

Unexpected Interactions between Sol–Gel Silica Glass and Guest Molecules. Extraction of Aromatic Hydrocarbons into Polar Silica from Hydrophobic Solvents

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Properties of a solute may differ greatly between a free solution and that solution confined in pores of a sol–gel glass. We studied the entry of various aromatic organic compounds from solution into the monolith of sol–gel silica immersed in this solution. Partitioning of the solute is quantified by the uptake coefficient, the ratio of its concentrations in the glass and in the surrounding solution at equilibrium. The dependence of this coefficient on the solvent gives insight into possible interactions between the solute and the silica matrix. We report the uptake of 31 compounds altogether: 18 halogen derivatives of benzene; 5 condensed (fused) aromatics; and stilbene and three substituted derivatives of it, each in both *cis* and *trans* configurations. When the solvent is hexane, the uptake coefficients are as follows: 1.0–1.9 for the halobenzenes; 3.0–4.6 for the hydrocarbons; and 3.3–4.9 for the stilbenes. When the solvent is carbon tetrachloride or dichloromethane, the uptake coefficients become 0.82–1.39 for the hydrocarbons and 0.90–1.25 for the stilbenes. The excessive uptake of organic compounds from hexane is unexpected, for it amounts to extraction of nonpolar or slightly polar solutes from a nonpolar solvent into a polar interior of silica glass. The solute–silica interactions responsible for this extraction are not of the van der Waals type. Our findings are consistent with hydrogen bonding between the aromatic π system in the solutes and the hydroxyl groups on the silica surface. Hexane cannot interact with this surface but dichloromethane and carbon tetrachloride can: they shield the hydroxyl groups from the organic solvents and thus suppress the hydrogen bonding. This explanation is supported by the emission spectra of the aromatic compound pyrene when it is dissolved in acetonitrile, dichloromethane, cyclohexyl chloride, and hexane and when it is taken up by monoliths of sol–gel silica from these four solutions. The relative intensities of the emission bands designated III and I change greatly when pyrene is taken up from hexane but remain unchanged when it is taken up from the other three solvents. Evidently, hexane does not, whereas the other three solvents do, line the silica surface and shield it from approach by pyrene molecules. Even though solute molecules are much smaller than the pores in the sol–gel glass, diffusion of these molecules into the monolith may result in an uneven partitioning at equilibrium. This fact must be taken into consideration in the design of biosensors, immobilized catalysts, and other composite materials because their function depends on the entry of analytes, substrates, and other chemicals into the glass matrix.

Introduction

The preparation of glasses by the sol–gel method is very useful in many branches of chemistry and materials science. Mild reaction conditions allow encapsulation of various organic, inorganic, and biological compounds into porous and transparent matrices.^{1–6} Because physical and chemical properties of the doped glasses can be altered by varying the experimental conditions during the preparation process, this method can be used for the fabrication of sensors, catalyst supports, coatings, special polymers, and other new materials.^{7–14}

The guest compounds can be encapsulated in silica as this matrix is being formed, or they can be diffused into the preformed glass from solution. The interactions at the molecular level between the glass matrix and the guest molecules may change the physical and chemical properties of the confined molecules. Understanding and control of these interactions are essential for purposeful design of doped sol–gel materials having desired properties.^{15–19}

Work in our laboratory has shown that interactions between the silica matrix on the one side and proteins, metal complexes, and organic compounds on the other can change the mobility and chemical reactivity of these guests.^{20–23} After studies of electrostatic interactions and of classical hydrogen bonding involving heteroatoms,²⁰ we turn our attention to even subtler and weaker forces, such as van der Waals interactions and nonclassical hydrogen bonding. These interactions of the guests with the surface of the sol–gel host may change the reaction rate inside the porous host, the availability of the immobilized molecules to the guests, and chemical equilibria inside the silica matrix. The interactions are important because they may affect the properties and performance of biosensors, immobilized catalysts, and other composite materials.

Experimental Procedures

Instrumentation. Proton, ¹⁹F, and ¹³C NMR spectra were recorded with a Varian 400 MHz instrument; UV absorption spectra with a Perkin-Elmer Lambda 18 spectrophotometer; and emission spectra with a Jobin Yvon Fluoromax-2 fluorimeter.

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Chemicals. Tetramethyl orthosilicate, acetonitrile, dichloromethane, and hexane were purchased from Fisher Chemical Co.; carbon tetrachloride, naphthalene, cyclohexyl chloride, 2,7-di-*tert*-butylnaphthalene, 4-methylbenzyl bromide, 2',4',6'-trimethylacetophenone, triphenylphosphine, carbon tetrabromide, 18-crown-6, and anthracene were from Aldrich Chemical Co.; pyrene, azulene, *trans*- and *cis*-stilbene were from Fluka Chemical Co.; and 3,4,5-trifluorobenzaldehyde was from Oakwood Products Inc. Distilled water was further demineralized to a resistivity greater than 17 M Ω cm.

