

Anion-Exchange Material with pH-Switchable Surface Charge Prepared by Sol–Gel Processing of an Organofunctional Silicon Alkoxide

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A novel organofunctional silica material has been prepared by sol–gel technology. The material incorporates an organic substituent, propyl-*N,N,N*-trimethylammonium, which is linked to the silica matrix covalently. This material is anion exchangeable and exhibits an improved selectivity toward chloride over more lipophilic anions. It is optically transparent and has been characterized by thermogravimetric analysis, infrared spectroscopy, nitrogen sorption analysis, capillary electrophoresis, cyclic voltammetry, and measurement of membrane potential. The material is porous, and almost all the covalently linked organic substituents are active in the pore space. The surface charge of this material is switchable in sign and its magnitude is dependent on pH and type of buffer. The potential of this material as a charged surface coating for capillary electrophoresis or an anion-exchange film for potentiometric sensors has been explored.

Introduction

Anion exchange is important for a variety of applications such as water treatment, chemical separation, and electrochemical sensing. Today, most anion exchangers are organically based, which typically have high exchange capacities (3–4 mequiv/g) but limited thermal stability.¹ Organically modified anion exchangers based on silica matrix combine the physical properties of the glass, such as thermal stability, durability with organic solvents and oxidizing agents, rigidity, and a polar microenvironment, with the exchanging properties of the organic functional groups. Such anion-exchange glasses are produced by entrapment² or bonding^{2d,3} of a quaternary ammonium salt in or to a silica matrix.

The sol–gel process is very well adapted for coating of thin films on complex shapes.⁴ The porosity and pore size of these films can be controlled⁵ to maximize the

specific surface area and to ensure that the permeability of the film remain high. Furthermore, the sol–gel process involves low-temperature hydrolysis and condensation of appropriate monomeric precursors and is highly suitable for inclusion of organic moieties that cannot withstand high temperatures. Hence, the sol–gel technique is very promising for fabrication of anion-exchange films, which are potentially applicable to preparation of stationary phases in chromatography and electrochromatography, potentiometric sensors, and chemically modified electrodes. Previously, anion exchangers based on sol–gel processing by entrapment of quaternary ammonium salts were attempted.^{2a} However, leaching remained the problem. Hence, the use of an organofunctional precursor appears to be the most effective immobilization method in the sol–gel process because the resulting material does not leach at all.^{4b,6}

In this article we describe a new organically modified silica material prepared by the sol–gel process. The material, named propyl-*N,N,N*-trimethylammonium functionalized silica (PTMAFS), incorporates a quaternary ammonium functional group, propyl-*N,N,N*-trimethylammonium (PTMA), which is linked to the silica matrix covalently. Since the PTMA functional group is often used in many anion-exchange resins, the material is anion-exchangeable. Also, this material retains the nanoscale porosity and optical transparency of the parent sol–gel glass and can be processed into monoliths or coated as thin films of widely variable forms. We have also examined the exchange selectivity of PTMAFS toward various anions and explored its potential as an anion-exchange material for ion-exchange electrochromatography, ion chromatography, ion ex-

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changers, ion-selective electrodes, ion-selective field-effect transistors, and ion-exchange voltammetry.

Experimental Section

Materials. The following chemicals were used in the synthesis of sol-gel-derived materials: tetramethyl orthosilicate (TMOS, TCI), *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMSPTMA, 50% in methanol, Gelest), and hydrochloric acid (Merck). Potassium ferricyanide was obtained from Janssen Chimica. 1,3-Benzenedicarboxylic acids were purchased from TCI. All reagents were used as received without further purification. Fused silica capillaries (75- μm i.d., 375- μm o.d.) were obtained from Polymicro Technologies (Phoenix, AZ).

Preparation of Silica Sol-Gel Powder. Prehydrolysis of TMOS was performed by adding 180 μL of deionized water and 10 μL of 0.1 M HCl to 500 μL of TMOS. The mixture was sonicated in an ice bath for ≈ 30 min and then stored in the ice bath for an additional 6 h. Subsequently, 340 μL of TMSPTMA was added to the mixture. After about 8 min of shaking in an ice bath, a transparent and homogeneous sol-gel monolith resulted. The gel, PTMAFS-Cl⁻, was aged for 24 h under ambient room conditions (temperature = 21–25 °C, relative humidity = 81–87%) and was then lyophilized into powder.

