Study of the fluoride adsorption characteristics of porous microparticulate zirconium oxide

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ABSTRACT

Lewis acid sites are present on the surface of metal oxide chromatographic supports and are responsible for the very strong adsorption of Lewis bases. Such sites must be masked or modified to elute solutes which contain Lewis base groups. Fluoride ion coordinates strongly with these sites on zirconium oxide and forms a surface whose composition is pH and ionic strength dependent. Coverages range from 13.7 μmol/m^2 fluoride at pH 4.8 to 0 μmol/m^2 fluoride at pH 13. Washing the particles with 0.1 M sodium hydroxide quantitatively desorbs all bound fluoride without harming the underlying zirconium oxide particle. Readsorption of the fluoride can be accomplished by equilibrating the particles in a buffer of suitable fluoride concentration. Such fluoride modification has been found to occur on a time scale suitable for displacement chromatography on the Lewis acid sites.

INTRODUCTION

Recently, there has been a resurgence of interest in the use of transition metal oxide particles as stationary phases for high-performance liquid chromatography (HPLC). Among the many possible oxide materials, zirconium oxide and titanium oxide show the greatest potential for successful use [1–5]. These materials have many characteristics of an ideal support including: mechanical strength, chemical stability, high surface area and a high percentage of mesopores. However, they lack the chemical homogeneity desired in an ideal phase.

The surfaces of these metal oxides, like other metal oxides, are very complex. A number of distinct classes of sites exist which can significantly contribute to the retention of a given solute. These sites include Brönsted acid sites, Brönsted base sites and Lewis acid sites [6–12]. These species are shown schematically in Fig. 1. Brönsted acid sites arise from the acidity of surface bound hydroxyls and tightly bound water molecules. The relative acidity is dependent on the metal ion, the mode of bonding and to a lesser extent the local environment.
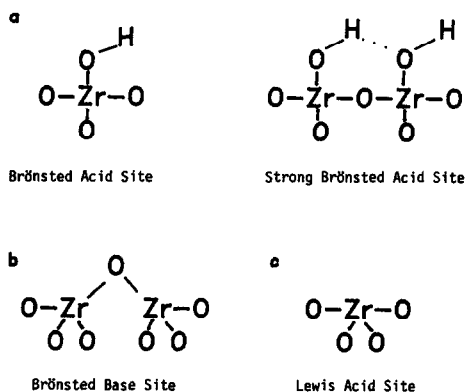
a

O–Zr–O with H on top O and O on bottom

Brönsted Acid Site

O–Zr–O–Zr–O with H...H bridging

Strong Brönsted Acid Site

b

O–Zr   Zr–O with bridging O

Brönsted Base Site

c

O–Zr–O

Lewis Acid Site

Fig. 1. Schematic of surface sites on zirconium oxide. (a) Brönsted acid sites; (b) Brönsted base sites; (c) Lewis acid sites.

Brönsted base sites arise from species such as bridging oxygen atoms shown in Fig. 1b. On the surface, such species can accept protons to form a cationic complex and have been observed spectroscopically [8,9,13]. Mono-, bi- and tridentate oxygen species have been identified on zirconium oxide surfaces [9,14,15] and it is expected that each will differ in Brönsted basicity.

The Lewis acid sites arise in a different manner. In the interior of metal oxides, such as zirconium oxide, the bonding of metal ions and oxygen atoms is governed by the coordination geometry of the metal ion. The metal ions bond to more oxygen atoms than charge stoichiometry would ordinarily allow, but the strength of each bond is less than in a stoichiometric bond. The result is an extensive network of bonding which gives metal oxides their high mechanical strength. When this bonding continuity is interrupted, at a surface for example, the coordination of the metal ions by oxygen atoms is not possible. As a result, a number of coordination sites are exposed at the surface. These sites are very electropositive and readily accept electron pairs, analogous to the coordination chemistry of soluble metal ions. To satisfy the coordination sphere of the metal ion, electron pair donors are coordinated to the available coordination sites. In aqueous solutions, these donors would include such species as water molecules, hydroxide ions and other available Lewis bases.

Within a given type of site, a great deal of heterogeneity can exist because of the varied geometries, surface defects and bonding types involved with a particular site. These complex surfaces can give rise to such interactions as ligand exchange on the exposed surface metal ions, hydrogen bonding to hydroxyl groups and ion exchange. The ion-exchange sites may be either cation or anion exchange or both due to the amphoteric nature of these metal oxides.

Undoubtedly, the most chromatographically troublesome sites on a zirconium oxide surface are the Lewis acid sites. These sites can form coordination complexes with a number of Lewis bases and are responsible for the irreversible adsorption of proteins and other solutes in systems where they are not blocked. For example, carboxylic acids could only be eluted from zirconium oxide when there was a high concentration of acetate ion (competing ion) in the eluent [2]. Phosphate is also observed to effectively block these sites [1].

However, these sites can be blocked by species other than oxyanions. The effectiveness of the blocking of the Lewis acid sites should be related to the strength of the interaction between the Lewis base used and the zirconium ion coordination site. Zirconium ion forms some of its strongest coordination compounds with fluoride ion [16]. We therefore tested fluoride as a mobile phase additive to control the Lewis acid properties of the material. This interaction is the subject of this investigation.