Hazards. Aromatic compounds used in our study are either toxic or carcinogenic. Protective gloves and effective fume hoods must be used in experiments with these compounds!

Preparation of Silica Monoliths. The silica sol was prepared by a standard procedure.²⁴ A mixture of 15.76 g of tetramethyl orthosilicate, 3.38 g of water, and 0.30 g of 0.040 M HCl was kept in an ice-cooled ultrasonic bath for 30 min. Upon addition of 36.3 mL of a 10 mM sodium phosphate buffer at pH 7.00, gelation began. The sol was quickly poured into polystyrene cuvettes sized 10 \times 10 \times 40 mm and left at 4 $^{\circ}$ C. During the aging period (14 days), the monoliths were kept soaked and were washed with water twice a day. The aged monoliths were exposed to air, still at 4 $^{\circ}$ C, for another 14 days of partial drying and shrinking. The resulting transparent monoliths, prisms sized 8 \times 8 \times 27 mm, were soaked in acetonitrile and stored at 4 $^{\circ}$ C for further use. Defective monoliths and those deviating from the standard dimensions were rejected for the sake of reproducibility and accuracy of the experiments.

Dehydration of Silica Monoliths. Two silica monoliths sized 8 \times 8 \times 27 mm were soaked together in a series of stirred solvents in a capped Erlenmeyer flask. The first soaking was in 300 mL of acetonitrile, which was changed three times, after 2, 24, and 48 h; soaking then continued for an additional 24 h. The second soaking was in 150 mL of carbon tetrachloride, which was changed after 24 h; soaking then continued for an additional 24 h. The third soaking was in 300 mL of hexane, which was changed three times, after 2, 24, and 48 h; soaking then continued for an additional 24 h. In one series of experiments, the third step (instead of hexane) was 150 mL of cyclohexyl chloride, which was changed after 24 h; soaking then continued for an additional 24 h. In another series of experiments, two monoliths were similarly soaked first in 300 mL of acetonitrile, as above, and then in 300 mL of dichloromethane, which was replaced three times, after 2, 24, and 48 h. In all experiments, the Erlenmeyer flasks were chosen according to the solvent volume and were capped, to protect the dry solvents from the moist air. Dehydrated silica monoliths were stored for further experiments in a fresh portion of the solvent in which they had last been soaked.

General Procedure for Uptake Experiments. The concentration of each guest compound in stock solution was 1.8×10^{-5} M. The dehydrated silica monoliths sized 8 \times 8 \times 27 mm were the hosts. Each monolith was soaked in 50.0 mL of a stock solution in a capped vial. The monolith stood upright, with one of its small sides resting on the flat bottom of the vial and the other five sides exposed to the solution. From time to time, the monolith (without the surrounding solution) would be transferred to a quartz cuvette, sized 10 \times 10 \times 40 mm, that was kept in the sample holder of the spectrophotometer. An identical but undoped silica monolith made in the same batch as the doped monolith would be placed in another quartz cuvette that was kept in the reference holder. Each monolith would be held in the same place and in the same position in all experiments so that the absorbances could be accurately

compared. The UV spectra would be scanned at the rate of 120 nm/min, and the doped monolith would be returned to the solution of the guest compound (the dopant) and soaked further. Ultraviolet–visible spectra of different undoped monoliths prepared in the same batch were identical. Moreover, UV–vis spectra of doped monoliths did not change when different undoped monoliths from the same batch were kept in the reference beam of the spectrophotometer. The UV measurements were more frequent early in the experiment, when the uptake was relatively fast, and less frequent later, when the uptake slowed. The uptake was considered finished when the absorbance of the guest in the silica monolith ceased to change over time.

Uptake Coefficients. We define the uptake coefficient as the ratio at equilibrium of the guest concentrations in the glass (internal) and the surrounding solution (external) at the end of the uptake process. The external concentration was kept nearly constant during the uptake. To correct the absorbance for the path length, the raw ratio is divided by the width of the monolith, determined with the caliper. This final number is the uptake coefficient that we report. The standard deviation of all the absorbance ratios between the internal and external guest populations taken at every 0.2 nm over the UV–vis spectral range examined constitutes the error margins in tables of uptake coefficients. Since these coefficients may depend on the external concentration of the guest, we kept that constant, at 1.8×10^{-5} M. This concentration gave absorbances in the range of the greatest photometric accuracy. We avoided low or high absorbances because of the inherent inaccuracy in their recording. With stilbene as the guest, we varied the concentration while keeping the stilbene absorbance in the accurate range and found only small variations (less than 20%) in the uptake coefficients.

General Procedure for Fluorescence Experiments. Steady-state fluorescence spectra of pyrene were recorded both in solution and in the sol–gel silica monolith. The excitation was at 330 nm, and each spectrum was an average of three scans. The ratio of emission intensities at 383.2 nm (band III) and 371.8 nm (band I) is the III/I quotient.

