

In Situ Adsorption Studies at Silica/Solution Interfaces by Attenuated Total Internal Reflection Fourier Transform Infrared Spectroscopy: Examination of Adsorption Models in Normal-Phase Liquid Chromatography

Dion Rivera, Pete E. Poston,[†] Rory H. Uibel, and Joel M. Harris*

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112-0850

ATR-FT-IR spectroscopy was employed to the study the adsorption of ethyl acetate and 2-propanol to the surface of thin silica sol-gel films in contact with *n*-heptane solutions. In situ vibrational spectra of silica-adsorbed species provided information regarding the mechanisms of solute retention and elution in normal-phase chromatography. Previous normal-phase chromatographic studies of ethyl acetate adsorption revealed nonlinear isotherms which were explained by both bilayer and adsorbate delocalization models. Infrared spectra of ethyl acetate at the silica surface versus concentration showed that nonlinear adsorption can be attributed to site heterogeneity, where adsorption to free silanols and surface-adsorbed water can be distinguished. Least-squares modeling of the data produced resolved spectra for the two sites and adsorption equilibrium constants that differed by about an order of magnitude. Adsorption of 2-propanol was best modeled by a single Langmuir isotherm showing no significant difference in adsorption energy for the two sites; 2-propanol was shown to easily displace ethyl acetate from the silica surface. Ethyl acetate could also displace 2-propanol from the silica, and least-squares modeling again revealed two-adsorbed-component spectra for ethyl acetate that were indistinguishable from spectra obtained when ethyl acetate adsorbed directly onto the surface.

Chemical interactions at the liquid/solid interface of silica are important for the differential retention of solutes in normal-phase liquid chromatography. Previous studies that have addressed the nature of the molecular interactions at the silica surface have relied primarily on indirect evidence derived from chromatographic retention behavior of solutes^{1–4} or the ex situ determination of absorption isotherms.^{5,6} From these studies, the equilibrium

constant for adsorption of polar compounds was found to decrease with adsorbate coverage. Two possible mechanisms have been advanced to explain this nonlinear adsorption behavior: the formation of an adsorbate bilayer^{5,6} and the delocalization of adsorbates from specific surface sites.^{1–4} The delocalization model has been used to explain retention behavior of compounds on silica gel,^{7–10} amino-, cyano-, and diol-functionalized silica,^{11–14} and even a Florisil stationary phase;¹⁵ proponents of this theory have pointed out inconsistencies in the bilayer model based on thermodynamic concepts.¹ Despite the success of the delocalization theory in explaining nonlinear adsorption behavior, there has been no direct evidence as to whether either of these models is an accurate representation of normal-phase adsorption interactions at higher coverages; both theories are still mentioned to explain experimental results.^{16,17}

The delocalization model describes the adsorption of polar adsorbates as initially interacting directly with surface sites in optimal, lowest energy conformations that are localized on those sites.^{1–4} Components of solutions containing multiple adsorbate molecules will compete at the surface for these sites. Localization increases the relative solvent strength of the adsorbate when it can optimize its interactions with the surface. After the surface coverage of the adsorbate exceeds about 75% of the total possible coverage, the remaining surface sites cannot be accessed directly due to the steric hindrance from the adsorbate already on the surface. Accumulation of more molecules at the surface will disrupt the localization of adsorption until the surface is completely delocalized at a full monolayer of coverage. This mechanism will not follow a simple Langmuir isotherm but is analogous to a Frumkin model, where the mutual repulsion of molecules at the

[†] Current address: Division of Natural Science and Mathematics, Western Oregon University, 345 N. Monmouth Ave., Monmouth, OR 97361.

(1) Snyder, R. L.; Poppe, P. *J. Chromatogr.* **1980**, *184*, 363–413.

(2) Snyder, R. L.; Glajch, J. L. *J. Chromatogr.* **1981**, *214*, 1–19.

(3) Snyder, R. L.; Glajch, J. L.; Kirkland, J. J. *J. Chromatogr.* **1981**, *218*, 299–326.

(4) Snyder, R. L. *J. Chromatogr.* **1983**, *255*, 3–26.

(5) Scott, R. P. W.; Kucera, P. *J. Chromatogr.* **1978**, *149*, 93–110.

(6) Scott, R. P. W.; Kucera, P. *J. Chromatogr.* **1979**, *171*, 37–48.

(7) Burrell, G. J.; Hurtubise, R. J. *Anal. Chem.* **1988**, *60*, 564–568.

(8) Ruchmick, S. C.; Hurtubise, R. J. *J. Chromatogr.* **1986**, *360*, 343–352.

(9) Olsen, L. D.; Hurtubise, R. J. *J. Chromatogr.* **1989**, *474*, 347–361.

(10) Olsen, L. D.; Hurtubise, R. J. *J. Chromatogr.* **1989**, *479*, 5–16.

(11) Snyder, L. R.; Schunk, T. C. *Anal. Chem.* **1982**, *54*, 1764–1772.

(12) Smith, P. L.; Cooper, W. T. *J. Chromatogr.* **1987**, *410*, 249–265.

(13) Salotto, A. W.; Weiser, E. L.; Caffey, K. P.; Carty, R. L.; Racine, S. C. *J. Chromatogr.* **1990**, *498*, 55–65.

(14) Lübke, M.; Quere, J.; Barron, D. *J. Chromatogr., A* **1995**, *690*, 41–54.

(15) Adams, J.; Giam, C. S. *J. Chromatogr.* **1984**, *285*, 81–89.

(16) Chang, C. A.; Huang, C. *Anal. Chem.* **1985**, *57*, 997–1005.

(17) Cheong, W. J.; Choi, J. D. *Anal. Chim. Acta* **1997**, *342*, 51–57.

surface raises the free energy of adsorption with increasing coverage.¹⁸ The model also assumes that the surface is homogeneous and that all the molecules in the delocalized monolayer adsorb at the same energy onto the silica surface. Within this model, displacement is also governed by the delocalization of the surface monolayer.¹ Delocalized regions of a surface are those initially displaced by a competing solute; as more of this solute accumulates on the surface, it delocalizes the rest of the solute that was initially adsorbed, which allows it to be displaced.

The bilayer model for adsorption describes the initial accumulation of a polar adsorbate monolayer followed by the adsorption of a second layer of molecules which adsorb to the initial layer at higher surface coverages.⁵ Strongly hydrogen-bonding adsorbents interact directly with the surface and form a hydrogen-bonded surface phase. These adsorbents are presumed not to be displaced by other polar solutes so that adsorption interactions are between the polar solute and the hydrogen-bonded surface phase.⁵ Within this model, polar solutes can displace the second, weaker layer of the bilayer but do not displace the primary monolayer and therefore do not interact directly with the silica surface. In the absence of a primary adsorbed layer, it has been proposed that adsorbates do not interact directly with the silica surface but instead interact with a layer of water that is adsorbed to the silica surface.¹⁹

ATR-FT-IR is a spectroscopic technique well suited to the study of interfacial phenomena. Internal reflection elements (IREs) that are coated with a thin layer of high surface area adsorbent materials can provide direct spectral evidence regarding the exact nature of the adsorbate/surface interactions.^{20–22} Sol–gel films have been grown on silicon substrates waveguides and have been shown to increase the sensitivity of ATR measurements due to the large surface area that can concentrate analyte at the interface.²³ In our laboratories, we recently showed that fumed silica can be deposited onto a broad-band ZnSe IRE with a simple dip-coating procedure and used to observe adsorbates at the silica/solution interface.²⁴ Results from our initial experiments showed that ethyl acetate adsorbs onto a silica surface at two sites, which suggested the bilayer adsorption model for ethyl acetate was not valid for these silica systems. This work was not the first to suggest a dispersion in adsorption site energies affecting chromatographic retention; two-site and multisite adsorption models were developed by Giddings.^{25,26} Such models have been used to account for band broadening in gas chromatography on bare- and derivatized-silica surfaces.^{27,28} Distributions of site energies have

also been used to interpret peak tailing in normal-phase liquid chromatography.²⁹

The present paper expands prior ATR-FT-IR experiments on fumed-silica films²⁴ by employing a porous sol–gel film whose surface chemistry should more closely resemble that of a chromatographic silica gel. Because of its porous nature, the sol–gel film provides much greater surface area than a fumed silica and allows spectra of weaker bands to be obtained. Interactions of ethyl acetate at this surface were investigated to substantiate the existence of two adsorption sites and to determine the chemical nature of these sites. Studies were also performed with 2-propanol to investigate the behavior of strong hydrogen-bonding adsorbates at the silica surface. The competition between ethyl acetate and 2-propanol for adsorption at the *n*-heptane/silica interface was also studied to gain insight into displacement mechanisms in normal-phase chromatography.