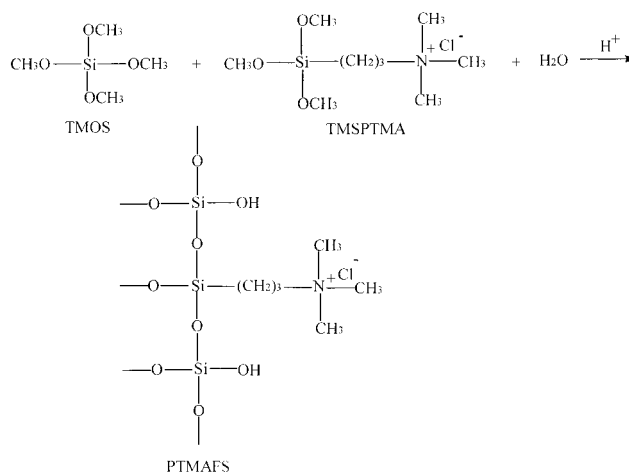
Preparation of PTMAFS-Coated Capillary. Upon addition of a prehydrolyzed TMOS sol to TMSPTMA, the mixture was shaken in an ice bath for 30 s. Subsequently, the sol-gel solution was forced through a silica capillary by a water pump for 10 s. Immediately after the coating, deionized water was forced through the capillary for 30 s. The capillary was then filled with deionized water, sealed at both ends, and annealed at 50 °C for 24 h. This procedure was employed to avoid cracks during aging⁷ and to give a more reproducible column. After this aging step, the capillary was stored under ambient room conditions. Prior to use and between runs, the coated capillary has to be pretreated with 0.1 M NaOH, deionized water, 0.1 M HCl, and the running buffer for appropriate times so that the column was maintained at identical conditions for each run. Detailed pretreatment procedures will be reported elsewhere.⁸

Amperometric Measurements. The PTMAFS films were prepared by casting the sol-gel solution on a spinning ITO-coated electrode at 1500 rpm. The coated electrodes were then dried under ambient room conditions for 24 h and stored in deionized water. Cyclic voltammetry was performed in a one-chamber, three-electrode cell. The area of the working electrode exposed in the cell was 0.48 cm². The reference and auxiliary electrodes were a silver-silver chloride and a platinum electrode, respectively. The electrolyte and sample solutions used were degassed with N₂ prior to cyclic voltammetric measurements.

Ion-Exchange Studies. PTMAFS-NO₃⁻ powder was prepared by soaking PTMAFS-Cl⁻ powder in 1 M HNO₃ for 17.5 h to replace Cl⁻ in PTMAFS by NO₃⁻. The powder was then washed with deionized water until the pH of the filtrate was nearly neutral. Exactly 0.1 g of PTMAFS-NO₃⁻ powder was added to 10 mL of various stock anion solutions. All anion stock solutions were made to be 0.03 M. The mixtures were mechanically shaken for 3 h. Subsequently, the powder in the mixtures was allowed to settle and the clear solutions were analyzed using an UV-vis spectrometer. Since NO₃⁻ has a characteristic absorption peak at 300 nm, the increase of absorbance at 300 nm was monitored.

Potentiometric Measurements. Cell potentials were measured with a voltmeter at an ambient temperature of 25 °C. The potentiometric cell used was as follows: Ag/AgCl(s)/3 M NaCl/sample solution/PTMAFS-based membrane/0.01 M

Scheme 1^a



^a Key Reaction Involved in Sol-Gel Process with TMOS and TMSPTMA as Precursors

NaCl/3 M NaCl/AgCl(s)/Ag. The membrane was prepared by placing an aliquot (5 μL) of the sol-gel solution on a glass pipet tip. The internal diameter of the tip was ≈ 1 mm while the thickness of the membrane was ≈ 2 mm. After standing in air for ≈ 1 min, the membrane was immediately immersed in a 0.01 M NaCl solution for 24 h to avoid cracks during aging.⁷ Before use and between each measurement, the membrane was immersed in a 5 M NaCl solution for 20 min so that the membrane was maintained at identical conditions for each measurement. Selectivity coefficients, $k_{\text{Cl}^-,X}$, were obtained by using the separate solution method.⁹ The sample solutions contained 0.1 M of the tested anion in 1 mM phosphate buffer (pH 3.6).