A 1.0×10^{-5} M aqueous stock solution of pyrene in a 100-mL volumetric flask was purged with nitrogen for 10 min, and a 2.5-mL aliquot was transferred to a 10-mm fluorescence cuvette, which was capped and put in the fluorimeter.

The silica monolith sized 8 \times 8 \times 27 mm was immersed upright in 50.0 mL of the pyrene stock solution held in a vial, as in the uptake experiments. From time to time, the vial would be opened and the solution purged with nitrogen for 5 min. First the monolith, and then 1.0 mL of the surrounding solution, were transferred to a cuvette, which was then capped, and the fluorescence spectrum was recorded. During the acquisition, the monolith adhered to those two walls of the cuvette that faced the light source and the detector. In this way, the excitation beam avoided the surrounding solution, the emission from pyrene in the glass was maximized, and the emission from pyrene in the surrounding solution was minimized. This external solution was necessary to avoid cracking of the glass monolith during acquisition of the spectrum.

Synthesis of the Substituted Benzyl Alcohol, (1). 3,4,5-Trifluorobenzyl Alcohol (**1c**). Sodium tetrahydroborate (0.23 g, 6.3 mmol) was added over 5 min to a stirred solution of 3,4,5-trifluorobenzaldehyde (2.0 g, 12.5 mmol) in 15 mL of ethanol. Stirring was continued for 30 min at room temperature. The volume was reduced in vacuo to ca. 2 mL, and 50 mL of water was added. The mixture was extracted with diethyl ether (3 \times 50 mL). The combined organic phases were washed with

saturated NaCl solution (2×50 mL) and dried over MgSO_4 . The evaporation of the organic phase yielded the crude alcohol, which was purified by flash chromatography on silica (hexane: acetone, 9:1). ^1H NMR in CDCl_3 , δ : 2.51 (br, 1 H), 4.61 (s, 2H), and 6.96 (m, 2H); ^{13}C NMR in CDCl_3 , δ : 63.6 (s), 110.3 (m), 137.1 (m), 138.9 (m), and 151.2 (m).

3,4,5-Trimethylbenzyl Alcohol (1b). The synthesis followed a published procedure.^{25,26} Baddeley rearrangement of 2',4',6'-trimethylacetophenone in the presence of AlCl_3 yielded 3',4',5'-trimethylacetophenone. Oxidation of this compound by NaOCl to 3,4,5-trimethylbenzoic acid, followed by reduction with LiAlH_4 , afforded the desired alcohol. ^1H NMR in CDCl_3 , δ : 2.17 (s, 3 H), 2.29 (s, 6H), 4.59 (s, 2H), and 7.01 (s, 2H); ^{13}C NMR in CDCl_3 , δ : 15.2, 20.6, 65.4, 126.5, 134.6, 136.8, and 137.7.

Synthesis of the Substituted Benzyl Bromide, (2). A solution of the derivatized benzyl alcohol **1b** or **1c** (10.5 mmol) in 25 mL of diethyl ether containing triphenylphosphine (2.75 g, 10.5 mmol) and carbon tetrabromide (3.48 g, 10.5 mmol) was stirred at 25 °C for 40 min, filtered, and concentrated in vacuo. The residue was subjected to flash chromatography on silica with hexane as an eluent, to yield the pure bromide derivative **2b** or **2c**.

3,4,5-Trimethylbenzyl bromide (2b). ^1H NMR in CDCl_3 , δ : 2.14 (s, 3 H), 2.25 (s, 6H), 4.41 (s, 2H), and 7.02 (s, 2H); ^{13}C NMR in CDCl_3 , δ : 15.4, 20.6, 34.2, 128.3, 134.6, 135.8, and 137.1.

3,4,5-Trifluorobenzyl bromide (2c). ^1H NMR in CDCl_3 , δ : 4.37 (s, 2 H), and 7.03 (m, 2H); ^{13}C NMR in CDCl_3 , δ : 31.0 (s), 113.3 (m), 133.9 (m), 139.6 (m), and 151.1 (m).

Synthesis of Alkylphosphonium Salts, (3).²⁷ A solution of the derivatized benzyl bromide **2a**, **2b**, or **2c** (1.1 mmol) and triphenylphosphine (0.29 g, 1.1 mmol) in benzene (10 mL) was stirred under reflux for 12 h. The initially clear solution rapidly become cloudy, and the phosphonium salt precipitated as a colorless solid. The solution was cooled in ice, filtered, and washed with 100 mL of cold benzene (carcinogen!). The benzene was evaporated in a rotary evaporator, and the phosphonium salt was recrystallized from benzene; both procedures were done inside an effective fume hood.