EXPERIMENTAL

Chemicals

Tris[hydroxymethyl]aminomethane (TRIS), cyclohexylaminopropane sulfonic acid (CAPS), 2-[N-morpholino]ethane sulfonic acid (MES), iminodiacetic acid (IDA) and N-tris[hydroxymethyl]methyl-3-aminopropane sulfonic acid (TAPS) were obtained from Sigma (St. Louis, MO, USA). Hydrochloric and acetic acids and sodium sulfate were obtained from EM Science (Gibbstown, NJ, USA). Sodium hydroxide was obtained as a 50% solution from Curtin Matheson Scientific (Houston,TX, USA). Sodium fluoride and sodium carbonate were obtained from J. T. Baker (Phillipsburg, NJ, USA) and sodium nitrate from MCB (East Rutherford, NJ, USA). Sodium thiocyanate, lithium chloride, sodium chloride, potassium chloride and ammonium chloride were obtained from Mallinckrodt (Paris, KY, USA). Sodium bromide, sodium perchlorate, sodium acetate, boric acid, oxalic acid and disodium phosphate were obtained from Fisher Scientific (Fairlawn, NJ, USA). Tetramethylammonium chloride and tetraethylammonium chloride were obtained from Aldrich (Milwaukee, WI, USA). All chemicals were reagent grade or better.

Water was prepared by passing house deionized water through a Barnstead Nanopure deionizing system with an organic free cartridge and a 0.2-μm final filter. The water was then boiled and cooled to remove any disolved carbon dioxide.

The porous zirconium oxide spherules were provided by the Ceramic Technology Center of the 3M Company. The spherules were prepared by a proprietary process and have been described previously [1–4]. Two types of particles were used in this investigation. The first type had a nominal diameter of 12.8 ± 1.2 μm, an average pore diameter of 308 Å by mercury porosimetry and an average BET surface area of 50.5 m^2/g. The second type had a nominal diameter of 37 ± 3 μm, an average pore diameter of 308 Å by mercury porosimetry and an average BET surface area of 33 m^2/g.

Apparatus

Solution fluoride measurements were made using an Orion Research (Boston, MA, USA) Model 96-09 combination fluoride electrode and a Model 501 Digital Ionalyzer. Polyethylene bottles were obtained from Nalge (Rochester, NY, USA).

Diffuse reflectance infrared spectroscopy was performed on a Bio-Rad (Cambridge, MA, USA) Digilab FTS-40 spectrometer with a Barnes Analytical/Spectra Tech (Stamford, CT, USA) Diffuse Reflectance Accessory. Spectral correction was performed with an internal Kubelka-Munk algorithm and a beam blocker was used during spectral acquisition.

Particle pretreatment

In order to remove as many of the manufacturing impurities as possible, the zirconium oxide particles were pretreated. This treatment consisted of three washes with 1 l of 0.5 *M* hydrochloric acid followed by three rinsings with 500 ml of treated water. The particles were then washed three times with 1 l of 0.5 *M* sodium hydroxide and then rinsed five times with 500 ml of treated water.

Fluoride adsorption rate studies

Three time domains were evaluated for the uptake of fluoride ion by zirconium oxide: minutes, hours and days. For the short term uptake studies, 1 g of particles was added to 49 ml TAPS buffer at pH 8.4 or MES buffer at pH 5.5. The solution was then stirred using a Teflon stir bar. An aliquot of 1 ml of a sodium fluoride solution was added using an Eppendorf pipette (Brinkman, Westbury, NJ, USA). The electrode response was monitored over the course of thirty minutes at 22°C.

The study of fluoride adsorption on the hour and day time scale was accomplished by placing 1 g of zirconium oxide particles in 50 ml of 0.1 *M* acetate buffer at pH 4.8 or 0.1 *M* TAPS buffer at pH 8.4. The slurry was ultrasonicated under vacuum and put into a waterbath at 35°C for an appropriate interval of time. Fluoride content was measured by adding 1 ml of the supernatant to 50 ml of 4 *M* acetate buffer at pH 4.8. The resulting solution was measured with the fluoride electrode and compared to similarly prepared standards.

Fluoride adsorption versus pH

Samples (1 g) of zirconium oxide were equilibrated with 50 ml of the appropriate buffer at 22°C. After 16 days, the supernatant solutions were analyzed for fluoride content in the same manner as for the timed adsorption assay.

Fluoride adsorption isotherm

Samples (1 g) of zirconium oxide were placed in 60 ml polyethylene bottles containing 50 ml of either 0.1 *M* acetate buffer at pH 4.75, 0.1 *M* TAPS buffer at pH 8.40 or 0.1 *M* MES buffer at pH 6.10. Various amounts of sodium fluoride were added to each bottle and the pH was readjusted by adding either concentrated hydrochloric acid or 50% sodium hydroxide solution. The bottles were placed in a shaker bath at 35°C for two days. The supernatant solutions were then analyzed for fluoride content in the same manner as for the timed assay. The supernatant solution was also submitted for inductively coupled plasma (ICP) analysis for zirconium.