Instrumentation. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 analyzer from 25 to 1000 °C under a nitrogen atmosphere. IR spectra were measured with a 16-PC Perkin-Elmer FTIR spectrometer by dispersing PTMAFS powder in KBr and pressed into pellet form. Thermal treatment of PTMAFS samples was performed in a Lenton LTF12/50/300 tube furnace. The specific surface area and mean pore diameter of PTMAFS were obtained from nitrogen sorption measurements at 77 K with a Micromeritics ASAP 2000 micropore analyzer according to the BET method.¹⁰ UV-vis spectra were obtained with a Shimadzu UV-160A spectrophotometer. Cyclic voltammograms were recorded with an EG&G PARC Model 173 Potentiostat and an EG&G PARC Model 175 Universal Programmer. All the EOF measurements and CE separations were performed in a Waters Quanta 4000 CE unit (Mildford, MA).

Results and Discussion

Synthesis and Characterization. Scheme 1 depicts the key sol-gel reaction involved in the present study. Several parameters were attempted to achieve a homogeneous sol-gel monolith. These parameters included the amount of catalyst, the water/silane ratio, and the prehydrolysis time of TMOS. All these factors primarily affect the rates and extents of hydrolysis of the two precursors, TMOS and TMSPTMA, and their subsequent condensation rates. Under acidic conditions, previous work suggests that the hydrolysis rate of silicon alkoxides is increased by an electron-donating

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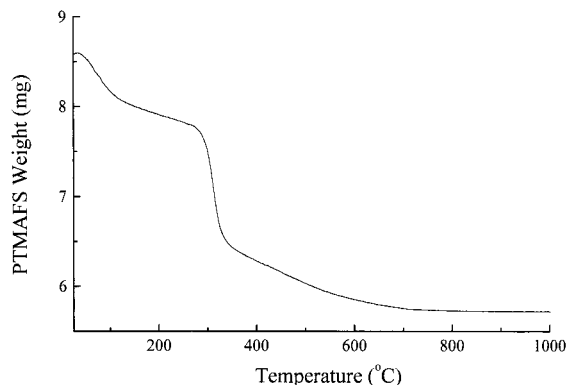


Figure 1. TGA thermogram of PTMAFS, rate of heating = 10 °C/min.

substituent and vice versa.¹¹ Thus, the difference in rates of hydrolysis between TMSPTMA and TMOS may cause phase separation and result in an opaque gel.¹² Our experimental results showed that either coexisting of the two sol-gel precursors, TMSPTMA and TMOS, at the beginning of the sol-gel reaction or prehydrolysis of TMSPTMA prior to the addition of TMOS always yielded opaque gels, even though various compositions of TMSPTMA, TMOS, water, and HCl were tried extensively. As such, the propyl-*N,N,N*-trimethylammonium (PTMA) group behaves as an electron-donating group. Normally, a visually transparent sol-gel monolith was formed with ≈ 6 h of prehydrolysis of TMOS. Otherwise, opaque gels were obtained (for <6 h of prehydrolysis of TMOS).

The final products were characterized by using FTIR spectroscopy, TGA, nitrogen sorption analysis, and UV-vis absorption spectroscopy. The IR spectra confirm the formation of a silica network (e.g., Si-O-Si stretching at 1000–1200 cm^{-1})¹³ and the presence of a $-\text{N}(\text{CH}_3)_3^+$ functional group (e.g., N-CH₃ bending at 1494 cm^{-1}).¹⁴ The IR spectra also suggest that there are a number of terminal Si-OH's on the PTMAFS surface, as identified by the band at 950 cm^{-1} .¹⁵ All the samples exhibit excellent optical transparency to visible light. When coated on glass slides, the transmittance of PTMAFS is close to that of the TMOS-derived sol-gel silica in the wavelength range 400–700 nm.

Thermogravimetric profiles for the lyophilized xerogels all contained similar features, as shown in Figure 1. Between 24 and 135 °C, the material presents an initial mass loss of 6.9% due to physically adsorbed water.¹⁶ The high initial mass loss indicates that the surface is very hydrophilic.¹⁷ Thermal decomposition of the organic moieties (PTMA and remaining unhydrolyzed methoxyl groups) occurred at about 236 °C. At 870 °C, the organic components were completely decomposed

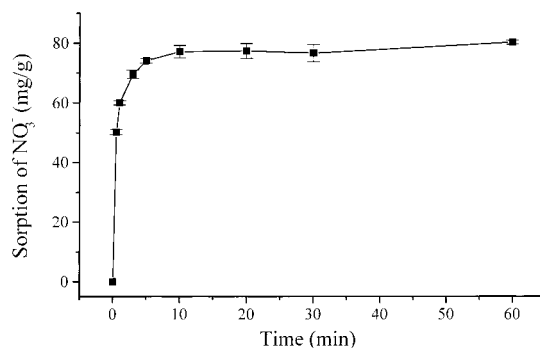


Figure 2. Amount of NO_3^- sorption in milligrams by 1 g of PTMAFS-Cl⁻ in 25 mM NO_3^- solution at pH 1.2 with respect to time.