Synthesis of Stilbene, (5).²⁸ To the alkylphosphonium salt **3** (0.9 mmol) and potassium *tert*-butoxide (0.10 g, 0.9 mmol) in dichloromethane (10 mL) were added 3,4,5-trifluorobenzaldehyde **4** (0.13 g, 0.8 mmol) and 18-crown-6 (15 mg). The mixture was stirred overnight at room temperature, and then the solvent was evaporated. The residue was washed three times with 50 mL of hexane, and the washings were filtered through silica gel. Evaporation of the solvent yielded a crude mixture of the trans and cis isomers **5**, which were then separated and purified by column chromatography on silica with hexane as an eluent.

trans-3,4,5-Trifluoro-4'-methyl Stilbene. ^1H NMR in CDCl_3 , δ : 2.36 (s, 3H), 6.86 (d, 1 H, $J = 16.4$ Hz), 6.97 (d, 1H, $J = 16.4$ Hz), 7.06 (m, 2H); 7.17 (d, 2H), and 7.37 (d, 2H); ^{13}C NMR in CDCl_3 , δ : 21.3 (s), 110.0 (m), 124.7 (m), 126.7 (s), 129.6 (s), 131.0 (m), 133.5 (s), 133.9 (m), 137.0 (s), 139.0 (m), 151.4 (m); ^{19}F NMR in CDCl_3 , δ : -133.1 (m) and -160.2 (m); LRMS-Cl: calcd for M^+ of $\text{C}_{15}\text{H}_{11}\text{F}_3$ 248, found 248.

cis-3,4,5-Trifluoro-4'-methyl Stilbene. ^1H NMR in CDCl_3 , δ : 2.33 (s, 3H), 6.35 (d, 1 H, $J = 12.0$ Hz), 6.63 (d, 1H, $J = 12.0$ Hz), 6.83 (m, 2H); and 7.08 (m, 4H); ^{13}C NMR in CDCl_3 , δ : 21.3 (s), 112.8 (m), 126.5 (m), 128.7 (s), 129.3 (s), 132.5 (s), 133.0 (s), 133.5 (m), 137.8 (s), 138.9 (m), and 151.0 (m); ^{19}F NMR in CDCl_3 , δ : -133.4 (m) and -160.5 (m); LRMS-Cl: calcd for M^+ of $\text{C}_{15}\text{H}_{11}\text{F}_3$ 248, found 248.

trans-3,4,5-Trifluoro-3',4',5'-trimethyl Stilbene. ^1H NMR in CDCl_3 , δ : 2.18 (s, 3H), 2.30 (s, 6H), 6.84 (d, 1H, $J = 16.4$ Hz), 6.91 (d, 1H, $J = 16.4$ Hz), 7.05 (m, 2 H), and 7.13 (s, 2H); ^{13}C NMR in CDCl_3 , δ : 15.5 (s), 20.7 (s), 109.9 (m), 124.3 (m), 126.0 (s), 131.2 (m), 133.1 (s), 134.1 (m), 135.9 (s), 136.9 (s), 139.0 (m), and 151.6 (m); ^{19}F NMR in CDCl_3 , δ : -133.1 (m), and -160.7 (m); LRMS-Cl: calcd for M^+ of $\text{C}_{17}\text{H}_{15}\text{F}_3$ 276, found 276.

cis-3,4,5-Trifluoro-3',4',5'-trimethyl Stilbene. ^1H NMR in CDCl_3 , δ : 2.15 (s, 3H), 2.20 (s, 6H), 6.30 (d, 1H, $J = 12.0$ Hz), 6.58 (d, 1H, $J = 12.0$ Hz), and 6.87 (m, 4 H); ^{13}C NMR in CDCl_3 , δ : 15.3 (s), 20.5 (s), 112.8 (m), 126.1 (m), 128.4 (m), 132.7 (br), 132.8 (s), 133.6 (m), 135.0 (s), 136.6 (s), 138.9 (m), and 150.9 (m); ^{19}F NMR in CDCl_3 , δ : -133.4 (m), and -160.5 (m); LRMS-Cl: calcd for M^+ of $\text{C}_{17}\text{H}_{15}\text{F}_3$ 276, found 276.

trans-3,3',4,4',5,5'-Hexafluoro Stilbene. ^1H NMR in CDCl_3 , δ : 6.84 (s, 2H) and 7.09 (m, 4H); ^{13}C NMR in CDCl_3 , δ : 110.5 (m), 128.0 (s), 132.5 (m), 139.6 (m), and 151.6 (m); ^{19}F NMR in CDCl_3 , δ : -132.2 (m) and -158.2 (m); LRMS-Cl: calcd for M^+ of $\text{C}_{14}\text{H}_6\text{F}_6$ 288, found 288.

cis-3,3',4,4',5,5'-Hexafluoro Stilbene. ^1H NMR in CDCl_3 , δ : 6.52 (s, 2H), and 6.80 (m, 4H); ^{13}C NMR in CDCl_3 , δ : 112.8 (m), 129.4 (s), 131.9 (m), 139.2 (m), and 151.3 (m); ^{19}F NMR in CDCl_3 , δ : -132.1 (m), and -158.8 (m); LRMS-Cl: calcd for M^+ of $\text{C}_{14}\text{H}_6\text{F}_6$ 288, found 288.

