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A CHROMATOGRAPHIC STUDY OF THE LEWIS ACID-BASE CHEMISTRY OF ZIRCONIA SURFACES

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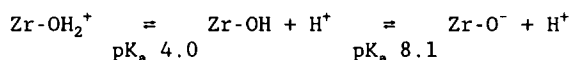
ABSTRACT

The chromatographic properties of porous microparticulate zirconium oxide surfaces in aqueous media are highly dependent upon the chemical composition of the eluent. In particular, retention is controlled by the type and concentration of "hard" Lewis bases when these species are present in the eluent. Ligand exchange is the dominant mechanism for the retention of solutes which are Lewis bases. Consequently, the capacity factor and plate height depend on both the thermodynamic and kinetic properties of whatever competing Lewis bases may be present in the eluent. These Lewis base eluent components act to control retention in two ways. They modify the net ligand exchange contribution to retention, and they serve as sites for secondary interactions, such as hydrogen bonding and hydrophobic interactions between solutes and the dynamic stationary phase.

INTRODUCTION

Over the past few years, there has been considerable interest expressed in materials which can serve as alternatives to silica as the basis of supports in different modes of HPLC [1-8]. Microparticulate zirconium oxide has extremely high chemical and mechanical stability relative to stabilized silicas, alumina and various porous polymeric materials [1,2]. It is resistant to chemical degradation over the pH range 1 to 13 and it maintains a physical (pressure) stability comparable to that of silica. The pore geometry and pore size distribution is favorable for the high performance separation of both small solutes and proteins. However, analogous to alumina, the surface chemistry of zirconia is much more complex than silica. While the surface chemistry of zirconia is closer to that of alumina than to silica, its chromatographic properties and performance are not the same as alumina [1].

Various studies have shown that the point of zero charge for zirconium oxide in water is approximately 6.7 [9]. Surface hydroxyl groups have a pK_a of about 8.1 while protonated surface groups have a pK_a of about 4.0:



Based on these pK_a values, in the absence of any species that can adsorb on the surface, zirconia should behave as an anion exchanger at pHs below 4.0 and as a cation exchanger above pH 8.1. Between these pHs, the material should retain both anions and cations, albeit more weakly than at higher or lower pH values.

The chromatographic performance of zirconia is more complicated than implied by the above description of a mixed anion/cation exchanger. In fact, the dominant feature of the surface chemistry of zirconia is the presence of coordinatively unsaturated zirconium (IV) sites which act as rather strong "hard" Lewis acids. Hard Lewis acids tend to form their strongest complexes with "hard" Lewis bases. Such bases are small, highly

charged species of low polarizability and include molecules and ions such as hydroxide, fluoride and carboxylates. These Lewis acid sites form labile coordination complexes with any Lewis bases, whether they are solutes or components of the eluent.

Chromatographically, the thermodynamic strength and slow dissociation kinetics of such strong interactions can give rise to extraordinarily poor chromatographic efficiencies unless a very strong competing Lewis base is added to the buffer. In this work, we take the existence of very broad peaks, even for weakly retained species, as prima facie evidence for the participation of ligand exchange processes in the overall retention mechanism. The buffer base moderates the net strength of the ligand exchange interaction. Earlier studies have shown that fluoride can effectively compete with even very strong polyvalent Lewis base solutes for such sites [10,11]. When used as an eluent additive, fluoride facilitates the efficient separation of a wide variety of low molecular weight solutes as well as many proteins [11].

The aim of the present study was to investigate the effect of various Lewis bases on the elution properties of a number of low molecular weight solutes. These small solutes were chosen to include a variety of moieties which had the potential for interacting with the anion, cation and ligand exchange sites present on the surface of zirconium oxide.

EXPERIMENTAL

Chemicals

2-[N-morpholino]ethanesulfonic acid (MES) was obtained from Sigma (St. Louis, MO). Hydrochloric acid and HPLC grade isopropanol were obtained from Fisher Scientific (Fair Lawn, NJ). Sodium hydroxide was obtained as a 50% solution from Curtin Matheson Scientific (Houston, TX). All other chemicals were obtained from commercial sources and were reagent grade or better.

Water used in these studies was prepared by passing house deionized water through a Barnstead NanoPure water system with an additional organic-free cartridge and a 0.2 μm final filter. The

water was subsequently boiled for five minutes then cooled to room temperature immediately prior to use to remove dissolved carbon dioxide.