The particles were then washed twice with 25 ml of treated water and 50 ml of 0.1 *M* sodium hydroxide was added to desorb the adsorbed fluoride. The samples were then placed in a shaker bath at 35°C for two days. The supernatant solution was analyzed for fluoride in the same manner as above.

A separate isotherm study was performed by placing 1-g samples of treated zirconium oxide particles into bottles and adding 50 ml of 20 m*M* sodium fluoride buffered to pH 8.4 with 0.1 *M* TAPS. Various amounts of sodium chloride were added to alter the total ionic strength of each sample. Following the addition of salt, the pH was readjusted to the desired pH. The bottles were placed in a shaker bath at 35°C for one day. The supernatant solutions were assayed for fluoride in the same manner as above. The base desorption procedure was the same as for the other isotherm studies with the incubation period shortened to one day.

Adsorption and desorption cycling

Polyethylene bottles containing 1 g of zirconium oxide particles were filled with 50 ml of either 0.1 M acetate buffer at pH 4.8, 0.1 M MES buffer at pH 6.1 or 0.1 M TAPS buffer at pH 8.4. Each solution was 20 mM in sodium fluoride. The bottles were then placed in a shaker bath at 35°C for 24 h. The supernatant solution was then assayed for fluoride in the same manner as for the timed assay. The remaining supernatant solution was removed and the particles were washed twice with 25 ml aliquots of treated water. The particles were then treated with 50 ml of 0.1 M sodium hydroxide solution at 35°C for 24 h. The supernatant solution was then assayed for fluoride. This procedure was repeated four times for each sample.

A fifth repetition of the cycle was performed on each sample, but after removing the excess supernatant buffer, the particles were washed twice with 50 ml aliquots of 1 M sodium chloride solution. This was followed by a washing with 50 ml treated water then base treatment in the usual manner. Each of the washing aliquots were assayed for fluoride.

Fluoride adsorption versus other salts

Solutions of the salts (1 M, except oxalate, lithium chloride and IDA which were 0.1 M) in 0.1 M TAPS buffer were made up with 20 mM sodium fluoride and the pH adjusted to 8.4. Zirconium oxide (1 g) was placed in a polyethylene bottle with 50 ml of a salt buffer. The bottles were transferred to a shaker bath at 35°C for two days. The fluoride content of the supernatant was measured in the same manner as in the timed adsorption assay.

Diffuse reflectance infrared (DRIFT) spectroscopy

Three samples of zirconium oxide particles were analyzed by DRIFT spectroscopy. The first sample consisted of the acid/base pretreated particles. The second sample consisted of particles which had been equilibrated for 16 days at 35°C with 0.1 M acetate buffer at pH 4.0 containing 0.5 M sodium fluoride. The last sample consisted of particles which had been equilibrated for 16 days at 35°C with 0.1 M sodium hydroxide containing 0.5 M sodium fluoride. The DRIFT cell was filled with sample and a beam blocker was put into place to decrease the amount of specular reflectance signal entering the detector. The samples were pulsed 256 times in the region of 400 to 4000 wavenumbers. Absorbances were corrected using a Kubelka–Munk algorithm.

RESULTS AND DISCUSSION

Because fluoride forms one of the strongest known zirconium complexes [16], it should be a very powerful displacing agent towards any Lewis base on a zirconium oxide surface. Previous studies have shown that metal oxides in general have a high affinity for fluoride ion [17–21]. However, its use as a modifier for controlling the retention of solutes on metal oxide surfaces has not yet been explored.

Zirconium ion is stable as a tetravalent cation. It has an especially high charge to radius ratio characteristic of hard metal ions and as such forms very strong coordination complexes with oxygen containing ligands [22,23]. It also displays a high affinity for other strong hard Lewis bases such as fluoride ion. Although these coordination properties are normally considered when dealing with solution species, we
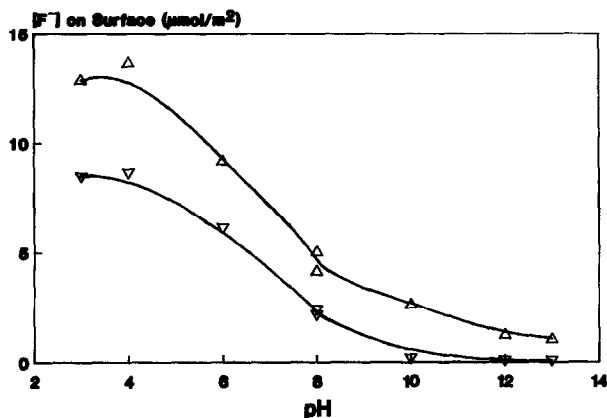
Fig. 2. Fluoride adsorption as a function of pH at 25°C. $\triangle$ = Fluoride adsorption; ∇ = fluoride desorption at pH 13. Buffers are all 0.1 M and contain 20 mM sodium fluoride except where noted: pH 3, 0.001 M HCl; pH 4, acetate; pH 6, MES; pH 8, TAPS (top) and TRIS (bottom); pH 10, CAPS; pH 12, 0.01 M NaOH; pH 13, 0.1 M NaOH.

believe that they are also relevant to the chemical properties of the "vacant" coordination sites (Fig. 1c) on the surface of zirconium oxide.