Results and Discussion

Interactions between Silica Glass and Guest Compounds.

It is widely assumed that molecules (including ions) smaller than the pores of the sol-gel glass can freely diffuse in and out of this glass when it is immersed in the solution of these molecules. This assumption underlies the design of various biosensors, which can function only if the guest concentrations in the matrix and in the surrounding solution are equalized relatively quickly. We refer to this equalization or near equalization, regardless of the time required for its attainment, as balanced uptake. Research in our laboratory²⁰⁻²³ has shown that when repulsive or attractive interactions exist between the glass and the guests, the sol-gel silica matrix takes up the guest partially or excessively. We call this uptake imbalanced.

Electrostatic interactions and conventional hydrogen bonds between sol-gel silica and guests have been documented.^{15,20,22,23} Now, we search for even subtler and weaker interactions. Study of the adsorption of aromatic compounds on silica has begun, but little is known about this phenomenon.²⁹⁻³³ Our goal is not to analyze these weak interactions as such, but to examine their unexpected consequences for the doping of sol-gel glasses with chemicals and for the function of these doped glasses. This study deals less with spectroscopy and more with materials science.

Dehydration of Silica Monolith. After aging and partial drying, the pores in the sol-gel silica monoliths contain water that must be removed lest it affect, or altogether prevent, the interaction of silica with the guests. We extracted water with a succession of solvents chosen so that each dilutes and removes the previous one. Over time, this exhaustive procedure achieved the overall dilution factor of ca. 10^{16} . Smaller factors probably would have sufficed, but we strove for accurate experiments.

The average pore size of silica xerogel prepared by the sol-gel method and completely dried at high temperature is ca. 20 Å.³⁴ The average pore size of our silica glass, which is only partially dried at 4 °C, is greater than ca. 30 Å²⁰ but smaller than ca. 100 Å. Indeed, our slabs do not scatter visible light.²³

TABLE 1: Partitioning at Equilibrium of Halo Derivatives of Benzene between Hexane Solution and Monoliths of Porous Sol–Gel Silica Glass at 25 °C

guest	polarizability (10^{-24} cm ³)	dipole moment (D)	uptake coefficient ^a
fluorobenzene	10.3	1.5	1.3 ± 0.2
1,2-difluorobenzene	10.4	2.4	1.4 ± 0.1
1,4-difluorobenzene	10.2	0	1.4 ± 0.2
1,2,3- trifluorobenzene	10.4	3.0	1.7 ± 0.2
1,3,5-trifluorobenzene	10.2	0	1.3 ± 0.1
chlorobenzene	14.1	1.6	1.3 ± 0.1
1,2-dichlorobenzene	14.2	2.2	1.3 ± 0.1
1,4-dichlorobenzene	14.4	0	1.3 ± 0.1
1,2,3-trichlorobenzene		2.4	1.9 ± 0.1
1,3,5-trichlorobenzene	16.1	0	1.0 ± 0.1
bromobenzene	14.7	1.7	1.3 ± 0.1
1,2-dibromobenzene	16.3	2.0	1.3 ± 0.1
1,4-dibromobenzene	13.5	0	1.3 ± 0.1
1,2,3-tribromobenzene			1.8 ± 0.1
1,3,5-tribromobenzene		0	1.1 ± 0.1
iodobenzene	15.5		1.5 ± 0.1
1,2-diiodobenzene	20.0	1.7	1.7 ± 0.1
1,4-diiodobenzene		0	1.7 ± 0.1

^a Ratio of concentrations in glass and the surrounding solution.

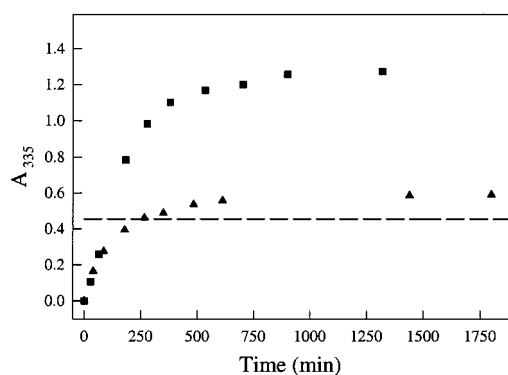


Figure 1. Uptake of pyrene by monoliths of porous sol–gel silica glass sized $8 \times 8 \times 27$ mm soaked in 50.0 mL of 1.8×10^{-5} M solutions of pyrene in carbon tetrachloride (\blacktriangle) and hexane (\blacksquare). As pyrene enters, its absorbance in the glass increases. The dashed line marks the absorbance of the external solution. Uptake is nearly balanced in carbon tetrachloride and excessive in hexane.