EXPERIMENTAL SECTION

Reagents and Silica Film Preparation. Tetraethoxysilane was purchased from Aldrich and absolute ethanol from Omnisolve. Both were used without further purification. Spectroscopic grade *n*-heptane, ethyl acetate, and 1-propanol were purchased from Fisher and dried over 4 Å molecular sieves prior to use.

Silica particles were prepared from a modified version of the Stöber synthesis.³⁰ Approximately 7.5 mL of tetraethoxysilane was added to 150 mL of absolute ethanol followed by addition of 7 mL of an aqueous solution of 25% ammonia. The mixture was stirred for 36 h, after which it was allowed to stand for 2 weeks to ensure reaction of any residual ethoxy groups. Then 50 mL aliquots of the resulting suspension were diluted to 200 mL in ethanol. This procedure produces porous spherical particles with a nominal diameter of 50 nm³⁰ in an ethanol suspension at a concentration (w/v) of 0.3%.

A germanium 45°, 10 × 50 × 2 mm single-pass parallelepiped internal reflection element (IRE) from Harrick Scientific was dip-coated in the silica suspension using a motorized stage to control the withdrawal rate at 1 cm/s. Fifteen dips were performed to give a sol–gel film having a mass of 82 µg/cm²; see Figure 1. The deposited silica films were characterized by ellipsometry using a single-angle ellipsometer (Gaertner Scientific Corp., Chicago, IL).

Attenuated Total Internal Reflection Infrared Spectroscopy. The ATR flow cell was a Teflon twin-parallel-mirror reflection attachment modified for liquid sampling (Harrick Scientific); the germanium IRE provides 24 internal reflections. Before spectra were acquired, the IRE was placed in the sample compartment of the FT-IR spectrometer, and the compartment was evacuated to sub-milliTorr pressures for 10 min to evaporate weakly adsorbed water from the silica surface. This step served to activate the silica, and it gave spectra similar to those of films that had been heated to 200 °C for 1 h. Liquid solutions were allowed to flow through the ATR cell using a peristaltic pump at a flow rate of 5.5 mL/min; the sol–gel film was allowed to equilibrate with the solution for 10 min before spectral measurements.

(18) Frumkin, A. N.; Damaskin, B. B. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., Eds.; Butterworth: Washington, DC, 1964; Vol. 3.

(19) Scott, R. P. W. *J. Chromatogr. Sci.* **1980**, *18*, 297–306.

(20) Hug, S. J.; Sulzberger, B. *Langmuir* **1994**, *10*, 3587–3597.

(21) Connor, P. A.; Dobson, K. D.; McQuillan, A. J. *Langmuir* **1995**, *11*, 4193–4195.

(22) Billingham, J.; Breen, C.; Yarwood, J. *Clay Miner.* **1996**, *31*, 513–522.

(23) Han, L.; Niemczyk, T. M.; Lu, Y.; Lopez, G. P. *Appl. Spectrosc.* **1998**, *52*, 119–122.

(24) Poston, P. E.; Rivera, D.; Uibel, R.; Harris, J. M. *Appl. Spectrosc.* **1998**, *52*, 1391–1398.

(25) Giddings, J. C. *J. Chromatogr.* **1960**, *3*, 443–453.

(26) Giddings, J. C. *Dynamics of Chromatography*; Marcel Dekker: New York, 1968; Chapter 4.

(27) Waksmundzki, A.; Rudzinski, W.; Suprynowicz, Z.; Leboda, R. *J. Chromatogr.* **1974**, *92*, 9–23.

(28) Sorrel, J. B.; Rowan, R. *Anal. Chem.* **1970**, *42*, 1712–1715.

(29) Suprynowicz, Z.; Jaroniec, M. *J. Chromatogr.* **1976**, *117*, 11–21.

(30) Coenen, S.; De Kruij, C. G. *J. Colloid Interface Sci.* **1988**, *124*, 104–110.

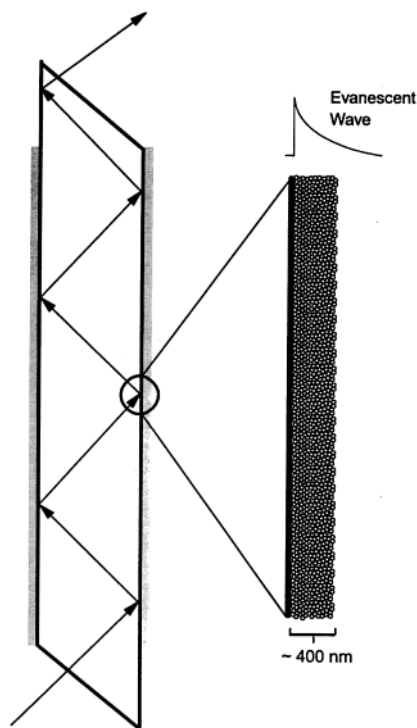


Figure 1. The silica-coated germanium internal reflection element. A germanium IRE is coated with a thin silica sol-gel film, comparable in thickness to the depth of penetration of the evanescent infrared intensity.

A Bruker IFS 66v FT-IR spectrometer was used to gather all infrared spectra; the sample compartment was purged with dry nitrogen. The background spectrum was acquired from an uncoated germanium IRE. Each spectrum required 1000 scans at 4 cm^{-1} resolution using a liquid-nitrogen-cooled MMT (HgCdTe) detector and a sampling rate of 200 kHz. Due to the short-wavelength cutoff of the germanium substrate, spectra could be undersampled by a factor of 3 (high folding limit of 5266 cm^{-1}) to reduce the data acquisition time. To observe adsorbate spectra free of significant solvent interferences, difference spectra were generated by subtracting an *n*-heptane blank spectrum on the coated IRE from subsequent ATR spectra where the solution contained adsorbate species. After subtraction of the solvent blank, the baseline was corrected to be at a zero offset using the appropriate flat region of the spectrum ($1900\text{--}1800$, $3900\text{--}3800$, or $900\text{--}920\text{ cm}^{-1}$). Spectral subtraction and baseline correction were performed using Bruker Opus software, and all modeling was done using QuatroPro version 5.0 and Matlab version 4.2 for Windows.

Since the ATR measurements involve a finite number of interfacial reflections, spectra obtained are not a true absorbance measurements since Beer's law requires integration over a continuous path.³¹ For this reason, the spectral data are reported as the negative logarithms of the attenuated reflectances ($-\log R$). For small optical losses per reflection, typically $\leq 2\%$ in this work, $-\log R$ is proportional to the solute absorptivity and interfacial concentration and deviates from linearity by less than 1%.

