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Abstract

A procedure to immobilize quaternary ammonium salts in solid silica supports is described. The process is based on the doping of sol–gel glasses by organic anion-exchange compounds during the polymerization of the glasses. Sol–gel glasses doped with Aliquat 336, cetyltrimethylammonium bromide, or cetylpyridinium bromide may serve as solid anion exchangers, exhibiting selectivity properties similar to strong base ion exchangers. This process provides a simple method for the preparation of silica-based ion exchangers.

INTRODUCTION

During the last few years, low temperature production of silica glasses by hydrolysis and condensation of tetralkoxysilanes (e.g., tetramethoxysilane or tetraethoxysilane) has found many applications, particularly for electric insulation, protective coating, and construction of optical equipment (*1*). It has been demonstrated (*2–4*) that it is possible to entrap organic compounds in those solid porous glasses during the low temperature polymerization process. Braun et al. produced biochemically active sol–gel glasses doped with enzymes (*5*). Zusman et al. (*6*) exploited this

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phenomenon to produce colorimetric sensors, and Lev et al. (*7*) prepared high sensitivity spectrophotometric detectors by trapping chromophoric organic reagents within the sol–gel glasses. We hereby report on the immobilization of quaternary ammonium salts in sol–gel glasses and discuss the advantages and limitations of these new silica-based ion exchangers.

Anion exchangers based on a silica matrix combine the physical properties of the glass, such as thermal stability, rigidity, and polar microenvironment, with the exchanging properties of the organic functional groups (*8*). These anion-exchange glasses are produced by covalent bonding of onium salts to a commercial silica gel (*9*). The proposed method to construct ion exchangers is much simpler than covalent bonding and may be used to manufacture glasses in any desired shape, including membranes, supported thin layers, and granular resins.

EXPERIMENTAL DETAILS

Reagents

Tetramethoxysilane was obtained from Petrarch Inc. Aliquat 336 (technical grade methyltrioctylammonium chloride), Alamine 304 (mainly trilaurylamine), and Alamine 336 (mainly trioctylamine) were purchased from General Mills, Inc. DINA (mixed isomers of di-isononylamine) and D_2EHA (di-2-ethylhexylamine) were purchased from Hoechst Celanese. Primene JM-T (principally t-$C_{18}H_{37}NH_2$ to t-$C_{22}H_{45}NH_2$) was purchased from Rohm and Haas Co. TEHA (tris-(2-ethylhexyl) amine) was purchased from Sigma. Cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB) were purchased from Fluka. Triple distilled water and analytical-grade reagents were used.

Analytical Equipment

A Tracor HPLC equipped with a Tracor 970 UV/Vis detector (330 nm) was used for ion chromatography. The anions were separated by a Wescan 269001 anion-exchange column. A dilute solution (approximately 2 m*M*) of potassium hydrogen phthalate (pH 4.5) was used as eluent. A Dohrmann Carbon Analyzer (DC-80) was used for the determination of total organic carbon. The analyzer was calibrated with a dilute solution (2000 mg/L) of potassium hydrogen phthalate.

Preparation of Sol–Gel Glasses

Quaternary ammonium compounds were immobilized in the glasses by the following procedure: A solution of methanol, water, and the anion-exchange compound (e.g., Aliquat 336, CTAB) was prepared and mixed with tetramethoxysilane (TMOS) in a 20-mL bottle. Typical weight ratios employed were (H_2O/methanol/TMOS/organic dopant) = (2.9/3/2.2/0.1–0.4). The pH of the solution was adjusted to the required level by addition of HCl or NaOH solution. The bottles were covered with aluminum foil and were let to stand for several days. After the gel was formed, the glasses were transferred to a 40°C incubator for 2 weeks and until no further weight changes could be detected. The glasses were then ground prior to the selectivity and leaching tests.

Selectivity Experiments

The glasses containing quaternary ammonium groups were immersed in a 1-*N* NaCl (or NaBr when appropriate) solution for several hours to remove traces of undesirable anions. The glasses were then washed thoroughly with distilled water and dried in a 50°C oven. Approximately 1 g of the glass was immersed in 100 mL distilled water and allowed to stand for 1 day, after which stock solutions containing the counterion (Br^-, SO_4^{2-}, NO_3^-) were added. The glasses were shaken gently on an Arig-Levi shaker for several hours until equilibrium was reached. The concentrations of the anions in the solution were analyzed by ion chromatography. Glasses containing immobilized amine groups were equilibrated in a 1-*N* HCl solution, rinsed with a 1-m*M* HCl solution, the pH was adjusted to pH 5, and the selectivity isotherms were determined following the above procedure.