In neutral solutions, these "vacant" sites are occupied by either water molecules, hydroxyl ions, or other Lewis bases. When the vacant sites are occupied by weakly held ligands, solutes containing stronger Lewis base groups will be retained until displaced by a yet stronger base. The strength of this interaction can be quite high. Fluoride's first formation constant [K_1] with zirconium ion [24] is $10^{8.8}$ which gives a Gibbs free energy of formation of 12.4 kcal/mol at 35°C. Thus a base such as fluoride can serve two functions: it can block Lewis acid sites occupied by weaker bases or it can displace coordinated solutes.

Since hydroxide ion is a Lewis base and also forms a strong complex with zirconium ion [25] ($K_1 = 10^{14.3}$), the adsorption of fluoride ion on zirconium oxide should have a very strong dependence on pH as shown by the data in Fig. 2. In very basic solutions, fluoride cannot effectively compete with the high concentration of hydroxide ions in solution. Above pH 13, fluoride does not adsorb at all on the zirconium oxide surface.

At low pH, the fluoride was more easily adsorbed onto the surface due to less effective competition from hydroxide ion. A maximum was reached at about pH 4 where 13.7 μmol/m^2 of fluoride was adsorbed on the large diameter particles. Adsorption of fluoride then decreases as the pH is lowered due to the protonation of fluoride.

At pH 8, less fluoride adsorbed in a TRIS buffer than in a TAPS buffer under the same conditions. TRIS is known to specifically solubilize zirconium phosphate by complexation of zirconium (IV) ion [1]. When TRIS molecules block some of the Lewis acid sites, decreased fluoride adsorption is expected.

A major consequence of the strong pH dependence is that it implies that fluoride adsorption can be reversed. Fluoride adsorbed at lower pH should be readily

TABLE I

REPETITIVE ADSORPTION AND DESORPTION OF FLUORIDE (μmol/m^2 ± S.D.)[a]

Cycle	Stage	pH 4.8	pH 6.1	pH 8.4
1	Adsorption[b]	11.3 ± 0.4	7.9 ± 0.3	3.4 ± 0.1
	Desorption[c]	8.4 ± 0.3	6.1 ± 0.2	1.8 ± 0.1
2	Adsorption	10.7 ± 0.3	8.3 ± 0.3	3.4 ± 0.1
	Desorption	8.1 ± 0.3	6.1 ± 0.2	2.1 ± 0.1
3	Adsorption	10.4 ± 0.3	7.9 ± 0.3	3.4 ± 0.1
	Desorption	8.1 ± 0.3	6.1 ± 0.2	2.0 ± 0.1
4	Adsorption	10.4 ± 0.3	7.9 ± 0.3	3.4 ± 0.1
	Desorption	8.1 ± 0.3	6.3 ± 0.2	2.0 ± 0.1
5	Adsorption	10.1 ± 0.3	7.9 ± 0.3	3.4 ± 0.1
	1st NaCl wash	0.5 ± 0.0	0.6 ± 0.0	0.7 ± 0.0
	2nd NaCl wash	0.3 ± 0.0	0.4 ± 0.0	0.4 ± 0.0
	Water wash	1.2 ± 0.0	0.9 ± 0.0	0.5 ± 0.0
	Desorption	8.4 ± 0.3	6.3 ± 0.2	2.0 ± 0.1
	Total desorbed	10.4 ± 0.3	8.2 ± 0.2	3.6 ± 0.1

[a] See Experimental for details.

[b] This amount is computed by measuring the decrease in fluoride concentration in solution upon contact with the zirconia particles.

[c] This amount is computed by measuring the concentration of fluoride in the base solution used to desorb fluoride. Note the particles are first washed with water to remove interstitial fluoride.

displaced by washing the particles with 0.1 M sodium hydroxide solution. It has previously been shown [2] that zirconium oxide is chemically and physically stable from pH 1 to 14. Equilibration with the appropriate fluoride containing buffer should restore the column to its original condition. This is shown quantitatively in Table I. Cyclic adsorption and desorption of fluoride showed that, at all three pH values tested, base treatment quantitatively removed the fluoride. Recovery of fluoride appears to be incomplete because the particles were washed with water to remove interstitial fluoride then adsorbed fluoride was released by washing with base. However, in each cycle, the base washing step restored the original capacity of the particles for adsorption of fluoride.