Data Analysis. Least-squares regression analysis was employed to test adsorption models and to resolve the spectra of

interfacial species. To carry out this analysis, $-\log R$ was assumed to be linear with concentration and the optical absorptions of various species were assumed to be independent and additive. ATR spectra were typically acquired for a series of different solute concentrations and were assembled into the columns of a data matrix, **D**, which contained *r* rows denoting the index on the spectral dimension (wavenumbers), and *c* columns, which denoted samples containing different concentrations of solute. This data matrix could then be expressed as the product of the spectral and concentration behaviors of the *n* individual components in the sample:

$$\mathbf{D} = \mathbf{A}\mathbf{C} \quad (1)$$

where **A** is an $r \times n$ matrix of *n* pure-component spectra and **C** is a $n \times c$ matrix that describes the changes in the interface concentrations with changes in solution concentration of the solute. Given an appropriate isotherm model for the concentrations of species at the interface and their dependence on the solution concentrations of solutes, matrix **C** could be built from estimates of the adsorption constants in the model. A least-squares estimate of the pure-component spectra, $\hat{\mathbf{A}}$, could be found by right-multiplying the data matrix **D** by the pseudoinverse of the **C** matrix.^{32,33}

$$\hat{\mathbf{A}} = \mathbf{D}\mathbf{C}^T[\mathbf{C}\mathbf{C}^T]^{-1} \quad (2)$$

The best-fit adsorption constants in the isotherm model were found by using a Nelder-Mead simplex algorithm³⁴ to minimize the sum of the squares of the residuals **R**:

$$\mathbf{R} = \mathbf{D} - \hat{\mathbf{A}}\mathbf{C} \quad (3)$$

For an optimal fit to a good model, the residuals **R** should be random and should be without structure; to test the quality of fit of various models, the values of $\chi^2 = (1/\sigma^2) \mathbf{R}^T\mathbf{R}$ were compared using an *F* test. To illustrate the quality of fit of the data to a particular model, a one-dimensional representation of the concentration variation, $\hat{\mathbf{C}}$, was determined by a least-squares projection of the component spectra, $\hat{\mathbf{A}}$, back onto the data.³⁵

$$\hat{\mathbf{C}} = [\hat{\mathbf{A}}^T\hat{\mathbf{A}}]^{-1}\hat{\mathbf{A}}^T\mathbf{D} \quad (4)$$

The least-squares-projected concentration variation derived from the data, $\hat{\mathbf{C}}$, was compared graphically with the optimized isotherm model, **C**, to examine how the amplitudes of the resolved spectra vary in comparison to those of the isotherm model.

Errors in estimated parameters were calculated by mapping the χ^2 surface within 20% of the best-fit values and fitting the surface in each parameter dimension to a parabola to find the curvature of the surface; the variance in the estimated parameter is³⁶ $\sigma_p^2 = 2/(\partial^2\chi^2/\partial p^2)$, and the parameter uncertainties are quoted

(32) Draper, N. R.; Smith, H. *Applied Regression Analysis*, 2nd ed.; John Wiley and Sons: New York, 1981; Chapter 2.

(33) Wilson, R. M.; Miller, T. L. *Anal. Chem.* **1975**, *47*, 256–266.

(34) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308–313.

(35) Tauler, R.; Kowalski, B.; Fleming, S. *Anal. Chem.* **1993**, *65*, 2040–2047.

(36) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; Chapter 11.

(31) Schlemmer, H.; Katzer, J. *Fresenius' Z. Anal. Chem.* **1987**, *329*, 435–439.

as $\pm\sigma_p$. A broader range of the χ^2 surface was also analyzed to make sure the best-fit value did not represent a local minimum. Replicate experiments (different sol–gel films and solutions on different days) produced the same spectra and adsorption constants within their estimated error.

RESULTS AND DISCUSSION

Sol–Gel Film and Surface Site Characterization. The dip-coated silica sol–gel films were characterized by ellipsometry at a single angle using a germanium internal reflection element as a substrate that was dip-coated five times to optimize the ellipsometry response. The measured film thickness averaged $0.14 \pm 0.02 \mu\text{m}$, and the refractive index at 633 nm was $1.2 (\pm 0.1)$. The refractive index indicates that the films are porous since the film index is less than that of solid fused silica ($n = 1.46$). The thickness for a 15-dip film was estimated by multiplying the 5-dip result by 3 since the linearity of the dip-coating process was confirmed by gravimetric analysis. The thickness of the 15-dip films is, therefore, estimated to be $0.40 \pm 0.05 \mu\text{m}$.

The amount of silica deposited in the film can be predicted from the solution film thickness that should remain on the surface upon withdrawal from the silica dispersion; on the basis of the viscosity, the surface tension, the density of ethanol, and the velocity of withdrawal, the solution film thickness for a single withdrawal at a velocity of 1.0 cm/s should be $9 \mu\text{m}$.^{37,38} Since the ethanol solution was a 0.3% (w/v) dispersion of silica sol, the solution film will leave behind $2.7 \mu\text{g}/\text{cm}^2$ silica after evaporation; 15 dips of the substrate should deposit a total of $40 \mu\text{g}/\text{cm}^2$ of silica on the substrate. This prediction is about half of the measured $82 \mu\text{g}/\text{cm}^2$ increase in the substrate mass from the deposited film determined gravimetrically; some of the discrepancy is expected from the influence of the silica sol on the dip-coating process;³⁹ additional mass is also expected from the adsorption of water onto the active silica surface. From the mass of the deposited film and the thickness from ellipsometry, the film density is estimated to be 2.0 g/mL which is 0.30% lower than that of solid fused silica and is consistent with a porous film.

Compared to those for silica films prepared from a fumed silica sol,²⁴ the intensities of adsorbate spectra for the sol–gel films indicate an approximately 3-fold greater surface area. Sol–gel deposition also leads to a more active silica with very strong signals from surface silanols and adsorbed water (see below). The greater density of active silanols on the precipitated sol leads to a strong network of Si–O–Si and hydrogen bonds between silica particles, which stabilize the films and make them much more robust compared to films prepared from fumed silica;⁴⁰ fumed silica films could not withstand exposure to solvents more polar than acetonitrile,²⁴ while the precipitated sol–gel films could withstand exposure to methanol or water without measurable loss of silica or other apparent damage. This robustness is consistent with the reported stability of films less than $1 \mu\text{m}$ thick deposited near their gel point.⁴¹

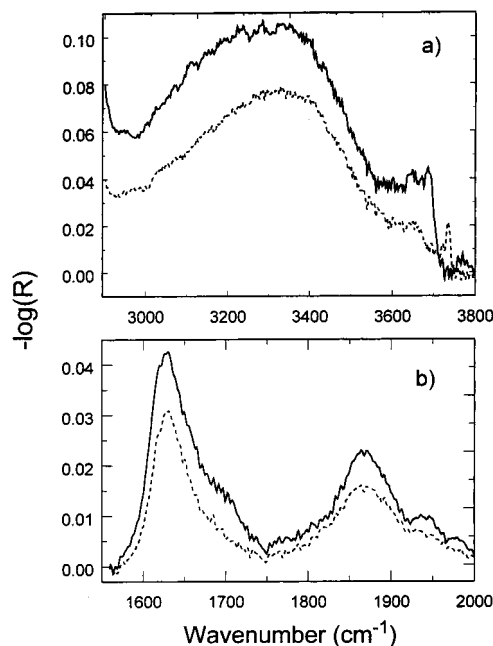


Figure 2. ATR-FT-IR spectra of the silica sol–gel film in contact with nitrogen (dashed lines) and *n*-heptane (solid lines).

Infrared spectra of the silica film under nitrogen and in contact with *n*-heptane are shown in Figure 2 for two spectral regions. Small increases in the intensities of the SiO_2 combination band⁴⁰ at 1868 cm^{-1} , the water deformation band⁴⁰ at 1628 cm^{-1} , and the hydrogen-bonded water OH stretching band⁴⁰ at 3400 cm^{-1} are observed when the sample is transferred from nitrogen to *n*-heptane. These small increases are primarily due to the higher index of refraction of *n*-heptane, which yields a greater depth of penetration into the silica film; these modes are not greatly affected by interactions with solvent, and the intensities of all three bands increase by the same factor of 1.3. If the *n*-heptane does not interact with surface silanols as postulated in the normal-phase chromatography literature,¹⁹ then the intensities of all the bands in the spectrum would increase by the same factor due to the change in the depth of penetration. When silica is in contact with *n*-heptane, however, the free silanol band⁴⁰ at 3742 cm^{-1} disappears completely, while the intensity of the silanol band at 3690 cm^{-1} increases by a factor 3 (average from duplicate sets of results). This large spectral shift is likely due to the *n*-heptane interacting with surface silanols through van der Waals or dipole–induced dipole interactions and shows direct spectral evidence of solvent interaction with the silica surface.