and vaporized, leaving behind only the inorganic silica, as evidenced by the disappearance of C-H and N-CH₃ bands in the IR spectra. Excluding the weight loss due to residual methanol and water, the total weight loss is 26.7% for the hybrid material, which is slightly higher than the calculated value of 24.1% organic content (percent PTMA), assuming that all the methoxy groups are hydrolyzed and condensed. This discrepancy is probably due to incomplete hydrolysis of TMSPTMA at the gelation point since the addition of TMSPTMA to the hydrolyzed TMOS sol caused gelation in only about 8 min.

The total surface area and average pore radius of the material were found to be 404 m^2/g and 3.65 nm, respectively. These numbers are typical for pure sol-gel silica prepared under similar conditions.^{5c,18} The porous nature of the material is also illustrated by the response curve as shown in Figure 2, which was presented as the amount of NO_3^- sorption by PTMAFS powder with respect to time. The response time was <10 min, suggesting that the PTMAFS powder is porous enough for anions to diffuse into and out of the powder freely. The response time should be further improved when it is coated as a thin film. Previously, we showed that a sol-gel material when coated as a thin film had a response time as short as 0.3 s.^{4c}

Isoelectric Point. The isoelectric point of the PTMAFS surface was characterized by capillary electrophoresis using dimethyl sulfoxide as the neutral marker. The effect of having both PTMA and silanol on the PTMAFS surface can be illustrated by measuring the electroosmotic flow (EOF) in the capillary coated with PTMAFS. Curve a of Figure 3 depicts the electroosmotic mobility obtained in 15 mM phosphate solutions (buffered at constant ionic strength) in the pH range of 2.5–6.0. Both magnitude and direction of the EOF change with the pH of the running electrolyte. At pH above 5, the direction of the EOF is from anode to cathode and the EOF increases as the pH increases, as is the case in a bare fused-silica capillary. At pH below 5, however, the direction of the EOF is reversed and becomes from cathode to anode, and the EOF increases as the pH decreases. At pH 5, the EOF is suppressed ($<4 \times 10^{-5}$

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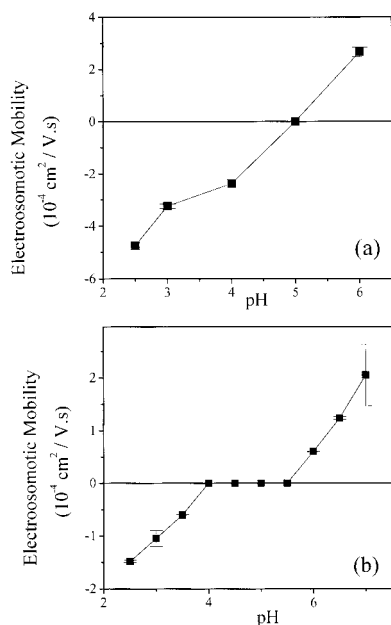


Figure 3. Plots of electroosmotic mobility versus the pH of the running electrolyte: (a) 15 mM phosphate and (b) 40 mM citrate. In both plots, EOF in the upper panel moved toward the cathode while EOF in the lower panel moved toward the anode. PTMAFS-coated capillary: 30 cm \times 75 μm i.d.

cm^2/Vs). The EOF in this pH range was monitored for about 60 min using both positive and negative polarities of the power supply. A signal corresponding to the neutral marker was not observed during the time monitored. As such, we assume the EOF at this pH to be zero. These results indicate that a desirable EOF direction can be switched by adjusting the pH of the running electrolyte. Such phenomena were also observed on other modified columns.^{3,19}

Curve b of Figure 3 depicts the electroosmotic mobility obtained in 40 mM citrate solutions (buffered at constant ionic strength) in the pH range of 2.5–7.0. At pH above 5.5, the direction of the EOF is from anode to cathode and the EOF increases as the pH increases, as is the case in a bare fused-silica capillary. However, the direction of the EOF is reversed and becomes from cathode to anode at pH below 4.0, and the EOF increases as the pH decreases. Interestingly, in the pH range 4.0–5.5, the coated capillary exhibits no EOF, indicating a net zero charge on the coating surface at more than a single pH.