The experimental methods for determination of surface area (BET) and pore size distribution (BJH) are inapplicable to our partially dried silica monoliths because they shrink, and therefore change their physical properties, during their preparation for the experiment. The infrared spectrum of a pulverized silica monolith used in the uptake experiments does not show residual water or carbon-containing compounds.²⁰

Nearly Balanced Uptake of Aromatic Halides by Silica Glass. Monosubstituted, 1,2- and 1,4-disubstituted, and 1,2,3- and 1,3,5-trisubstituted halo derivatives of benzene differ in dipole moment and polarizability (Table 1).³⁵ We tested whether these compounds form van der Waals interactions with the sol–gel silica glass. The experiments were done in hexane since this solvent is nonpolar and has very low polarizability and therefore is not expected to compete with the guest molecules for the host sites on silica. (This assumption was vindicated in experiments with pyrene emission, to be discussed later.) The results of uptake exemplified by Figure 1 are shown in Table 1. The uptake coefficients for all the aromatic halides examined fall between 1.0 and 1.9. The 1,2,3-trisubstituted derivatives, which have the greatest dipole moments, showed the highest values. The 1,3,5-trisubstituted and 1,4-disubstituted chloro and bromo derivatives, which have no dipole moments, showed low values. Iodo derivatives, especially 1,4-diiodo benzene, and

TABLE 2: Uptake Coefficients for Partitioning of Polynuclear and Conjugated Aromatic Hydrocarbons between Various Solvents and Monoliths of Porous Sol–Gel Silica Glass at 25 °C

guest	solvent		
	hexane	dichloro- methane	carbon tetrachloride
naphthalene	3.0 ± 0.2	1.00 ± 0.02	0.94 ± 0.08
2,7-di- <i>tert</i> -butylnaphthalene	3.0 ± 0.1	0.85 ± 0.03	0.95 ± 0.02
azulene	3.6 ± 0.1	0.99 ± 0.03	1.35 ± 0.02
anthracene	3.6 ± 0.3	0.82 ± 0.03	1.39 ± 0.08
pyrene	3.7 ± 0.5	0.88 ± 0.02	1.30 ± 0.03
<i>trans</i> -stilbene	4.6 ± 0.2	0.95 ± 0.02	1.24 ± 0.08

some other compounds in Table 1, however, refute the correlation between the dipole moment of the guest and the extent of its uptake by the silica matrix. Likewise, there is no correlation between the polarizability of compounds and their uptake coefficients. We conclude that dipolar and van der Waals interactions are not responsible for the uptake of aromatic halides with the coefficients exceeding 1.0.

Uptake of Polynuclear Aromatic Hydrocarbons and Control of It. We chose six aromatic hydrocarbons that differ in polarizability, size, and structure. Their uptake by sol–gel silica from the solutions in hexane, dichloromethane, and carbon tetrachloride is quantified in Table 2. The uptake coefficients in the range 3.0 to 4.6 show that all the six compounds are excessively taken up from hexane into the silica matrix. On the contrary, the coefficients in the range 0.82 to 1.39 show balanced or nearly balanced uptake from carbon tetrachloride and dichloromethane. The excessive uptake from hexane by sol–gel glass amounts to extraction of nonpolar hydrocarbons from a nonpolar hydrocarbon solvent into the polar environment characteristic of porous silica. This finding intrigued us, for it violates the well-known principles of extraction and partition chromatography.^{36–38}

The propensity of aromatic compounds to act as hydrogen-bond acceptors is well documented,^{39–46} but there is no scale quantifying this propensity. We assume that it generally increases as the size (and also polarizability) of the molecule increases. Silanol groups in the sol–gel silica are hydrogen-bond donors. As Table 2 shows, the uptake coefficients generally increase downward, as the guest molecules become larger. This finding is consistent with hydrogen bonding involving the aromatic system as the cause of the unexpected extraction. All the solvents used in uptake experiments have near-zero α and β Kamlet–Taft parameters, which reflect hydrogen-bonding acceptor and donor abilities, respectively.^{47,48} Therefore, these solvents do not make hydrogen bonds with guest molecules. The π^* parameter, which reflects dipolarity/polarizability, is -0.081 , 0.82 , and 0.28 for hexane, dichloromethane, and carbon tetrachloride, respectively.^{49,50} Therefore, these solvents may differ in their van der Waals interactions with the guest molecules and the silica matrix. Dichloromethane and carbon tetrachloride are known to adsorb on silica.^{30,51,52} This silica–solvent interaction would suppress the silica–guest interaction; the solvent molecules, present in great excess, would displace the aromatic molecules from the pore surfaces in sol–gel glass. The result is balanced or nearly balanced uptake of the aromatics.