This type of shift in the SiOH stretching frequency is not unprecedented; isolated silanols on Cabosil, dosed with methane and cyclohexane at low surface coverage from the gas phase, exhibit shifts in the frequency for the SiOH stretching vibration of 32 and 34 cm^{-1} , respectively.⁴² The same study showed that liquid nitrogen and argon on Cabosil shift the SiOH stretch by 40 and 43 cm^{-1} , respectively.⁴² Solution-phase experiments on Cabosil in carbon tetrachloride also demonstrated a shift in the free silanol bands from 3747 cm^{-1} in the gas phase to about 3690 cm^{-1} in contact with the solvent.⁴³ On the basis of these results, it seems

(37) Landau, L.; Levich, B. *Acta Physicochim. URSS* **1942**, *17*, 42–54.

(38) Lacy, W. B.; Olson, L. G.; Harris, J. M. *Anal. Chem.* **1999**, *71*, 2564–2570.

(39) Strawbridge, I.; James, P. F. *J. Non-Cryst. Solids* **1986**, *86*, 381–93.

(40) Wood, D. L.; Rabinovich, E. M.; Johnson, D. W., Jr.; MacChesney, J. B.; Vogel, E. M. *J. Am. Ceram. Soc.* **1983**, *66*, 693–699.

(41) Iler, R. K. *The Chemistry of Silica*; John Wiley and Sons: New York, 1979; Chapter 4.

(42) McDonald, R. S. *J. Am. Chem. Soc.* **1957**, *79*, 850–854.

(43) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 1215–1219.

reasonable that *n*-heptane could shift the isolated SiOH stretching frequency by 52 cm⁻¹ as observed. On the basis of the spectra for the silica sol-gel surface and the changes in bands upon contact with the *n*-alkane solvent, the sites that are available as candidates for adsorption of polar molecules are solvent-perturbed free silanols and hydrogen-bonded surface water.

Ethyl Acetate Adsorption on Silica. Solvent-subtracted ATR-FT-IR spectra were acquired for ethyl acetate adsorption onto the silica sol-gel film from *n*-heptane solution, for adsorbate concentrations ranging from 1 to 200 mM. The resulting difference spectra are plotted for the 1220–1800 cm⁻¹ and 2800–3800 cm⁻¹ spectral regions in Figure 3. As the concentration of ethyl acetate in the solution increases, the intensities of adsorbate bands at 1270 and 1290 cm⁻¹ and at 1701 and 1708 cm⁻¹ rise at different rates, indicating changes in the populations of adsorbed species versus surface coverage. The bands at 1750 and 1240 cm⁻¹ that correspond to ethyl acetate in *n*-heptane solution appear only at the highest solution concentrations, which shows that the surface area is large enough to allow adsorbed species to dominate the spectra until the surface becomes saturated at high solution concentrations. Vibrational frequency shifts of the adsorbed versus solution-phase ethyl acetate are due to interactions between hydrogen-bonding donor sites on the surface and π electrons in the carbonyl groups of the ethyl acetate molecules. These interactions draw electron density from the carbonyl groups, lowering the bond order and decreasing the frequency of the C=O stretching vibration.⁴⁴ The frequency of the symmetric C–C–O stretch at 1240 cm⁻¹ is increased upon adsorption due to greater electron density in these bonds coinciding with destabilization of the carbonyl bond.²⁴

One source of hydrogen-bonding interactions for this adsorbate is the surface silanols on the silica, which is apparent in the behavior of the OH stretching region (Figure 3b); the band associated with the silanols at 3700 cm⁻¹ (weakly perturbed by *n*-heptane; see above) shows a marked decrease with increasing ethyl acetate concentration as *n*-heptane is displaced from these sites. A proportional increase in the band at 3400 cm⁻¹ is observed which corresponds to the growth of silanols interacting with adsorbate. Silanols have been shown to shift from ≈ 3742 to ≈ 3400 cm⁻¹ when polar molecules such as acetone are adsorbed onto a silica surface.⁴³ These observations strongly suggest a displacement mechanism for the direct adsorption of ethyl acetate to silanols on the silica surface with the accompanying displacement of *n*-heptane from these sites.

Adsorption of a solute onto a surface from solution is generally accompanied by displacement of a species that was previously interacting with the surface:^{46,47}



where A is the adsorbate in solution and AS is the adsorbate

(44) Silverstein, M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed.; John Wiley and Sons: New York, 1991; Chapter 3.

(45) Folman, M.; Yates, D. J. C. *J. Phys. Chem.* **1959**, 63, 183–187.

(46) Snyder, L. R. *Principles of Adsorption Chromatography*; Marcel Dekker: New York, 1968.

(47) Ross, S.; Morrison, I. D. *Colloidal Systems and Interfaces*; John Wiley and Sons: New York, 1988.

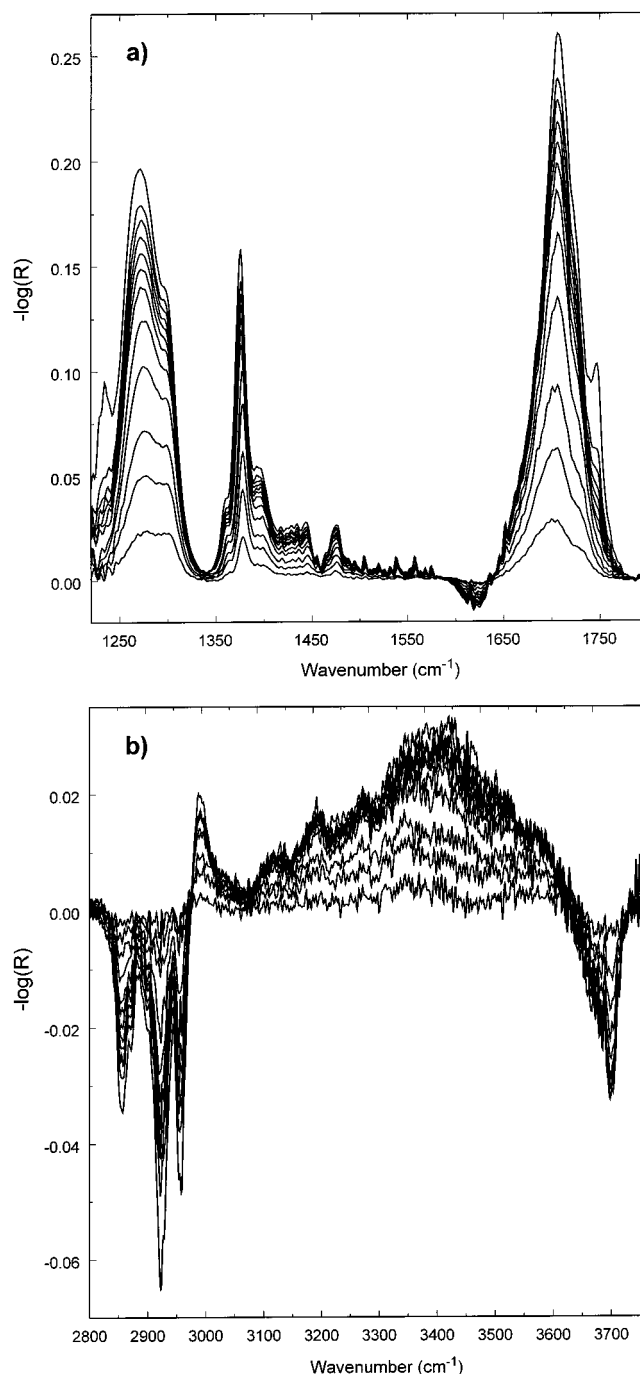


Figure 3. ATR-FT-IR difference spectra for the adsorption of ethyl acetate onto silica from *n*-heptane solution. The ethyl acetate concentration ranges from 1 to 200 mM.

interacting with the surface S and where *n* molecules of the species M are displaced from the surface by the adsorption of A. To predict the surface concentration of adsorbate AS versus its solution concentration, a model for the adsorption equilibrium is needed, the simplest form of which is a Langmuir isotherm.⁴⁷ This model is based on localized adsorption of noninteracting adsorbates and is found by equating the rates of adsorption and desorption of molecules at the surface.⁴⁸ For competitive adsorption, a Langmuir isotherm can be derived from the independent rates of change in the surface concentrations of each species.

(48) Langmuir, I. *J. Am. Chem. Soc.* **1918**, 40, 1361–1370.