Chromatographic Supports

The porous zirconium oxide particles were provided by the Ceramic Technology Center of the 3M Company and were described earlier [1,2,8,10-15]. The particles used in this investigation had a nominal diameter of $5.3 \mu\text{m} \pm 1.3 \mu\text{m}$, an average pore diameter of 308 Å by mercury porosimetry and an average B.E.T. surface area of 32.5 square meters per gram. The particles were initially pretreated in order to remove as many of the manufacturing impurities as possible as described earlier [10,11].

Chromatographic columns were prepared in 50 mm by 4.6 mm column blanks fitted with 1/4" Parker® end fittings. Titanium screens with 2 μm mesh were used instead of frits to minimize any potential extraneous metal ion contamination from the frits. Columns were packed by the upward slurry technique using isopropanol as the solvent. Packing pressure was 4500 psi (300 atm.). Following the packing procedure, all columns were flushed with freshly boiled water to displace all of the packing solvent prior to introduction of the buffer.

Chromatographic Systems

Chromatographic studies were carried out on a Hewlett Packard (Avondale, PA) Model 1090M liquid chromatograph with a DR5 ternary solvent delivery system and a diode array detector. The optional expanded pH range kit as well as ultrahigh molecular weight polyethylene piston seals (UPC-10) obtained from Bal Seal Engineering (Santa Ana, CA) were installed. Data were processed using a Hewlett Packard 9000/Series 300 computer outfitted with ChemStation software. A guard column (50 x 4.6 mm) filled with 10-20 μm zirconia particles was placed before the injection valve to scavenge any trace contaminants in the eluent.

Solute Retention Studies

Solutes were dissolved in freshly boiled water to make a final solute concentration of approximately 10mM. Because of the small injection volumes involved, sample pHs were not standardized. Ten microliter injections of each solute were made and elution was monitored at 230, 254 and 280 nm using a diode array detector. Capacity factor measurements were based on the peak maximum.

Following the analyses using a particular Lewis base eluent, the zirconium oxide columns were flushed with 45 mL of 0.1M sodium hydroxide to strip any "irreversibly" bound solutes. This was followed by rinsing with 50 mL of freshly boiled water to remove excess hydroxide from the column. Periodically, the chloride elution study was repeated to ensure that the long term selectivity and efficiency were constant. In all cases, the reproducibility was better than 5% for capacity factors and 7% for reduced plate heights despite repeated base stripping.

RESULTS AND DISCUSSION

Effect of Eluent Lewis Base Type

Chemical insight into the surface properties of zirconia was gained by studying retention as a function of eluent composition. The results are given in Table 1. In sodium chloride media, the cationic solutes were not retained. This is not surprising since only a small fraction of the surface hydroxyl groups are ionized at neutral pH and the ionic strength of the eluent is high enough to displace any solutes bound only by ion exchange. Uracil had been previously shown to be retained on zirconium oxide by ligand exchange [11]. In the absence of any stronger Lewis base, uracil is retained.

When a stronger Lewis base eluent was used, the retention times of the cationic solutes changed significantly. Uracil was no longer retained since the stronger Lewis base prevented any ligand exchange interaction between uracil and the zirconia surface. The other cationic solutes were more retained than in the chloride

TABLE 1

Retention as a Function of Displacing Lewis Base^a

Solute	capacity factor			
	sodium chloride	glycolic acid	malic acid	succinic acid
guanidine	n/a	0.8	1.6	0.7
imidazole	0.0	0.4	0.7	0.3
benzylamine	0.0	0.5	0.8	0.4
uracil	0.5	0.0	0.0	0.0
benzamide	0.0	0.0	0.0	0.0
benzyl alcohol	0.0	0.0	0.0	0.0
benzyl mercaptan	0.1	0.0	0.1	0.1
phenylacetic acid	eno	0.9	0.0	0.2
benzenesulfonic acid	0.9	0.1	0.1	-0.1
phenol	0.2	0.0	0.0	0.0
benzenephosphonic acid	eno	eno	eno	eno