The magnitude and direction of the EOF depend on the number and sign of net charges^{3,19} and hence the relative concentration of PTMA and ionized silanol on the inner surface of the capillary. Because of the existence of two types of surface silanols²⁰ that have different pK_a values²¹ on the PTMAFS surface, an increase of solution pH will cause dissociation of the two types of surface silanols to different extents. This manifested the plot of surface SiO^- concentration versus pH for a silica surface as two separate titration curves.²¹ Since PTMA has a positive charge over the whole pH

range in this study, the ionization of the surface silanols essentially determines the number and sign of the net charges on the PTMAFS surface. At pH values above 5 (with 15 mM phosphate solutions), the number of ionized silanols is higher than that of PTMA; therefore, the PTMAFS surface bears a net negative charge and the EOF is from anode to cathode. At pH below 5 (with 15 mM phosphate solutions), there is more PTMA than ionized silanols. As a result, the EOF is reversed. At a pH of ≈ 5 , the coated capillary exhibits no EOF, indicating a net zero charge on the PTMAFS surface. This surface isoelectric point, however, slightly shifted according to the preparation conditions since a small change in the sol-gel condition (e.g., temperature or relative humidity) may lead to a change in the number of surface silanols. It should also be noted that the surface isoelectric point is a weak function of solution ionic strength since the acid dissociation constants of the surface silanols depend on the solution ionic strength as well.

Surprisingly, with 40 mM citrate solutions as the running electrolyte, the coated capillary exhibits no EOF in the pH range 4.0–5.5, indicating an almost net zero charge on the PTMAFS surface over a wide pH range. It has been shown that the effective charge (or ζ potential) at the plane of shear²² is a function of the charge per unit surface area and the thickness of the electrical double layer.²³ Citric acid has a pK_2 at 4.76, which is close to the isoelectric point of the PTMAFS surface. With an increase in solution pH around 4.8, the thickness of the electrical double layer decreases because of the increased number of higher charged citrate molecules in the diffuse layer.²⁴ On the other hand, the number of ionized silanols increases in the same pH range. Consequently, the two effects cancel each other between pH 4.0 and pH 5.5 and results in an isoelectric range.

Capillary electrophoresis (CE) has shown great potential in becoming a powerful separation tool for the analysis of complex mixtures,²³ in which permanent coatings have often been used to modify the capillary wall to gain more control of the EOF and/or provide an alternative separation mechanism. It has been very difficult, however, to prepare capillary coatings with characteristics such as simplicity, good reproducibility, sufficient retention, high loadability, and long lifetime. Recently, it has been shown that coatings fabricated by sol-gel processing offer good retentive characteristics and hydrolytic stability compared to phases prepared by more conventional methods.^{4a,19,25} In addition to the above characteristics, the three-stage EOF pattern offered by PTMAFS is beneficial for the separation of a wide range of species using only a single capillary column. The applications of PTMAFS to CE using such three-stage EOF patterns will be reported elsewhere.⁸

The isoelectric point of the PTMAFS surface was further characterized by cyclic voltammetry. As shown

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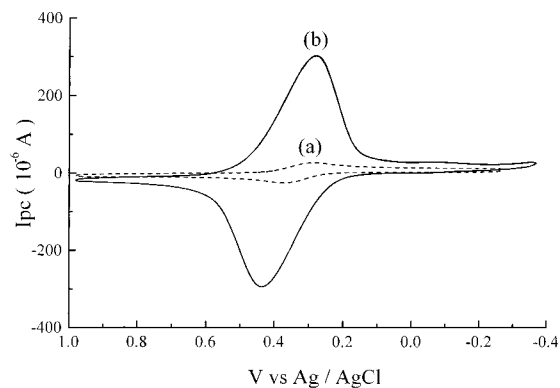


Figure 4. Cyclic voltammograms of 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$ in 0.1 M NaNO_3 (pH 3.0) at (a) a bare ITO electrode and (b) a PTMAFS-coated ITO electrode; scan rate = 100 mV/s.