   The desorption of fluoride in the water washes was monitored closely in cycle five. If fluoride were held by a simple ion-exchange rather than by a ligand-exchange mechanism, washing with 1 M sodium chloride should quantitatively displace fluoride. This is because on all ion exchangers, fluoride is more weakly held than is chloride due to the lower charge to radius ratio of the hydrated fluoride anion *versus* chloride ion. During the salt wash, a small amount of fluoride ion was removed. This can be attributed to the small fraction of fluoride held by ion-exchange forces and to the presence of fluoride ion in solution in the pores of the particles. However, when a water wash followed the salt washes, an increased amount of fluoride ion was recovered. We believe that this resulted from desorption of coordinated fluoride due to the lower ionic strength. The favorable thermodynamic driving force for coordination of
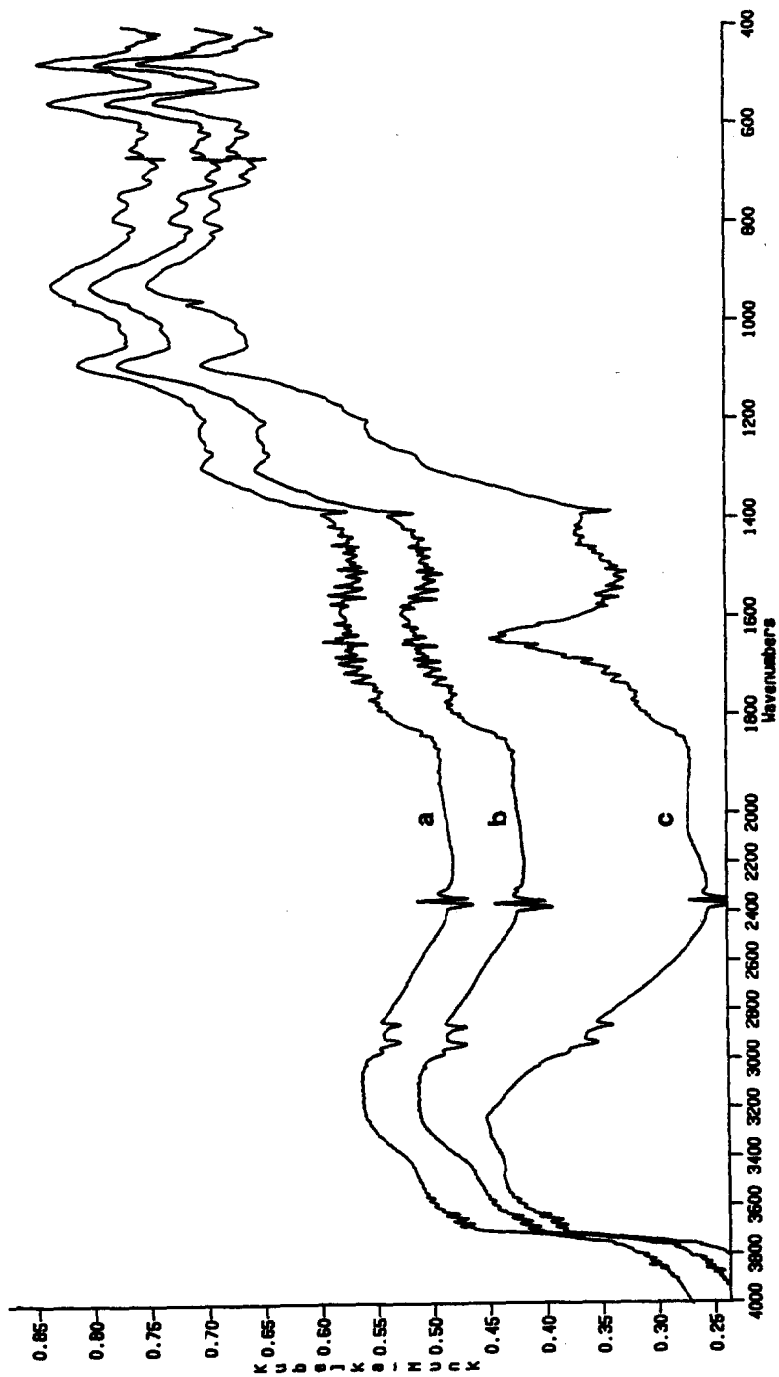
Fig. 3. DRIFT spectrum of (a) pretreated zirconium oxide particles, (b) particles treated with 0.5 *M* sodium fluoride at pH 13, (c) particles treated with 0.5 *M* sodium fluoride at pH 4.8.
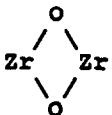
fluoride is somewhat offset by the ionic repulsion between fluoride ions when two or more fluoride ions attempt to occupy the small Lewis acid site. In solutions of high ionic strength (as in 1 M sodium chloride), this ionic repulsion is screened (in a Debye sense) and a larger amount of fluoride can adsorb onto the surface. When the ionic strength is decreased, coulombic repulsion causes some surface fluoride ions to desorb.

The reversibility of fluoride adsorption is demonstrated spectroscopically by the results shown in Fig. 3. Spectrum 3a is for the acid and base pretreated zirconium oxide particles before exposure to fluoride. After equilibrating the particles in 0.5 M sodium fluoride solution, a noticeable difference in the spectrum was observed as shown in spectrum 3c. Spectrum 3b is for the same particles after treatment with 0.1 M sodium hydroxide in the presence of 0.5 M sodium fluoride. The spectrum is identical to that of the untreated particles indicating no modification to the particles under these conditions.