When the molecular areas of the adsorbate A and competing species M are nearly equal, n is close to unity and the maximum surface coverages of the species are equivalent ($\Gamma_{\infty}^A \approx \Gamma_{\infty}^M$); on this assumption, the changes in the fraction of sites occupied by each species are given by

$$\frac{d\theta_{AS}}{dt} = k_a^A X_A (1 - \theta_{AS} - \theta_{MS}) - k_d^A \theta_{AS} \quad (6)$$

$$\frac{d\theta_{MS}}{dt} = k_a^M X_M (1 - \theta_{AS} - \theta_{MS}) - k_d^M \theta_{MS} \quad (7)$$

where θ_i , X_i , k_a^i , and k_d^i represent the surface coverage, solution mole fraction, and adsorption and desorption rates of the i th species, respectively. At equilibrium, the rates of change of both species are zero, and a Langmuir isotherm is derived for each component from eqs 6 and 7:

$$\frac{\theta_{AS}}{1 - \theta_{AS} - \theta_{MS}} = \frac{k_a^A X_A}{k_d^A} = K_a^A X_A \quad (8)$$

$$\frac{\theta_{MS}}{1 - \theta_{AS} - \theta_{MS}} = \frac{k_a^M X_M}{k_d^M} = K_a^M X_M \quad (9)$$

where K_a^i is the adsorption equilibrium constant for the i th species.

When the equilibrium constant for prior interaction between M and the surface is large ($K_a^M > 1/X_M$), the fraction of "free" sites is negligible ($1 - \theta_{AS} - \theta_{MS} \approx 0$) and the adsorption of A competes directly with that of M as in eq 5. Under these conditions, the ratio of sites occupied by A to those not occupied by A can be found from the ratio of eqs 8 and 9

$$\frac{\theta_{AS}}{1 - \theta_{AS}} = \frac{\theta_{AS}}{\theta_{MS}} = \frac{K_a^A X_A}{K_a^M X_M} = K_S^A X_A / X_M \quad (10)$$

since $\theta_{MS} = 1 - \theta_{AS}$. Here $K_S^A = K_a^A / K_a^M$ is a selectivity coefficient (ratio of adsorption equilibrium constants) for the adsorption of A relative to that of M. When M is the solvent and the adsorbate concentration is small ($X_A \ll 1$), $X_M \approx 1$ and eq 10 takes the form of a simple Langmuir isotherm, where the adsorption equilibrium constant K_a is equivalent to a selectivity coefficient for the adsorption of A compared to that of the solvent M.

The assumptions underlying a Langmuir-isotherm model for adsorption at a liquid/solid interface include ideal solution behavior for solutes, where the solution activities are equal to mole fractions and there are no interactions between solutes (note: a Raoult's law standard state is generally chosen for the solvent, $a_M \rightarrow X_M$ as $X_M \rightarrow 1$, while a Henry's law standard state is chosen for adsorbates in solution at low concentration, $a_A \rightarrow X_A$ as $X_A \rightarrow 0^{47}$). Evidence for the validity of this assumption can be found in the vibrational spectra of the adsorbates in solution; the C=O stretching band of ethyl acetate does not shift from its 1750 cm^{-1} frequency in *n*-heptane over the range of concentrations used in these studies. Furthermore, even in the presence of higher concentrations of 2-propanol (see below), this band does not shift

as would occur if there were any interaction between the 2-propanol and ethyl acetate in solution.

A Langmuir isotherm is also based on the assumption of no significant interactions between adsorbates at the surface, and therefore no change in the adsorption equilibrium constant with surface coverage. The accumulation of the ethyl acetate signal (integrated intensity of adsorbate bands) in Figure 3a versus solution concentration does *not* follow a Langmuir response and is consistent with nonlinear isotherms reported from chromatographic studies.⁵

This nonlinear isotherm behavior was first postulated to be due to accumulation of an adsorbate bilayer (ethyl acetate adsorbed to ethyl acetate) at high surface coverages;^{5,6} however, no evidence of a bilayer can be observed in the infrared spectra. Ethyl acetate molecules in a bilayer would reside at the interface between the *n*-heptane solvent and a primary adsorbate layer of ethyl acetate; thus, the adsorption environment should be intermediate between *n*-heptane and ethyl acetate. The C=O stretching frequency of ethyl acetate shifts only 7 cm^{-1} to 1743 cm^{-1} in pure ethyl acetate,⁴⁹ compared to 1750 cm^{-1} in *n*-heptane. Therefore, none of the intensity in the 1700–1710 cm^{-1} region can be attributed to bilayer adsorption. The weak intensity at 1750 cm^{-1} rises linearly with solution concentration of ethyl acetate, consistent with a solution-phase species; it does not exhibit the concentration dependence characteristic of bilayer adsorption.⁵⁰

Nonlinear adsorption of ethyl acetate onto silica has also been attributed to delocalization of the adsorbed layer at high surface coverages.^{1–4} There is no evidence for this mechanism in the interfacial infrared spectra since there is no shift in the adsorbate peak frequencies with coverage. At low coverages, for example, a C–C–O band at 1290 cm^{-1} dominates the initial adsorbate signal; this band is clearly still present, and neither shifted nor decreased in intensity, as the surface is saturated with adsorbate. Rather than a shift of the band frequency with coverage, which would be characteristic of a changing interaction with the surface, the relative amounts of two stationary bands appear to vary with surface coverage; this is a clear signature of multisite adsorption to a heterogeneous surface.

From the spectra in Figure 3a, the adsorption of ethyl acetate appears to be governed by two sites on the surface: a strong adsorption site appears to dominate ethyl acetate adsorption at low solution concentrations and produces C–C–O and C=O bands at 1290 and 1701 cm^{-1} , respectively. At higher concentrations, where the strong site begins to saturate, a weaker site giving rise to bands at 1270 and 1708 cm^{-1} accumulates more adsorbate at the surface. On the basis of this observation, the infrared absorptions in the C–C–O and C=O band regions were fit to two independent Langmuir isotherms of the form of eq 10 and a vector that is linear with solution concentration to capture the solution-phase ethyl acetate intensity. The values of the two adsorption equilibrium constants were refined on the basis of the quality of fit of the spectral data, minimizing the sum of squared residuals $\mathbf{R}^T \mathbf{R}$ from eq 3. The two-isotherm model made a significant reduction in the squared residuals compared to a single-isotherm model; the quality of fit improved by a significant *F* ratio of 2.91, while adding a third isotherm to the **C** matrix improved

(49) Schradler, B. *Raman/Infrared Atlas of Organic Compounds*, 2nd ed.; VCH: Berlin, Germany, 1989.

(50) Simpson, S. A.; Harris, J. M. *J. Phys. Chem.* **1990**, *94*, 4649–4654.

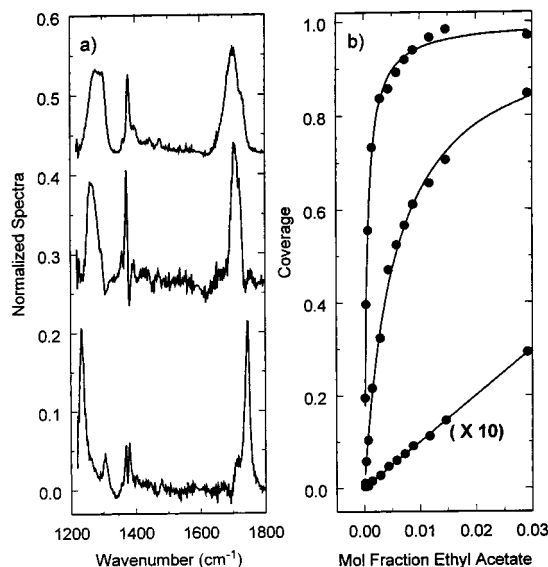


Figure 4. Modeling the accumulation of ethyl acetate at the silica solution interface: (a) component spectra $\hat{\mathbf{A}}$ resolved with isotherms for strong site adsorption (top), weaker site adsorption (middle), and the solution-phase solute (bottom); (b) model concentration dependence (lines) and projections of the spectra $\hat{\mathbf{A}}$ onto the data ($\hat{\mathbf{C}}$, points) for the strong adsorption site (top), the weaker site (middle), and the free solution solute (bottom).

the fit by an F ratio of only 1.044. The \mathbf{R} residuals for the two-isotherm model showed some proportional uncertainty but no systematic variation with concentration or frequency.