in Figure 4, a comparison of the bare electrode response to $\text{Fe}(\text{CN})_6^{3-}$ with the PTMAFS-coated electrode response indicates that $\text{Fe}(\text{CN})_6^{3-}$ preconcentrates into the PTMAFS film to enhance the current. We attribute this behavior to the interaction of negatively charged $\text{Fe}(\text{CN})_6^{3-}$ ions with the positively charged PTMA groups inside the sol-gel film. However, this interaction may be weakened when a neighboring surface silanol dissociates. On the other hand, the magnitude of the diffusion current depends not only on the concentration but also on the diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$ inside the film. It has been suggested that surface interaction was very important in determining the diffusion rate inside a porous film.²⁶ Such surface interaction should relate to the ζ potential at the plane of shear. Hence, the diffusion current of $\text{Fe}(\text{CN})_6^{3-}$ should be pH-dependent in a range determined by the pK_a of the surface silanol and the pK_a of the supporting electrolyte. To verify this, a pH study was carried out to determine the effect of solution pH on the diffusion current of $\text{Fe}(\text{CN})_6^{3-}$.

PTMAFS-coated electrodes were immersed into 1.0 mM $\text{Fe}(\text{CN})_6^{3-}$, 0.1 M phosphate solutions of varying pH for 2 min for uptake. The pH values for the solution had been adjusted from 1 to 10 using 0.1 M HNO_3 or NaOH . A voltammogram was taken after waiting 2 min for equilibrium to occur. Figure 5a shows the cathodic peak current, I_{pc} , measured from the voltammograms versus the solution pH. The condition (e.g., concentration of $\text{Fe}(\text{CN})_6^{3-}$ and scan rate, ν) at which the electrode processes occurred were predominately diffusion-controlled processes, as indicated by the linear dependency between I_{pc} and $\nu^{1/2}$.²⁷ The shape of the curve is sigmoidal, with a point of inflection at about 4.8. Between pH 8 and pH 10, the cathodic peak current is constant and relatively small, indicating that, under alkaline conditions, the surface silanols were essentially all deprotonated. Below pH 8, there is a gradual upturn in the curve. Apparently, more surface silanols in the PTMAFS film were protonated at lower solution pH, and the surface interaction between the negatively charged $\text{Fe}(\text{CN})_6^{3-}$ ions and positively charged PTMA groups increased. At the inflection point of the curve, it is likely that the surface is in an isoelectric condition.

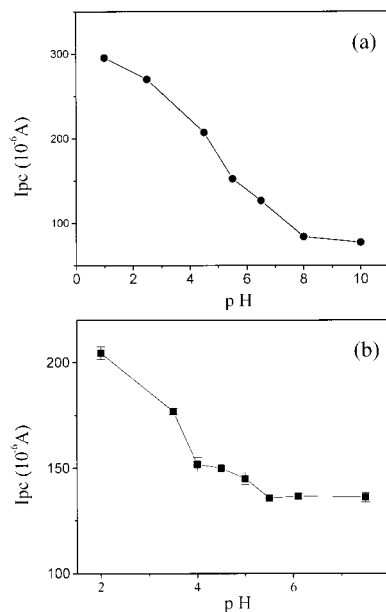


Figure 5. Effect of solution pH on cathodic peak current, I_{pc} , in (a) 1.0 mM $\text{Fe}(\text{CN})_6^{3-}$, 0.1 M phosphate, and (b) 1.0 mM $\text{Fe}(\text{CN})_6^{3-}$, 0.1 M citrate. Working electrode: PTMAFS-coated ITO electrode; film coating at 1500 rpm; immersion time, 2 min; scan rate = 100 mV/s.

As a result, a small change in solution pH will lead to a sharp change in the cathodic peak current. The solution pH at this inflection point also agrees with the surface isoelectric point determined by capillary electrophoresis.

The effect of the supporting electrolyte on the surface isoelectric point was also evaluated. PTMAFS-coated electrodes were immersed into 1.0 mM $\text{Fe}(\text{CN})_6^{3-}$, 0.1 M citrate solutions of varying pH for 2 min for uptake. The pH values for the solution had been adjusted from 2 to 7.5 using 0.1 M HNO_3 or NaOH . A voltammogram was taken after waiting 2 min for equilibrium to occur. Figure 5b shows the cathodic peak current measured from the voltammograms versus the solution pH. Between pH 5.5 and pH 7.5, the cathodic peak current is constant and relatively small, indicating that the surface silanols were essentially all deprotonated.

Interestingly, between pH 4 and pH 5, the cathodic peak current is also constant but is higher than that between pH 5.5 and pH 7.5. Below pH 4, there is a sharp upturn in the curve, indicating that protonation of surface silanols lead to increased surface interaction between $\text{Fe}(\text{CN})_6^{3-}$ and PTMA in the sol-gel film. Such a trend is consistent with Figure 3b determined by capillary electrophoresis, further confirming that the PTMAFS film has a surface isoelectric range with citrate as a supporting electrolyte.