Silica–Solvent Interactions Probed with Pyrene. We tested the hypothesis that some solvents do, while others do not, adsorb on the sol–gel silica glass under the conditions of our experiments. The emission spectrum of pyrene consists of five bands, designated I through V. The ratio of the intensities of the third and the first band, the III/I quotient, is widely used as

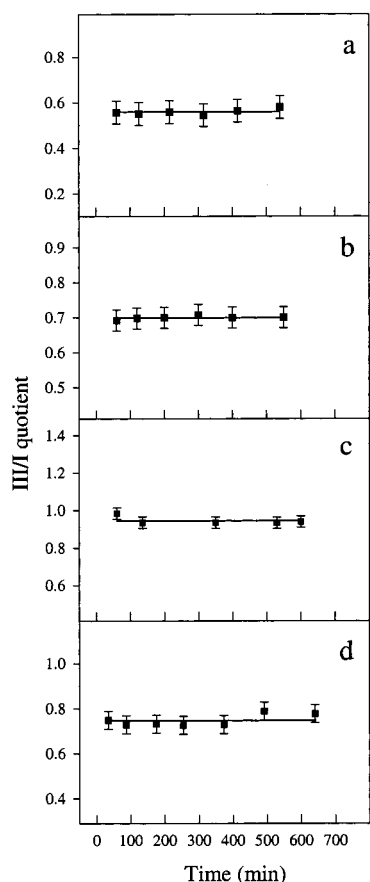


Figure 2. Relative intensity of bands III and I in the fluorescence spectra of pyrene taken up by monoliths of porous sol–gel silica glass sized $8 \times 8 \times 27$ mm from 50.0 mL of 1.0×10^{-5} M solutions of pyrene in (a) acetonitrile, (b) dichloromethane, (c) cyclohexyl chloride, and (d) hexane.

TABLE 3: Relative Intensity of the Bands III and I in the Fluorescence Spectra of Pyrene When Dissolved in Four Solvents and When Taken up from These Solutions into Monoliths of Porous Sol–Gel Silica Glass at 25 °C

solvent	III/I quotient		uptake coefficient
	solution	silica	
acetonitrile	0.55 ± 0.01	0.55 ± 0.05	0.93 ± 0.04
dichloromethane	0.71 ± 0.01	0.70 ± 0.03	0.88 ± 0.02
cyclohexyl chloride	0.93 ± 0.01	0.94 ± 0.03	0.88 ± 0.02
hexane	1.68 ± 0.01	0.75 ± 0.04	3.7 ± 0.5

a measure of the polarity of the medium surrounding the fluorophore.^{53–57}

Figure 2a, 2b, and 2c and the first three rows in Table 3 show that the III/I quotient remains unchanged as the fluorophore moves from the polar or chlorine-containing solvent into the glass interior. Evidently, pyrene “feels” the same environment in these solvents and inside the porous sol–gel silica monolith immersed in the solutions containing polar or chlorine-containing solvents. Figure 2d and the last row in Table 3, however, show that the III/I quotient changes greatly as the fluorophore moves from hexane into the glass. Evidently, pyrene “feels” greatly different environments when dissolved in hexane and inside the sol–gel glass impregnated by this solution. The III/I quotient of 0.75 ± 0.04 in our study is similar to the values of 0.65 – 0.75 reported for pyrene inside silica and modified silica.^{57–62}

Uptake of pyrene into silica from the first three solvents is nearly balanced—the coefficients are equal (within the margins of error) and near unity. But uptake from hexane is excessive.

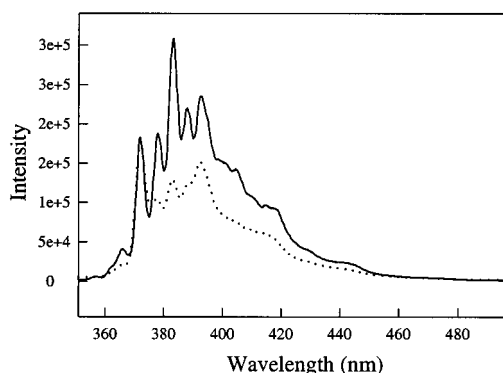
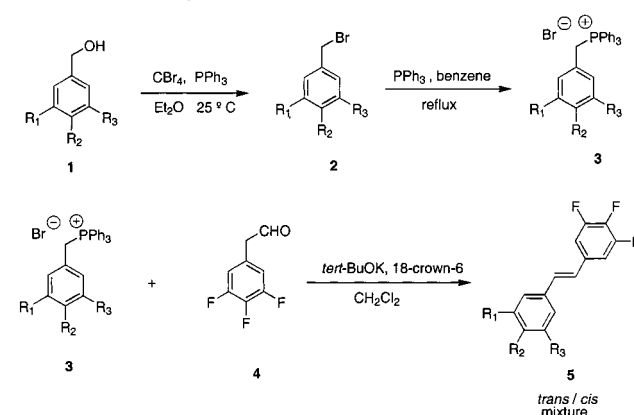


Figure 3. Fluorescence spectra of 1.0×10^{-5} M pyrene in hexane (solid line, III/I = 1.68 ± 0.01) and taken up from the hexane solution by monolith of porous sol–gel silica glass sized $8 \times 8 \times 27$ mm (dotted line, III/I = 0.75 ± 0.04). The last point in Figure 2d is based on the dotted-line spectrum here.