Optimized concentration vectors, \mathbf{C} , for the two-isotherm model were used in a least-squares step (eq 2) to resolve spectral components, $\hat{\mathbf{A}}$, for the 1220–1800 cm^{-1} region. Three distinct spectra were thereby extracted from the data, consisting of those for two adsorbate species and solution-phase ethyl acetate as shown in Figure 4a. The spectral component corresponding to the stronger adsorption site (top) has major peaks appearing at 1701 cm^{-1} and a broader band at approximately 1290 cm^{-1} , shifted from those of the solution-phase species by -49 and $+50$ cm^{-1} , respectively. The spectrum corresponding to the weaker adsorption site (middle) has bands at 1708 and 1270 cm^{-1} , corresponding to shifts from the solution-phase bands of -42 and $+30$ cm^{-1} , respectively. The pure-component spectra indicate that the more strongly bound adsorbate experiences greater changes in electron density due to stronger H-bonding interactions, as would be expected. The adsorbate spectra of the more weakly adsorbed component are shifted less, indicating that this species is interacting with less polar sites but is clearly distinguishable from solution-phase ethyl acetate. The spectrum of the component which is linear with concentration (bottom) is indistinguishable from the solution-phase spectrum of ethyl acetate in an n -heptane solution.

In Figure 4b are plotted the best-fit concentration dependences of the resolved spectral components, both adsorbate species and the linear solution-phase component. The lines represent best-fit Langmuir isotherms for the adsorption equilibrium constants, $K_a = 1.7 (\pm 0.3) \times 10^3$ and $1.8 (\pm 1) \times 10^2$ (mole fraction) $^{-1}$, respectively. Note that the reproducibility of the equilibrium constants for adsorption to the two sites is comparable to the fitting uncertainty of a single run; the average results for 3 samples (different sol–gel films and solutions; run on different days) show

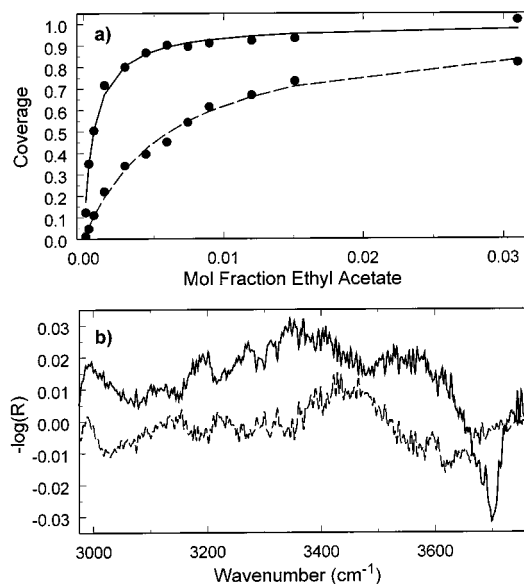


Figure 5. Analysis of the OH stretching region for adsorption of ethyl acetate onto silica from n -heptane: (a) curves representing \mathbf{C} , the best-fit Langmuir isotherms for strong-site (solid) and weak-site (dashed) adsorptions, and points $\hat{\mathbf{C}}$ representing projections of the resolved spectra onto the data; (b) spectra $\hat{\mathbf{A}}$ of the resolved components from strong-site (solid) and weak-site (dashed) adsorptions.

$K_a = 1.8 (\pm 0.2) \times 10^3$ and $1.7 (\pm 0.9) \times 10^2$ (mole fraction) $^{-1}$ for the strong and weak sites, respectively. The points in the isotherm plots in Figure 4b are the values of $\hat{\mathbf{C}}$, which are projections of the resolved spectra, $\hat{\mathbf{A}}$, onto the data determined by eq 4. The agreement between the model and data illustrated by these results shows that two Langmuir isotherms capture the concentration variation of the two adsorbed components. Both isotherms rise above 75% coverage, at which delocalization of the monolayers would occur according to a delocalization model. There is no spectral evidence to suggest that either of these monolayers becomes significantly delocalized at high coverage which would be manifested in deviations between $\hat{\mathbf{C}}$ and a Langmuir model and shifts in band frequencies as adsorbate is displaced from strong interactions with adsorption sites.

To elucidate the nature of the sites responsible for adsorption of ethyl acetate to the silica surface, the region between 2950 and 3800 cm^{-1} , plotted in Figure 3b, was tested for its fit to the adsorption model; this region contains OH stretching vibrations of water and surface silanols.^{40,41} The model that described the concentration dependence of these spectra was also a two-Langmuir-isotherm model, although no solution-phase component was needed since ethyl acetate does not absorb in this region. This two-component adsorption model gave a significantly better fit than a single isotherm, as evidenced by a significant F ratio of 1.8. The best-fit isotherms, \mathbf{C} , for the two-Langmuir-isotherm model along with the corresponding spectra or $\hat{\mathbf{A}}$ matrix are shown in Figure 5. Projecting the fitted spectra back onto the data gives the points $\hat{\mathbf{C}}$ in Figure 5a, which show that the data are well described by the model throughout the concentration range of the experiment. Best-fit values for the strong and weak adsorption equilibrium constants are $1.4 (\pm 0.6) \times 10^3$ and $1.6 (\pm 3) \times 10^2$ (mole fraction) $^{-1}$, respectively, which agree with values obtained from fitting the 1220–1800 cm^{-1} region (see above).

The spectrum corresponding to the strongly adsorbed component (solid line in Figure 5b) shows a significant decrease at 3700 cm^{-1} , which indicates that the sites for strong adsorption are isolated silanols that absorb at this frequency when in contact with *n*-heptane (see above). A corresponding increase in a broad band centered at $\approx 3350\text{ cm}^{-1}$ tracks the decrease in the silanol band and is comparable in frequency to that of silanols interacting with hydrogen-bond acceptors; for example, the frequencies of silanols interacting with adsorbed acetone also shift to a broad band at $\approx 3400\text{ cm}^{-1}$.⁴³ The spectrum corresponding to the weakly adsorbed component (dashed line in Figure 5b) exhibits the loss of a band at 3618 cm^{-1} with increasing concentration of ethyl acetate. Absorption in this region is not due to strongly or weakly hydrogen-bonded vicinal silanols, which adsorb at $3540\text{--}3550$ and $3650\text{--}3660\text{ cm}^{-1}$, respectively;⁴¹ most likely, this band is due to stretching vibrations of the adsorbed water layer and very weakly H-bonded vicinal silanols, which overlap in this region.⁴⁰ The corresponding increase in the broad band at 3450 cm^{-1} is consistent with the interaction of a hydrogen-bond acceptor with OH groups (see above). This site is less polar than the stronger adsorption site, however, since the band shift is only 168 cm^{-1} compared to 350 cm^{-1} for the stronger site.