Close examination of the DRIFT spectra revealed some subtle but important aspects of the surface modification. Table II lists the infrared absorptions relevant to this material [8,9,14,15,26–31]. The most striking feature is the lack of modification to the non-Lewis acid sites on the surface. The high frequency (3800–3200 cm^{-1}) absorbance region is due to freely vibrating surface hydroxyl groups [9,31] and was found to be identical in all three spectra. However, the lower frequency (3200–2600 cm^{-1}) region, due to coordinated water molecules [9,30,31], showed a decrease in absorbance for the fluoride treated sample. This is consistent with fluoride induced displacement of coordinated water molecules from the Lewis acid sites. Comparison of the low frequency (1200–400 cm^{-1}) region again showed that the surface hydroxyl

TABLE II

INFRARED ABSORBANCES FOR ZIRCONIUM OXIDES AND FLUORIDES [8,9,14,15,26–31]

Functionality	Frequency (cm^{-1})
Zr–O non-bridging	420
Zr–O bridging	450
Zr–O stretch	550
$\overset{\displaystyle O}{\underset{\displaystyle O}{Zr \diagup\diagdown Zr}}$ stretch	475
	610
asymmetric stretch	740
Zr–OH bend	700–1050
Zr–H	1371
	1562
O–H	2800–3800
H–O–H bend	1620
Coordinated H–O–H	2600–3500
Zr–OH stretch	3770
$(Zr)_n$–OH	3670
ZrF_6^{-2}	581
ZF_4	668

groups were intact. As a result, the surface retained its ionizable hydroxyl groups and thus its potential for cation exchange despite the presence of adsorbed fluoride ions.

A noticeable increase in absorbance at 1620 cm^{-1} was observed for the fluoride treated sample. This corresponds to the water bending frequency and reflects a difference in the water molecules bound to the surface of the particles. In the fluoride treated sample, the fluoride ions have displaced some of the coordinated water molecules and a decrease in the coordinated water absorptions was observed. Fluoride is normally hydrated to a great extent and when a fluoride ion is coordinated to the surface, the accessible surface of the fluoride ion is expected to be hydrated. This gives rise to an increased absorbance at 1620 cm^{-1} due to the bending frequency of these adsorbed water molecules. The untreated samples have their surface hydrated with water molecules coordinated to the Lewis acid sites whereas the fluoride treated surface has water bound due to fluoride hydration.

Zirconium forms a number of different types of compounds with fluoride and the final product is usually a mixture of complex hydroxyoxofluoro compounds [32]. As a result, there is a great diversity of binding types and strengths between zirconium and fluoride ions. From Fig. 3 it can be seen that the absorbance bands characteristic of the zirconium fluoride compounds showed no difference between the treated and untreated particles. In ZrF$_4$, fluoride is present entirely as bridging ions and this type of binding is not expected in adsorbed fluoride. A lack of definitive infrared absorbance data on the many types of zirconium fluoride compounds precludes any positive assignment of the bonding type from infrared spectroscopy.

Fluoride adsorption rate

Earlier studies on the adsorption of fluoride ion from solution by zirconium oxide indicated a relatively slow process [18]. However, under the conditions stated above, the adsorption rate for the zirconium oxide particles was faster than the response time of the fluoride electrode (less than two seconds). The discrepancy between our results and the previous findings are no doubt due to the differences in
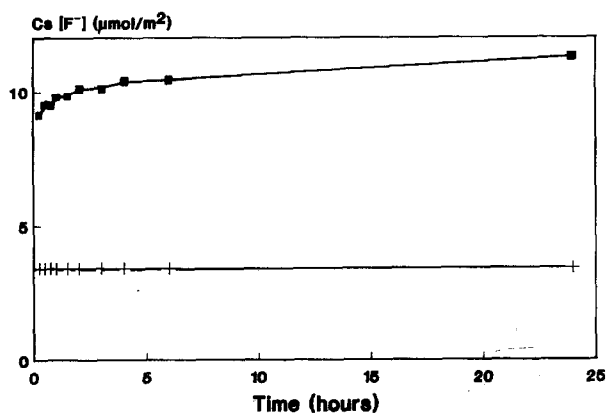

Fig. 4. Fluoride adsorption as a function of time. ■ = Fluoride adsorption in 0.1 M acetate buffer with 20 mM sodium fluoride at pH 4.75; + = fluoride adsorption in 0.1 M TAPS buffer with 20 mM sodium fluoride at pH 8.4 at 35°C. C_s = Surface fluoride concentration.

diffusion rates between the large, relatively non-porous particles used in prior studies and the small, highly porous particles used here.

When the adsorption rate was studied over much longer periods of time, a very slow increase in the amount of fluoride adsorbed was observed at low pH. Fig. 4 shows that at pH 8.4 there was no increase in fluoride adsorption while at pH 4.75, a slow increase was observed. We account for this by the slow dissolution of zirconium oxide by the hydrogen fluoride formed at this pH and the subsequent formation of fluorozirconates [32]. Such soluble fluoride species cannot be detected by the fluoride electrode and lead to high apparent adsorption of fluoride. It should be noted that this dissolution is a relatively slow process and rapid acid washing to remove base resistent species from the stationary phase may be tolerable. A very small increase in fluoride adsorption was observed over the period from one to sixteen days at pH 4.75, whereas no increase at all was observed at pH 8.4.