- a. Eluent contained 20 mM of displacing Lewis base with 20 mM MES at pH 6.1. Flow rate was 0.50 mL/min at 35°C. Injections were 5 μ L of 10 mM solute in 20 mM sodium chloride 20 mM MES pH 6.1. Detection was at 230 or 254 nm using a diode array detector. eno = elution not observed

buffer. The highest retention of cations was observed in the malic acid buffer. Such a strong dianionic Lewis base as malic acid is certainly adsorbed on zirconia. The increase in retention of cations can be explained by assuming that adsorption of the dianion leads to the development of a highly negatively charged surface. We believe that this also explains the effect of succinate buffer on retention. However, it cannot explain the effect of the increase in retention of the cations, relative to their retention in chloride media, in the glycolate buffer since this buffer anion is the salt of a monoprotic acid. It may be that a weak interaction between the surface when it is coated with an adsorbed layer of glycolate and the solute acts to increase retention in this eluent.

The fact that the nonelectrolytes are unretained in all the buffers shows that ionic interactions, and not simply hydrogen

bonding and/or van der Waals forces, are responsible for retention of the anions and cations. Therefore, retention of the ionic species must be primarily due to ion and/or ligand exchange interactions which may be modified by secondary van der Waals interactions.

In chloride media, all of the anionic solutes were retained, some exceedingly so. This is consistent with the formation of labile complexes between the anionic Lewis base solutes and the Lewis acid sites on the zirconia surface. It is also consistent with the existence of positively charged, protonated surface hydroxyl groups. The fact that the retention of phenylacetic acid is so strong ($k' > 50$) while benzenesulfonic acid, which from the perspective of size and charge is quite similar, is readily eluted strongly supports our view that the dominant retention process is ligand exchange and not simply ion exchange.

When anionic solutes are chromatographed in an eluent that contains a strong Lewis base, their retention times decrease greatly relative to that in chloride media. Both malic and succinic acid readily displace solutes except benzenephosphonic acid. Glycolic acid acts similarly, however, phenylacetic acid is substantially retained in this buffer. This may be due to the similarities in ligation strength between the phenylacetic acid and glycolic acid. The strong retention of benzenephosphonic acid in all of these Lewis base buffers is not surprising, since the elution of this solute could not be observed even with fluoride [11], an extremely powerful hard Lewis base.

Based on the results with these low molecular weight probe solutes, the effective displacing strength of various Lewis bases can be roughly estimated. Due to the complications with proton transfer, the ranking is limited to the pH of the experiment. Chloride shows little or no affinity for the Lewis acid sites. It is clearly the weakest eluent and, therefore, is ranked lowest of the Lewis bases. Conversely, no species is able to displace benzenephosphonic acid, therefore, it is ranked highest. Subsequent comparisons result in the following ranking of effective Lewis

TABLE 2
Retention in Citrate Buffers^a
capacity factors
(reduced plate heights)

Solute	pKa	pH					
		2.63	3.63	4.26	5.50	6.40	7.38
benzylamine	9.35	0.17 (5)	0.21 (4)	0.25 (4)	0.28 (5)	0.29 (6)	0.30 (5)
guanidine		0.82 (4)	0.78 (4)	0.72 (6)	0.71 (5)	0.67 (7)	0.67 (6)
uracil		0.08 (8)	0.03 (8)	0.03 (8)	0.03 (9)	0.04 (10)	0.03 (10)
benzamide		0.35 (131)	0.31 (158)	0.27 (138)	0.10 (55)	0.07 (48)	-0.02 (24)
benzyl alcohol		0.04 (7)	0.00 (7)	0.00 (6)	-0.01 (7)	0.00 (7)	-0.02 (8)
phenol	9.99	0.05 (7)	0.01 (7)	0.01 (6)	0.00 (7)	0.02 (8)	0.00 (8)
phenylacetic acid	4.31	0.12 (21)	0.10 (29)	0.10 (31)	-0.01 (34)	-0.01 (15)	-0.04 (11)
phenylsulfonic acid	2.55	0.00 (5)	-0.05 (5)	-0.05 (5)	-0.05 (6)	-0.04 (6)	-0.06 (7)
phenylphosphonic acid	1.83 7.07	eno n/a	2.60 n/a	1.70 (5600)	4.25 n/a	eno n/a	eno n/a

a. Eluent was 0.2M sodium chloride in 20mM citric acid with the pH adjusted with 50% sodium hydroxide solution. Flow rate was 0.5 mL/min at 35°C. Injections were 10 μ L volumes of 10mM solutions in water. Detection was at 230, 254 and 280 nm.

basicity: phosphonate > malate > succinate > glycolate > acetate > sulfonate > uracil > phenolate > chloride. This order of basicity parallels the sequence of solution formation constants of these species with zirconium (IV) ion¹². This correlation is very significant in that, in combination with knowledge of the ion exchange retention behavior of the various solutes, it permits prediction of retention properties of the various solutes on zirconium oxide .