Exchange Capacity and Selectivity. PTMAFS has a calculated 24.1% PTMA by weight (see previous section) and thus a theoretical anion-exchange capacity of 1.236 mequiv/g, assuming that all the PTMA substituents in PTMAFS are available for exchange in the lyophilized gel. The practical anion-exchange capacity of PTMAFS was determined by immersion of 0.1 g of PTMAFS- NO_3^- powder in Cl^- solution (10 mL, 1.24 M, the amount used is 100 times in excess of the number of exchange sites) at pH 2.1 for 3 h. Since silica has an

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Table 1. Selectivity Factors, $\alpha_{\text{NO}_3^-, \text{X}^{n-}}$ and $\alpha_{\text{Cl}^-, \text{X}^{n-}}$, of PTMAFS for Selected Anions at pH 6.9

anion, X^{n-}	$\alpha_{\text{NO}_3^-, \text{X}^{n-}}$	$\alpha_{\text{Cl}^-, \text{X}^{n-}}$	anion, X^{n-}	$\alpha_{\text{NO}_3^-, \text{X}^{n-}}$	$\alpha_{\text{Cl}^-, \text{X}^{n-}}$
NO_3^-	1	2.0	phosphate	0.67	1.4
citrate	0.95	1.9	Br^-	0.64	1.3
SO_4^{2-}	0.89	1.8	Cl^-	0.49	1
I^-	0.75	1.5	acetate	0.27	0.55

Table 2. Observed Membrane Potential and Potentiometric Selectivity Coefficients ($k_{\text{Cl}^-, \text{X}^-}$) of the PTMAFS-Based Membrane for Selected Anions at pH 3.6^a

anion, X^-	membrane potential (V)	$k_{\text{Cl}^-, \text{X}^-}$
NO_3^-	0.277 ± 0.004	3.0
Br^-	0.299 ± 0.004	1.3
Cl^-	0.305 ± 0.002	1
acetate	0.332 ± 0.017	0.35

^a A similar trend was also observed at pH 6.9. However, at this pH, the difference in the observed potentials for two succeeding anions in the selectivity order is barely larger than the measurement errors, probably because the dissociated silanols weaken the ion-exchange interactions.

isoelectric point at about pH 2,²⁸ the amount of NO_3^- released at the above solution pH was then used to calculate the practical exchange capacity. This value was found to be 1.14 ± 0.05 mequiv/g, which is $92.6 \pm 4.0\%$ of the theoretical anion-exchange capacity. In other words, the molar ratio of NO_3^- sorption to PTMA substituent in PTMAFS is close to 1, suggesting that almost all the PTMA substituents in PTMAFS are active and are exposed on the surfaces of the sol-gel-derived pores. The inactive PTMA substituents are probably buried in the inorganic matrix or form an ion pair with a neighboring surface silanol group. We presently do not have any means to distinguish these two features.

The selectivity factors (or separation factors)^{1,29} of PTMAFS- NO_3^- toward some selected anions was investigated by immersion of portions of 0.1 g of PTMAFS- NO_3^- powder in separate solutions of each anion (10 mL, 30 mM) at pH 6.9 for 3 h. The amount of NO_3^- released was used to calculate the selectivity factors of PTMAFS for the anions relative to NO_3^- . The material formed in this way exhibits a selectivity order similar to that of strong base anion exchangers^{29,30} (i.e., citrate > SO_4^{2-} > I^- > phosphate \approx Br^- > Cl^- > acetate), as shown in Table 1. For applications of PTMAFS to potentiometric sensors, the potentiometric selectivity order is more relevant. As such, the membrane potentials and hence the potentiometric selectivity coefficients of the PTMAFS-based membrane for several selected anions were determined, as shown in Table 2. In comparison with the selectivity order as shown in Table 1, the potentiometric selectivity order follows closely.