Adsorption isotherm

Fluoride adsorption isotherms showed that the surface was saturated with fluoride at fairly low fluoride concentrations. Fig. 5 shows the isotherm at pH 4.75. The desorption measurements show a maximum adsorption capacity of approximately 8 $\mu mol/m^2$ which was reached in 10 mM fluoride solutions and was maintained to 100 mM solutions. This high surface coverage is not entirely surprising. Lewis acid site density has been found to be approximately 6 $\mu mol/m^2$ by titration of such sites with sulfur trioxide [33]. Since the sites have a $+2$ charge [6,8,12], electronic neutrality can be reached with 2 fluoride ions per Lewis acid site, giving 12 $\mu mol/m^2$.

At fluoride concentrations greater than 100 mM, the zirconium oxide particle were attacked with formation of fluorozirconates. Fluorozirconates are slightly soluble in aqueous solutions and their solubility in higher fluoride concentration solutions is suppressed. This is obviously detrimental to the integrity of the particles, but is not surprising since at pH 4.75 a fair amount of fluoride ion is present as hydrofluoric acid, which is known to attack zirconium oxide.
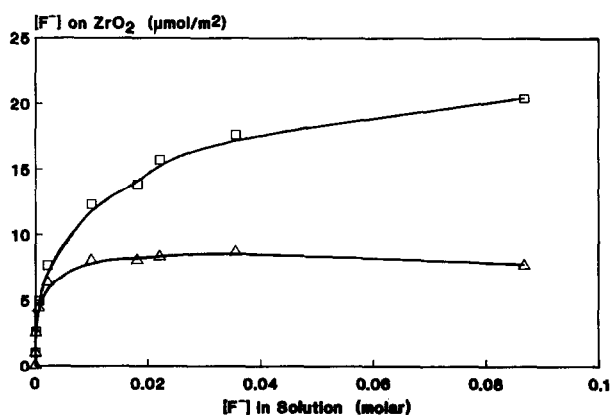

Fig. 5. Fluoride adsorption isotherm at pH 4.75. $\square$ = Apparent adsorption isotherm; $\triangle$ = base desorption isotherm. Buffer was 0.1 M acetate containing various amounts of sodium fluoride at 35°C for 48 h.
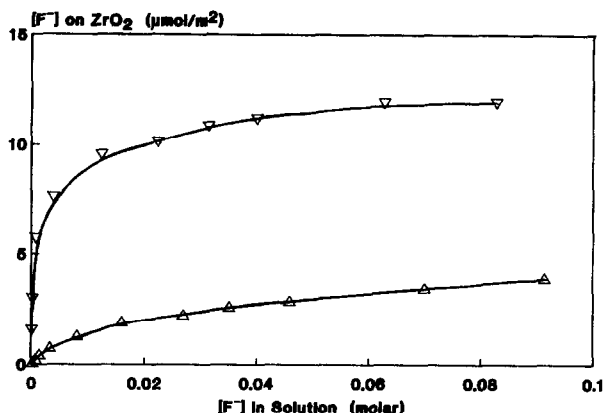
Fig. 6. Fluoride adsorption isotherm. ∇ = pH 6.1 0.1 M MES buffer; $\triangle$ = pH 8.4 TAPS buffer; both 35°C for 48 h. Measurements made by desorbing fluoride ion in 0.1 M sodium hydroxide.

At higher pH, the problems associated with hydrogen fluoride generation were alleviated. Fig. 6 shows the adsorption isotherm for fluoride under more hospitable conditions. The maximum adsorption of fluoride ion was lower than that found at lower pH due to increased competition from hydroxide ion. The adsorption of fluoride leveled off when the surface concentration reached approximately 4 μmol/m^2 at pH 8.4 and 12 μmol/m^2 at pH 6.1 at 35°C. In contrast to what was observed at lower pH, the zirconium oxide particle was not rapidly attacked. The solution concentrations of zirconium never exceeded 0.6 nmol/ml. In comparison, silica dissolves in neutral solutions to approximately 1.67 μmol/ml [34] and at pH 8.4 to a much greater extent.

When the amount of fluoride adsorbed onto the zirconium oxide was measured in the original solution, a much higher apparent capacity was observed. Fig. 5 shows
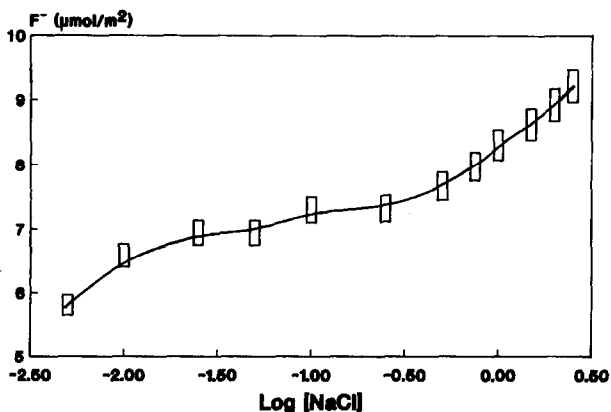

Fig. 7. Fluoride adsorption as a function of ionic strength. Buffer is 20 mM sodium fluoride in 0.1 M TAPS buffer at pH 8.4 and 35°C with added sodium chloride.

that the apparent capacity reached approximately 20 μmol/m^2 in 100 mM sodium fluoride solution. This higher apparent capacity is believed to be a result of the ionic strength masking of the electronic repulsion between adsorbed fluoride ions on the surface. As the ionic strength was increased, a greater number of fluoride ions could adsorb onto the surface. When the ionic strength was lowered to zero, as in the water washes, the ionic repulsion displaced excess fluoride until equilibrium was established. For comparison purposes, it was this equilibrium fluoride content which was measured in the isotherm studies at different pH values.