Leaching Experiments

We used a qualitative screening procedure and quantitative leachability tests.

a. Qualitative Procedure

Doped glasses were washed slowly with 1 L distilled water. The aliquot was collected and analyzed by a total organic carbon (TOC) analyzer. The glasses were then immersed in a solution containing a different counterion (0.01 *N* NaBr for onium-chloride and 0.01 *N* NaCl for onium-bromide compounds), and the solution was analyzed by ion chromatography after an equilibration of several hours. The absence of the original counterion in the solution signified a lack of exchanging capacity.

b. Quantitative Procedure

The glasses were immersed in distilled water for several days. The solution was sampled periodically and analyzed for chlorides (or bromides) and TOC.

RESULTS

Selectivity experiments were conducted using three immobilized quaternary ammonium exchangers in order to determine the total capacity

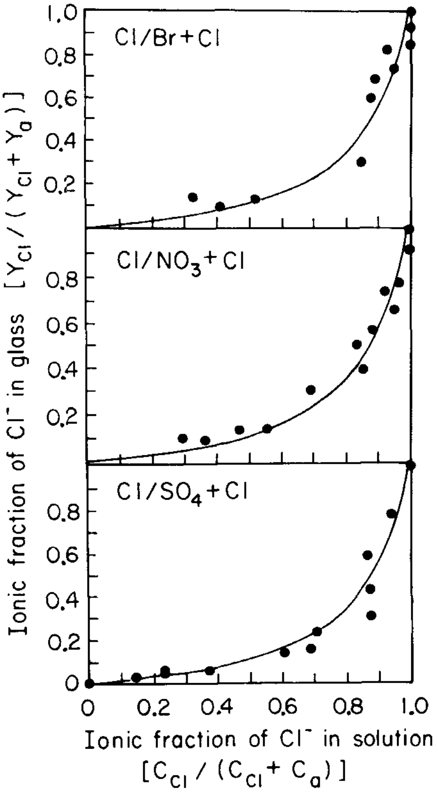

FIG. 1. Selectivity isotherms of glass immobilized Aliquat 336: (top) Br^-/Cl^-; (middle) NO_3^-/Cl^-; (bottom) SO_4^{2-}/Cl^- (C_a and y_a represent concentrations of the counterion).

and exchange selectivity of silica-based resins. Aliquat 336 exhibited the best chemical stability and was singled out for more extensive investigations. Figure 1 demonstrates the binary exchange isotherms of SO_4^{2-}, Br^- and NO_3^- versus Cl^- in glasses doped with Aliquat 336. Table 1 summarizes the best fit separation factor (K) for the anions tested:

$$K = C_a y_b / C_b y_a \qquad (1)$$

where C_a and C_b, y_a and y_b are the equilibrium concentrations of the counterions a or b in the solution and in the resin phase, respectively (*10*). Similar binary isotherms were constructed for immobilized CPB and CTAB. Table 2 compares the separation factors (K) obtained by selectivity experiments for nitrate versus bromide exchange by the immobilized quaternary ammonium compounds CPB, CTAB, and Aliquat 336.

TABLE 1
Separation Factors of Aliquat 336 Immobilized in Sol–Gel Glasses

	Br$^-$/Cl$^-$	NO$_3^-$/Cl$^-$	SO$_4^{2-}$/Cl$^-$
Separation factors (*K*)	7.0	7.5	8.7
Theoretical capacity (meq/g)	0.52	0.27	0.51
Practical capacity (meq/g)	0.22	0.11	0.22

TABLE 2
NO$_3^-$/Br$^-$ Separation Factors of CTAB, CPB, and Aliquat 336 Immobilized into Glass Supports

	CTAB	CPB	Aliquat 336[a]
Separation factor *K*	1.5	0.95	1.07
Theoretical capacity (meq/g)	0.22	0.3	0.5
Practical capacity (meq/g)	0.05	0.08	0.22

[a] Computed from Cl$^-$/NO$_3^-$ and Cl$^-$/Br$^-$ *K* values.