Effect of pH on Retention in Citrate Eluents

Table 2 summarizes the effect of the eluent pH on retention and efficiency. A series of dilute citrate buffers, whose pH ranged from 2.6 to 7.4, was employed. As shown in Table 2, the pH had a very large effect. Citric acid was chosen for this study since it has three reasonably distributed acid dissociation constants ($pK_a = 3.13, 4.76$ and 6.40) and thus has a reasonable buffer capacity. The citric acid competing ligand becomes increasingly anionic as the pH is increased. The retention behavior of benzylamine shows that the cation exchange capacity increased as the pH increased. This is due to the combination of increased ionization of surface hydroxyl groups and of the surface adsorbed citrate molecules. Even though the capacity factor for benzylamine is low, we believe that the surface density of negative sites must be reasonably high since the ionic strength (0.2M sodium chloride) is rather high.

In contrast to benzylamine, the capacity factor for guanidine decreased monotonically as the pH was raised. Both species show good efficiencies, but some other factor, such as hydrophobic enhancement of retention, must be involved to cause these solutes to act so differently. Uracil is retained primarily by ligand exchange processes and thus is only weakly retained due to intense competition with citrate.

Benzyl alcohol eluted in the void volume at all but the lowest pH. The very slight retention at the lowest pH may be due to hydrophobic or hydrogen bonding interactions with the largely uncharged surface bound citrate ligand. Under similar elution

conditions, benzamide is not usually retained. However, its high reduced plate height and the decrease in its capacity factor as pH is increased lead us to believe that it is retained to some extent by a ligand exchange process. However, secondary interactions with adsorbed citrate moieties may be responsible for its anomalous retention.

Anionic or potentially anionic solutes, such as phenol and phenylsulfonic acid, were not retained and were somewhat excluded from the pores of the stationary phase. This substantiates our view that the surface is negatively charged even at quite low pH. Hydrophobic or hydrogen bonding interactions at low pH may be responsible for the small increase in capacity factor. The capacity factor for phenylacetic acid decreases as the pH is increased and its reduced plate height are higher than those of the other anions, as expected for a species which is retained to some extent by ligand exchange. Surprisingly, phenylphosphonic acid elutes in the pH range of 3.6 to 5.5, albeit with extremely high reduced plate heights. The minimum in capacity factor for this solute versus pH does not coincide with any specific event (e.g. dissociation constant), but may be the result of competing retention processes.

Effect of Borate on Retention

Regazzoni [17], et.al., have shown that borate interacts with zirconium oxide in a decidedly different manner than do fluoride, sulfate and other Lewis bases. Using potentiometric and electrophoretic mobility measurements, they found that, rather than form Lewis acid/base complexes with zirconium, borate forms monovalent esters with the surface hydroxyl groups, thereby generating a negative charge on the surface. This negative charge is partially neutralized by forming a tight ion pair with available cations. The maximum adsorption capacity for these species was found to be very near the first dissociation constant of boric acid ($pK_a = 9.24$). In light of this, the chromatographic properties of zirconium oxide in borate media were investigated as a function of pH and boric acid concentration.

TABLE 3

Effect of pH Retention in 0.1M Borate Buffers^a

Solute	pH:	capacity factors (reduced plate heights)			
		4.8	7.0	9.0	11.0
benzyltributylammonium Cl		0.41 (19)	0.68 (14)	n/a n/a	0.11 (28)
benzylamine		0.79 (25)	1.64 (7)	0.72 (14)	0.08 (26)
benzyl alcohol		0.00 (14)	0.00 (17)	0.00 (14)	0.00 (17)
p-toluenesulfonic acid		-0.06 (16)	-0.18 (21)	-0.10 (21)	-0.06 (23)
benzoic acid		2.49 (137)	-0.09 (28)	-0.04 (25)	-0.05 (19)

a. Isocratic elution at 45°C with a flow rate of 0.5 mL/min. Detection was at 254 or 230 nm. Eluent was 0.1M boric acid with pH adjusted by adding 50% sodium hydroxide solution.