Interestingly, selectivity toward Cl^- over more lipophilic anions is significantly improved, deviating from the Hofmeister selectivity pattern.³¹ For an anion exchanger, the anion selectivity is governed by the ratio of the partition coefficients of primary and interfering anions in the sample solution. As such, the lack of

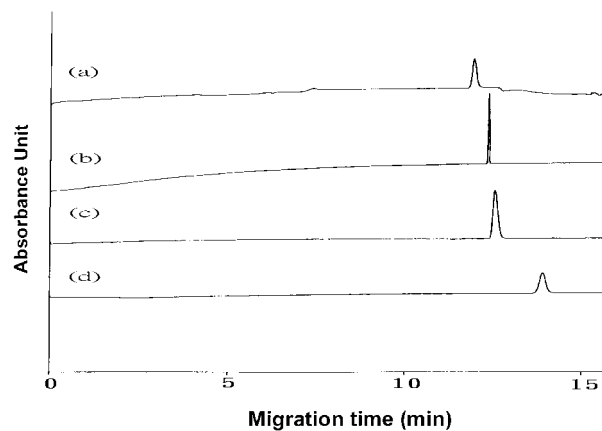


Figure 6. Electropherogram of 1,3-benzenedicarboxylic acid and the competing anion, X^{n-} : (a) citrate, (b) sulfate, (c) chloride, and (d) acetate. Conditions: mobile phase, 40 mM phosphate and 60 mM X^{n-} , pH 4.5; PTMAFS-coated capillary, 35 cm \times 75 μm i.d.; separation voltage, -5 kV; detection wavelength, 214 nm; temperature, 26.8 ± 0.5 °C.

lipophilic plasticizers in our sol-gel matrix improves selectivity toward Cl^- , which is more hydrophilic. For example, a 5.7-fold and 4.1-fold improvement in selectivity toward Cl^- over I^- were achieved for our material as compared to those of a Dowex 1 anion-exchange resin³⁰ and another sol-gel-derived material that was doped with tridodecylmethylammonium chloride (TDMAC),^{2b} respectively. Our PTMAFS also has a 5.4-fold and 1.5-fold improvement in selectivity toward Cl^- over Br^- as compared to those of other sol-gel-derived materials that were doped with trioctylmethylammonium chloride (TOMAC)^{2a} and TDMAC,^{2b} respectively. These differences in selectivity are probably because our PTMA group is less lipophilic than either TDMAC or TOMAC and our sol-gel matrix is less lipophilic than the organic Dowex 1 matrix. Such improvement in selectivity toward Cl^- over more lipophilic anions is important for development of ion-selective electrodes^{2b} and ion-selective field-effect transistors^{2d} for blood chloride measurements. Furthermore, the incorporation of a PTMA group through covalent bonding also avoids the problem of leaking.

In chromatography or electrochromatography, the ion exchange between the stationary phase and the mobile phase would be a nonequilibrium type. As such, it is important to compare the relative anion-exchange selectivity of PTMAFS in both equilibrium and nonequilibrium modes. Figure 6 shows a series of electropherograms of 1,3-benzenedicarboxylic acid and a competing anion (citrate, sulfate, chloride, or acetate) in a 40 mM phosphate buffer solution at pH 4.5. Under such conditions, the EOF is suppressed ($< 5 \times 10^{-5}$ cm²/Vs). The EOF at this pH was monitored for about 60 min using both positive and negative polarities of the power supply. A signal corresponding to the neutral marker was not observed during the time monitored. Thus, we assume the EOF at this pH to be zero. As shown in the figure, the migration time of 1,3-benzenedicarboxylic acid increases if the competing co-anion changes in the following order: citrate, sulfate, chloride, and acetate. This trend is consistent with the relative anion-exchange selectivity determined in our sorption studies. Furthermore, it demonstrates that the relative contributions of anion exchange and electromigration can

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potentially be controlled by a competing co-anion in the eluent. In general, it is more difficult to manipulate selectivity in CE than in ion chromatography.³² Nevertheless, the use of the PTMAFS stationary phase provides a way to manipulate the separation selectivity of anions in CE.

Conclusions

We have prepared a new organically modified silica material via the sol-gel process. The material has been shown to be effective for anion exchange. The ion-exchange capacity of the material is about 1.14 mequiv/g, which is comparable to many commercially available resins. The material also shows an improved selectivity toward chloride over more lipophilic anions such as iodide. This improved chloride selectivity is believed to be useful for blood chloride measurement. In addition, the improved selectivity toward more hydrophilic anions

may also provide an alternative to manipulate selectivity in ion chromatography and capillary electrochromatography. When the material was applied as a coating for fused-silica capillaries, a three-stage EOF pattern was observed in citrate solutions. This switchable EOF behavior is believed to be beneficial for the separation of a wide range of species using only a single capillary column. Moreover, the material can preconcentrate anions. This property is beneficial to the improvement of the detection limit in many sensing applications. Further research is underway to develop this material for sensing applications.

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