The nature of the weaker adsorption site on the silica surface is also evident in a small negatively moving band in the difference spectra centered at 1620 cm^{-1} that exhibits a displacement constant of $170\text{ (mole fraction)}^{-1}$, indistinguishable from the adsorption equilibrium constant for the accumulation of adsorbate at the weaker site. This negatively moving band is a water deformation mode and could indicate that the weaker adsorption site involves interactions with surface-bound water. As discussed above, the spectrum of ethyl acetate adsorbed to the weaker site shows a smaller perturbation of C=O and C–C–O band frequencies, indicating less acidic hydrogen-bonding interactions than those at the stronger adsorption site attributed to surface silanols. When the displacement isotherm for the 1620 cm^{-1} band is extrapolated to completion, typically about two-thirds of the band intensity remains. A possible explanation of this behavior is that water at the outer boundaries of a multilayer structure is less tightly adsorbed and can be displaced by the ethyl acetate, while water that interacts directly with the surface is more tightly bound and is not displaced. Far-IR studies of silica that has been heated to $400\text{ }^{\circ}\text{C}$ indicate that a significant amount of water bound to silanols remains.⁴⁰ In addition, solution-phase reaction studies of the first monolayer of water adsorbed to silica have shown very minimal reactivity of this layer toward the hydrolysis of chlorosilane reagents.⁵¹

The magnitudes of the adsorption equilibrium constants, which were determined by replicate isotherm measurements in the $1220\text{--}1800\text{ cm}^{-1}$ region (see above), can be used to determine the free energies of adsorption. For adsorption to the stronger site, $\Delta G_a = -RT \ln K_a = -18.6 (\pm 0.3)\text{ kJ/mol}$. This result is comparable in energy to a strong hydrogen-bonding interaction of $\approx 20\text{ kJ/mol}$ which would be expected for ethyl acetate adsorption to free silanols. On the basis of the behavior of the OH stretching region and the 1620 cm^{-1} band, less strongly adsorbed ethyl acetate is probably forming a monolayer at the interface between adsorbed water and *n*-heptane. The large difference between the surface tensions of water and *n*-heptane, 50.2 mN/m , compared to the surface tension difference between

ethyl acetate and water, 6.8 mN/m ,⁴⁷ would be a sufficient driving force to establish a layer of ethyl acetate at the water/*n*-heptane interface. The free energy of adsorption of ethyl acetate to the weaker site is $\Delta G_a = -12.7 (\pm 1.2)\text{ kJ/mol}$. This result can be compared to the free energy gain from the lowering of the interfacial tension by the adsorbate; this can be estimated⁴⁷ by dividing the expected lowering of the surface tension by the expected surface coverage of the adsorbate ($\approx 0.4\text{ }\mu\text{mol/m}^2$), predicting a change in free energy of -11 kJ/mol . While this value is an approximation, since the surface tension of adsorbed water will differ from that of bulk water, it nevertheless shows that lowering the interfacial surface tension can produce a free energy of adsorption that is comparable in magnitude to what is observed for adsorption of ethyl acetate to the weaker site. Note that displacement of weakly bound water is not always observed in the adsorption of ethyl acetate, since the water content of the film varies depending on the relative humidity. Both adsorbed ethyl acetate populations are observed, however, even when surface water is not displaced, which indicates that the adsorption mechanism is not greatly affected by the water content of the film.

In addition to providing structural and thermodynamic information regarding the adsorption mechanism, the interfacial spectra can also be used to determine the ratio of silanol sites to water sites. This is done by comparing the relative magnitudes of the unnormalized C=O and C–C–O bands for the strongly and weakly adsorbed populations on the assumption that the oscillator strengths of these vibrations are not strongly affected by the differences in H-bonding interactions. This analysis shows that the two surface sites when fully occupied are responsible for approximately the same population of adsorbed ethyl acetate on the surface; a 1:1 ratio for the two surface sites would yield an average free energy change for adsorption of $-15.7 \pm 0.6\text{ kJ/mol}$. Direct spectral evidence for this average energy of adsorption is found in the displacement of *n*-heptane from the surface in the $2800\text{--}2970\text{ cm}^{-1}$ spectral region. This region could be modeled with a single Langmuir isotherm and linear component (for displacement of solvent molecules by ethyl acetate in solution); the resulting fit of this region is reasonable, as illustrated by the agreement between the model **C** and concentration dependence projected from the data $\hat{\mathbf{C}}$ shown in Figure 6a. The solvent displacement from the surface is fit by an adsorption equilibrium constant for this region of $470 \pm 180\text{ (mole fraction)}^{-1}$, which corresponds to an adsorption free energy of $-15 \pm 1\text{ kJ/mol}$; this agrees well with the free energy change estimated by assuming a 1:1 ratio for the two surface sites. The spectra, $\hat{\mathbf{A}}$, corresponding to the concentration variation of the two vectors in **C** are plotted in Figure 6b and show that adsorbed *n*-heptane displaced from the surface by ethyl acetate can be distinguished from *n*-heptane displaced by ethyl acetate in free solution. Since the interactions between *n*-heptane and the surface are not strongly dipolar, there is an insufficient difference in adsorption energies to distinguish solvent displacements occurring from the two different surface sites.

Displacement of Adsorbates. In normal-phase chromatography, it is common to elute a solute from a column by the addition of a compound to the mobile phase that has a strong adsorption affinity for silica in order to displace the solute from the surface.⁴⁶ Isotherms for the displacement of ethyl acetate by 2-propanol have been used to investigate the mechanism of adsorbate interactions at the silica surface in chromatographic studies.^{1,5} On the basis

(51) Tripp, C. P.; Hair, M. L. *Langmuir* **1992**, *8*, 1120–1126.

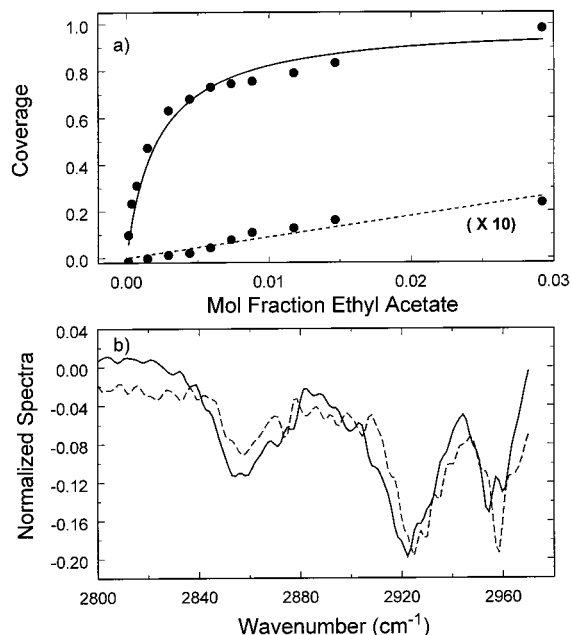


Figure 6. Displacement of *n*-heptane from the interface during the adsorption of ethyl acetate: (a) curves representing the model for the concentration dependence $\hat{\mathbf{C}}$ for displacement by adsorbed (solid) and solution-phase (dashed) ethyl acetate and points $\hat{\mathbf{C}}$ representing projections of the spectra onto the data; (b) spectra $\hat{\mathbf{A}}$ of the resolved components from displacement by adsorbed (solid) and solution-phase (dashed) ethyl acetate.

of this background, it was logical to use sol-gel ATR spectroscopy to study the displacement of adsorbates from silica.

To begin this investigation, the adsorption of 2-propanol from *n*-heptane onto silica was measured, and ATR difference spectra (solvent-subtracted) for a series of 2-propanol concentrations are plotted in Figure 7 for the 920–1010, 1200–1600, and 2970–3800 cm^{-1} regions. Unlike the ethyl acetate data, those for 2-propanol are less informative, since structural changes upon adsorption are difficult to detect in the infrared spectrum of this molecule. The methine (CH) stretching mode is very weak in the infrared spectrum⁴² and is not resolved in the 3000 cm^{-1} region; methyl (CH_3) groups are one carbon atom removed from the hydrogen-bonding interactions of the OH group, so that electron density changes in the CH_3 groups are weak and produce very small changes in the vibrational frequency. Interactions of the alcohol functional group with surface water or silanols produce a very broad band, as shown in Figure 7; the breadth of this band makes resolution of more than one spectral component from the data difficult. Figure 7 also shows that the disappearance of the free silanol band at 3700 cm^{-1} coincides with an increase in the feature at 3100 cm^{-1} . The shift to about 3100 cm^{-1} of the free silanol band is in agreement with IR studies of free silanols interacting with gas-phase hydrogen-bonding compounds.⁴⁵

A simple Langmuir isotherm plus a linear component for solution-phase 2-propanol captures the concentration variation of the spectra in Figure 7. The best-fit adsorption equilibrium constant was $2.86 (\pm 0.2) \times 10^3 (\text{mole fraction})^{-1}$, which corresponds to a larger adsorption free energy compared to that of ethyl acetate, $-19.7 (\pm 0.2) \text{ kJ/mol}$, which is expected. The best-fit isotherm is plotted in Figure 8, along with the $\hat{\mathbf{C}}$ projections for each of the three spectral regions; the best-fit adsorbate and solution-phase spectra, $\hat{\mathbf{A}}$, are plotted in Figure 9. Separation of