The retention properties of zirconium oxide in 0.1M boric acid buffer at various pHs are shown in Table 3. Both cationic species are fairly well retained at low pH due to the ionization of surface bound borate and transient formation of a strong ion pair. Retention is greater at higher pHs, consistent with increased ionization of the surface bound borate. However, the capacity factors decrease when the pH is increased above 7.0. This is most likely due to the increased ionic strength of the buffer as the solution borate species become increasingly ionized. The relatively good reduced plate heights, similar to those of unretained neutral species (benzyl alcohol) observed in borate media, also indicate that these cations are retained by ion exchange and not ligand exchange processes.

Phenylsulfonic acid was not retained under any of the conditions employed here. In fact, it was fairly well excluded from

TABLE 4

Effect of pH on Retention in 0.5M Borate Buffers^a

Solute	pH:	capacity factors (reduced plate heights)			
		4.8	7.0	9.0	11.0
benzyltributylammonium Cl	1.47 (6)	0.30 (11)	0.02 (17)	0.02 (31)	
benzylamine	2.21 (9)	1.09 (7)	0.20 (14)	0.01 (27)	
benzyl alcohol	0.00 (12)	0.00 (15)	0.00 (15)	0.00 (24)	
p-toluenesulfonic acid	-0.23 (21)	-0.10 (22)	-0.11 (18)	0.00 (25)	
benzoic acid	0.49 (196)	-0.10 (19)	-0.05 (16)	-0.01 (18)	

a. Isocratic elution at 45°C with a flow rate of 0.5 mL/min. Detection was at 254 or 230 nm. Eluent was 0.5M boric acid with pH adjusted with 50% sodium hydroxide solution.

the pores. Maximal exclusion was observed at neutral pH, where electrostatic repulsion is at a maximum due to the relatively high negative charge of the surface and low solution ionic strength. This is consistent with the explanation proffered for the retention of the cations. Except at low pH, benzoic acid acts like phenylsulfonic acid. At pH 4.8, benzoic acid competes well with the uncharged boric acid molecules for the Lewis acid sites. At low surface borate loading, benzoate may not be electrostatically repelled from the surface. The rather high reduced plate height for benzoic acid at this pH suggests that retention is at least partially controlled by a ligand exchange process.

By increasing the boric acid concentration and thereby increasing the amount adsorbed, several notable changes in retention occur (see Table 4). First, the capacity factors for cations at low pH increase. This may result from simple mass balance effects on the borate adsorption isotherm. Second, no maxima in capacity

factor vs pH is observed. Once the surface is nearly saturated with borate, a further increase in the eluent boric acid concentration can act only to decrease retention by virtue of the higher ionic strength. The capacity factor for benzoic acid also decreases as the eluent borate concentration increases, probably due to increased surface coverage of borate.

CONCLUSION

The chromatographic properties of Lewis base modified zirconium oxide can be explained by assuming the existence of four major types of interactions. First, cation exchange interactions take place between cationic solutes (which bear no Lewis base functional groups) and deprotonated surface hydroxyl groups and/or adsorbed negatively charged Lewis base components of the eluent. Second, non-coordinating anionic solutes undergo anion exchange at the positively charged Lewis acid sites, such as $\text{Zr}(\text{OH})_n^{\text{m}+}$, which are intrinsic to the zirconia surface. Third, ligand exchange reactions take place between Lewis base solutes and the Lewis acid surface sites. Finally, secondary interactions between adsorbed Lewis base components of the eluent and the test solutes can be significant. These secondary interactions may involve hydrophobic, hydrogen bonding, cation exchange or anion exchange interactions depending on the adsorbed Lewis base. These secondary interactions combine with the three primary retention processes to produce an overall selectivity which is unique for each type of buffer Lewis base. These interactions can be exploited to design a very wide variety of specific separations in very complex media. In many instances, these separations would not be possible with a support, such as alumina, which is chemically less stable than zirconia.

Comparison of the relative retention of various species in different eluents allows a relative ranking of the eluotropic strength of a number of Lewis bases. This ranking includes both the ligand exchange displacement strength of the particular Lewis base, but also its contributions to cation and anion exchange

displacement. It provides a useful, predicative, although qualitative scheme for choosing the appropriate Lewis base eluent for a particular separation. A more detailed quantitative eluotropic scale is the subject of further investigation.

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