The following test confirmed that the exchange capacity of the doped glasses is due to entrapped ammonium groups rather than adsorption phenomena. Porous glasses prepared by the sol–gel process without any addition of organic dopant were immersed in a saturated solution of Aliquat 336. The glasses were then washed with 1 L distilled water according to the same procedure applied to the doped glasses prior to the selectivity

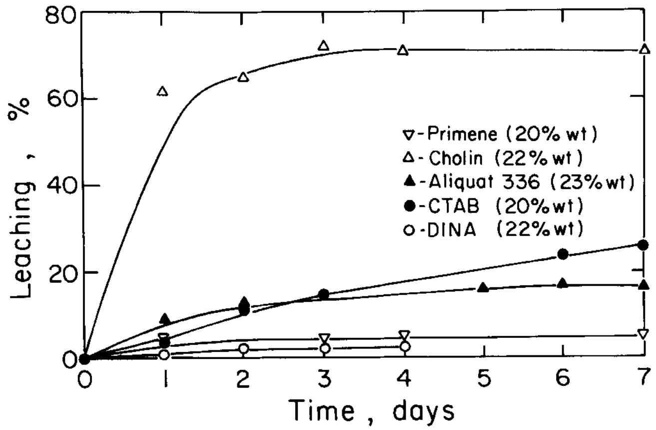

FIG. 2. Leaching of anion-exchange compounds immobilized in glass support by polymerization at pH 7.

tests. Exchange experiments with these glasses did not reveal any detectable exchange capacity, confirming that the immobilization of the ammonium salts in the polymerization process cannot be attributed to an adsorption mechanism only.

Leaching Tests

Leaching tests were conducted to investigate the stability of typical immobilized quaternary ammonium and primary, secondary, and tertiary organic amines. The quaternary ammonium compounds CTAB, CPB, and Aliquat 336 and the amines Primene JMT and DINA were successfully immobilized in the glass phase. D_3EHA, TEHA, Alamine 304, Alamine 336, and the choline chloride were leached from the glasses. Representative leaching curves are presented in Fig. 2. The concentration of the leachate in the solution rises until a plateau is reached. However, extensive washing of the glasses for several days under a continuous flow of water eventually leached all the dopants from the glasses. Figure 3 shows that the pH of the polymerization step had no significant effect on the leaching rate of Aliquat 336 from the glasses, despite the fact that pore size may be greatly increased by a higher pH.

DISCUSSION AND CONCLUSIONS

Our preliminary results indicate that it is possible to immobilize quaternary onium salts in a solid silica support by using the sol–gel polymerization procedure. The glasses formed in this way exhibit a selectivity

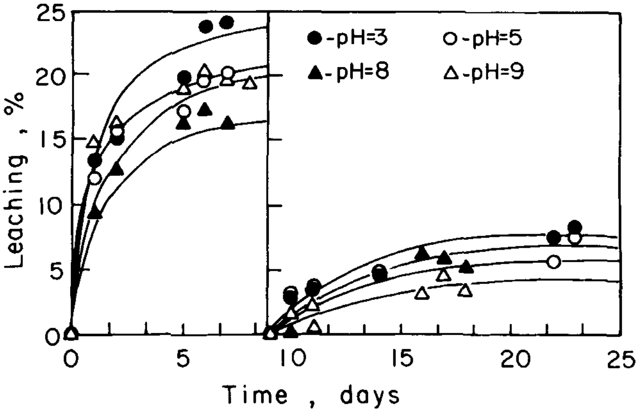

FIG. 3. Leaching of Aliquat 336 from sol–gel glasses produced at various acidities. The solution was replaced after 10 days.

order similar to strong base anion exchangers (i.e., $SO_4^{2-} >> NO_3^- > Br^- > Cl^- >> OH^-$). Chemical adsorption cannot account for the observed phenomenon because of the much higher chemical stability of the entrapped compounds relative to surface adsorption.