This ionic strength effect is shown in Fig. 7. An adsorption isotherm study was undertaken with a constant amount of fluoride in solution. The total ionic strength was increased by the addition of sodium chloride. Chloride ion has a formation constant of $10^{0.3}$ with zirconium ion [24] and therefore is not expected to form coordination compounds at pH 8.4. The surface concentration of fluoride rose from 5.8 μmol/m^2 at low ionic strength to 9.25 μmol/m^2 at high ionic strength. This 60% increase in capacity is believed to be due to the masking of the ionic repulsion of crowded surface fluoride ions thus allowing a greater mean coordination number of fluoride ions on each Lewis acid site.

Salt effects on fluoride adsorption

The effects on fluoride adsorption by a variety of salts is shown in Table III. A number of salts showed no effect other than to reduce the ionic repulsion between coordinated fluorides to increase the total adsorption capacity. Small differences exist

TABLE III

SALT EFFECTS ON FLUORIDE ADSORPTION[a]

| Salt	Fluoride capacity (μmol/m^2) $\pm$ S.D. ($n = 3$)
Tetraethylammonium chloride	8.8 $\pm$ 0.3
Sodium perchlorate	8.7 $\pm$ 0.3
Sodium nitrate	8.0 $\pm$ 0.3
Sodium bromide	8.0 $\pm$ 0.3
Sodium acetate	8.0 $\pm$ 0.3
Sodium thiocyanate	7.4 $\pm$ 0.3
Sodium chloride	7.4 $\pm$ 0.3
Sodium sulfate	6.7 $\pm$ 0.2
Potassium chloride	6.2 $\pm$ 0.2
Ammonium chloride	6.2 $\pm$ 0.2
Tetramethylammonium chloride	6.2 $\pm$ 0.2
Iminodiacetic acid (0.1 M)	4.5 $\pm$ 0.2
None	4.5 $\pm$ 0.2
Lithium chloride (0.1 M)	4.3 $\pm$ 0.2
Oxalic acid (0.1 M)	3.8 $\pm$ 0.1
Sodium carbonate	3.8 $\pm$ 0.1
Sodium phosphate	3.0 $\pm$ 0.1
Boric acid	0.6 $\pm$ 0.1

[a] See Experimental for details.
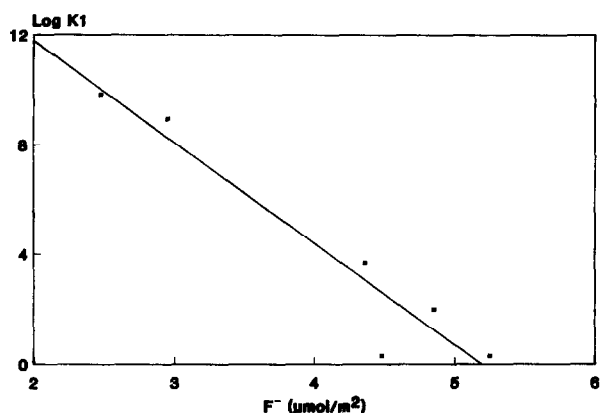
Fig. 8. Fluoride adsorption as a function of solution complex formation constant. Adsorption was in 0.1 M TAPS buffer with 20 mM sodium fluoride at pH 8.4 and 35°C.

between these salts and can be mainly ascribed to differences in the chaotropic nature of the salts. A second group of salts was effective in blocking a certain fraction of the available Lewis acid sites on the zirconium oxide surface. This was expected since these salts have stronger interactions with zirconium ion than does fluoride [35]. Using data for the formation constants of zirconium (IV) ion and the appropriate anion [25,26,35,36], Fig. 8 shows the relationship between fluoride adsorption and the strength of the coordination interaction.

Borate is an interesting case in itself since it is not a good Lewis base. Borate is known to form esters with polyhydroxy compounds [37] and may be preventing fluoride ion adsorption by sterically blocking the Lewis acid sites. The composition of such phases are known to vary strongly with the pH of the solution [38]. The resulting surface might be useful as a cation-exchange material and could also find use in the separation of sugars. This, however, is the subject of another investigation.

CONCLUSIONS

It has been demonstrated that the interactions of various ligands on the Lewis acid sites are similar to those of the soluble species. Since the composition of Lewis bases coordinated to the Lewis acid sites will be determined by the concentration and coordination thermodynamics of the bases in solution, the strength of these adsorptions can be modified to change the overall properties of the surface. In doing so, the zirconium oxide support can be modified to provide a more compatible and controllable surface for separation of solutes without losses due to irreversible adsorption on these strong sites.

It was also found that such interactions take place on a time scale suitable for their use in chromatography. In addition, the surface modification was found to be readily reversible by flushing the material with 0.1 M sodium hydroxide solution followed by re-equilibration with the appropriate buffer. However, care should be exercised when working with acidic solutions to prevent dissolution of the material when fluoride is present.

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