SCHEME 1: Synthesis of Stilbene Derivatives



group	a	b	c
R ₁	H	Me	F
R ₂	Me	Me	F
R ₃	H	Me	F

Even when pyrene was maximally extracted into silica from hexane, at the end of the uptake experiments, there was no sign of excimer formation in the emission spectrum (Figure 3), which is diagnostic of pyrene aggregation.^{63,64} Evidently, pyrene accumulates in the porous glass because it interacts with silica, not with itself.

These experiments confirm our conclusion in the preceding subsection. Polar or chlorine-containing solvents line the pore surfaces in the glass, so that the pyrene “feels” this solvent inside the glass as well as in the solution. Hexane, however, does not adsorb on the glass surfaces and does not shield pyrene from the silica matrix. Consequently, pyrene “feels” a great difference between the glass interior and the hexane solution. Pyrene, like the guest compounds in Table 2, accepts hydrogen bonds from silica and thus becomes extracted into the glass matrix from the hexane solution.

Uptake of Stilbene and Its Derivatives. Because stilbene showed the highest affinity for sol–gel silica, we examined its uptake in some detail. Besides the parent compound, we synthesized three of its derivatives, according to Scheme 1. Compounds **1a**, **1b**, **2a**, **3a**, and **4** are known. Compounds **1c**, **2b**, **2c**, **3b**, and **3c**, which are intermediates in the syntheses, have not been reported previously. Most important, all six compounds designated **5** (three substituted derivatives of stilbene, two geometrical isomers of each) are new.

TABLE 4: Uptake Coefficients for Partitioning of Stilbene and Its Derivatives between Solvent and Monoliths of Porous Sol–Gel Silica Glass at 25 °C

guest	isomer	solvent	
		hexane	dichloro- methane
stilbene	<i>trans</i>	4.6 ± 0.2	0.95 ± 0.02
	<i>cis</i>	4.4 ± 0.1	1.14 ± 0.01
3,4,5-trifluoro 4'-methyl stilbene	<i>trans</i>	3.5 ± 0.1	0.95 ± 0.08
	<i>cis</i>	3.3 ± 0.1	0.95 ± 0.02
3,4,5-trifluoro 3',4',5'-trimethyl stilbene	<i>trans</i>	4.4 ± 0.1	1.16 ± 0.01
	<i>cis</i>	3.4 ± 0.1	1.14 ± 0.01
3,3',4,4',5,5'-hexafluoro stilbene	<i>trans</i>	4.9 ± 0.1	0.90 ± 0.01
	<i>cis</i>	4.0 ± 0.2	1.25 ± 0.09

There are altogether eight guest compounds, which differ in configuration and aromatic electron density. A *trans* isomer is more nearly planar than its *cis* isomer. Hexafluoro stilbene is poorer in electrons than the other derivatives. As Table 4 shows, all the eight compounds are extracted by porous sol–gel silica from the hexane solution. The molecular configuration (*cis* and *trans*) has a small effect on the uptake coefficient, possibly because the pore surfaces are irregular. Because hydroxyl groups on these surfaces are capable of hydrogen bonding in various directions, the precise orientation of the aromatic rings is not critical for adsorption. The substituents do not seem to affect adsorption in a discernible way. Dichloromethane as a solvent suppresses adsorption of stilbene and brings about the balanced uptake of all eight guest compounds.

Conclusion

Extraction of aromatics into porous sol–gel silica from hexane but not from solvents capable of hydrogen bonding seems to be a general property of aromatic compounds. We document it with many halo derivatives of benzene and also with polynuclear and conjugated aromatic compounds. This unexpected behavior is consistent with hydrogen bonding between the aromatic guests and silanol groups on the surfaces of the glass pores. These interactions have recently been recognized.²⁹ Nothing, however, was known before this study about these interactions in sol–gel materials. The goal of this research was not to continue the study of hydrogen bonding itself, but to examine its consequences for the adsorption of aromatics on sol–gel silica and the unexpected extraction of organic compounds into an inorganic matrix from organic solvents. This phenomenon should be taken into consideration in the design and use of various composite materials containing sol–gel silica, such as enzymes in biosensors and in immobilized catalysts. If balanced uptake is required for the function of sensors and other molecular devices, the unwanted extraction can be suppressed by the use of hydrogen-bonding solvents, which reliably prevent the adsorption and cause the aromatic guests to be evenly distributed between the glass matrix and the surrounding solution.

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