The testing of a wide variety of anion exchangers show that in order to obtain good trapping and good exchange activity, one has to use quaternary salts and not free bases. Thus the quaternary Aliquat 336, CPB, and CTAB (Fig. 4) remained immobilized in the glass matrix and exhibited substantial ion-exchange capacity, while none of the free anions worked: these were either leached out easily (choline chloride, D_2EHA, and the tertiary amines TEHA, Alamine 336, and Alamine 304) or were trapped but remained nonactive (Primene JMT and DINA). The leached out amines are all bulky tertiary amines (Fig. 4) and a highly branched secondary amine (D_2EHA). These suffer from substantial steric hinderance which does not allow them to form the R_3N^+H—^-O—Si— bond which is necessary for good dispersion in the glass. They apparently form silanophobic clusters which are easily leached out (*11*). The less hindered DINA and the Primene JMT

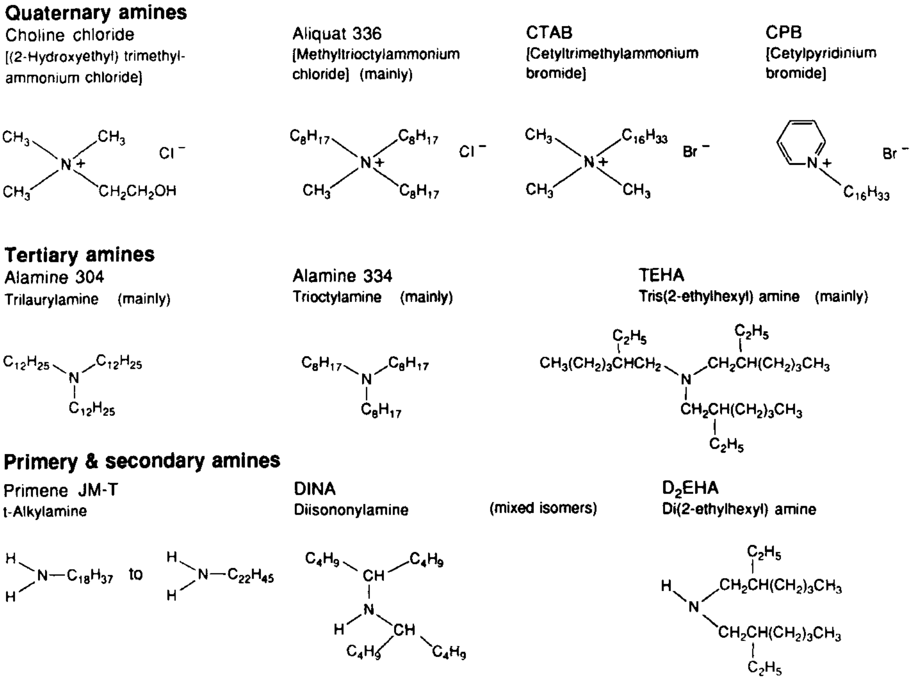

FIG. 4. Typical strong base ion-exchange compounds.

do form these bonds, but since these are exceedingly strong bonds (*12*), the formation of the ammonium chloride salts at the appropriate pH, which is necessary for efficient exchange activity, does not take place. Supporting evidence for this type of mechanism may be drawn from the fact that glasses doped with the amine groups did not exhibit the buffering capacity characteristic of amine compounds near their pK_a's.

These problems are avoided with the quaternary ammonium salts: They cannot form the strong bond just mentioned, but they still are capable of forming regular bonds of the form $(R_4N^+\cdots OH—Si—)Cl^-$ which allow good dispersion and trapping, and leaves the chloride for the necessary exchange activity. It should be noted that the quaternary choline chloride (Fig. 4) is an exception. It is only partially (30%) trapped, and it shows no exchange activity. A possible clue to this exception is the existence of $—CH_2—OH$ groups in its structure, allowing intermolecular (or even intramolecular) hydrogen bonding instead of the necessary bonding to the silanol.

Finally, it should be noted that there is a price for the advantages of using the glass matrix and of the simplicity of the preparation procedures: Not all the trapped molecules are open for reactivity with the environment, and a portion remains completely encapsulated. This shows up in the lower exchange capacities (Tables 1 and 2), but then one should recall that differences between actual and theoretical capacity (and dependence of the capacity on ionic size) is common to all the highly crosslinked commercial resins due to steric hinderance phenomena (*13*).

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