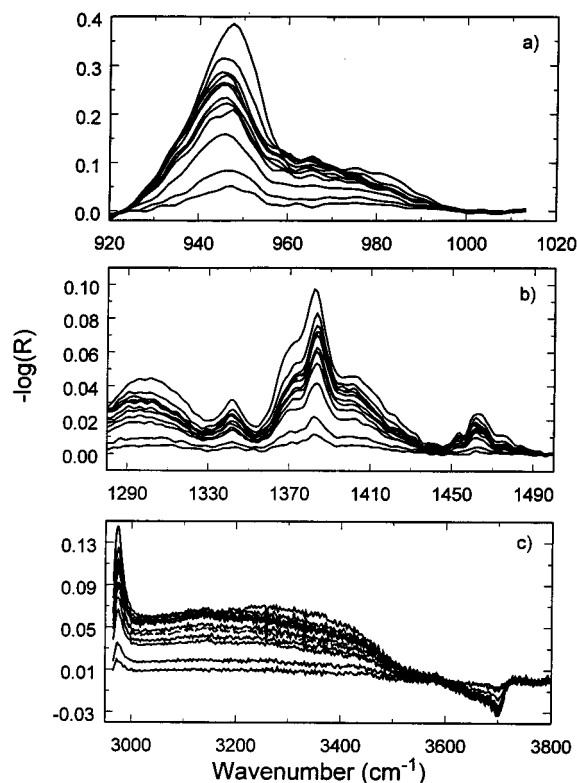


Figure 7. ATR-FT-IR difference spectra for the adsorption of 2-propanol onto silica from *n*-heptane solution. The 2-propanol concentration ranges from 0.5 to 210 mM.

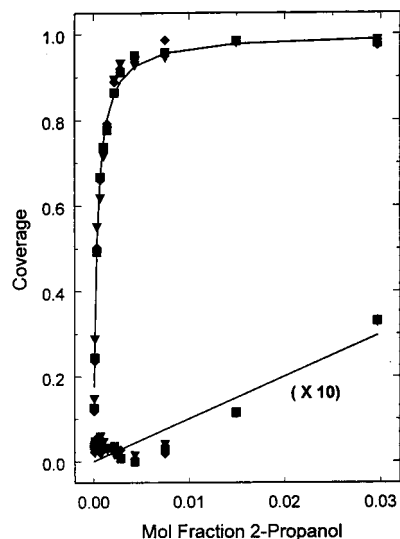


Figure 8. Least-squares optimized $\hat{\mathbf{C}}$ matrix (lines) describing the accumulation of 2-propanol at the silica interface from *n*-heptane solution. Points $\hat{\mathbf{C}}$ correspond to the projection of the spectra ($\hat{\mathbf{A}}$ plotted in Figure 9) onto the data; \blacksquare corresponds to Figure 9a, \blacklozenge corresponds to Figure 9b, and \blacktriangledown corresponds to Figure 9c.

the adsorbate and solution-phase bands by least-squares modeling in Figure 9b is near the resolution limit of the experiment of 4 cm^{-1} . To ensure that these small differences were not due to anomalous dispersion, solution-phase spectra of 2-propanol were collected using a bare germanium ATR element; peak shifting of no more than 0.5 cm^{-1} was observed with concentrations as high as 400 mM, which is almost twice the highest concentration used in the 2-propanol adsorption experiments.

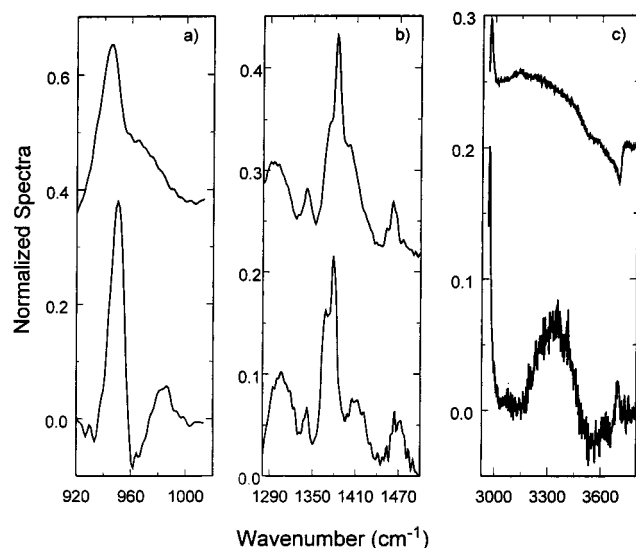


Figure 9. Least-squares-optimized spectra $\hat{\mathbf{A}}$ for the accumulation of 2-propanol at the silica surface. Top spectra correspond to the adsorbed component; bottom spectra are linear with the solution-phase concentration of 2-propanol.

While there is a small lack of fit in the residual difference between the model and $\hat{\mathbf{C}}$ results, a nonlinear least-squares optimization cannot resolve meaningful results from a two-isotherm fit of the data. Part of the difficulty in resolving the behavior of two sites in this case is due to the relatively small shifts in the 2-propanol bands upon adsorption. Nevertheless, the differences in the adsorption energies for the two sites must be significantly smaller for 2-propanol than for ethyl acetate, since all of the spectral regions return a consistent value for the adsorption equilibrium constant; the K_a 's determined from the individual C–C–C stretching, CH₃ bending, and OH stretching regions were $2.8 (\pm 4) \times 10^3$, $2.9 (\pm 4) \times 10^3$, and $2.8 (\pm 0.4) \times 10^3$ (mole fraction)⁻¹, respectively.

These results indicate that 2-propanol indeed experiences a more homogeneous adsorption equilibrium than does ethyl acetate on the same silica surface. While this finding seems contradictory, surface heterogeneities are not equivalent in the adsorptions of different compounds, since adsorption energies are composed of a mixture of specific interactions with the surface. For example, while ethyl acetate is simply a hydrogen-bond acceptor, 2-propanol can act as a hydrogen-bond donor as well as an acceptor. The amphiphilic nature of the alcohol adsorbate should make its interaction with surface water stronger; since 2-propanol is miscible with water, it could even dissolve to some extent into a water multilayer. These attributes of 2-propanol should increase the strength of the alcohol–water interactions so that they are comparable to alcohol–silanol interactions, leading to differences in adsorption energies for the two sites that are not detectable. The purely hydrogen-bond-accepting character of the ester, however, is very sensitive only to the large differences in hydrogen-bond acidity of silanols versus surface water, making the heterogeneity of the silica surface much more significant in the adsorption of this compound. In chromatographic separations, it is common to observe peak tailing for one class of compounds but not another. This behavior is usually attributed to a dispersion in site energies that affects a particular class of solute; from these results we have obtained spectroscopic evidence of compound-

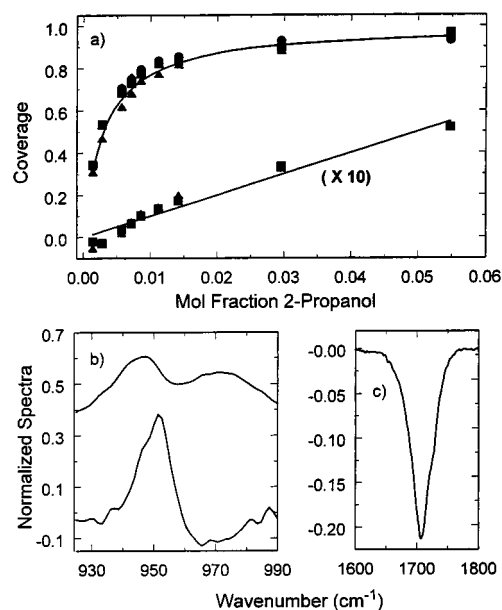


Figure 10. Modeling of the displacement of ethyl acetate from silica by 2-propanol. Part a shows the least-squares-optimized $\hat{\mathbf{C}}$ matrix (lines) with the points corresponding to the projection of the spectra onto the data; ■ corresponds to spectra in part b, ♦ corresponds to the 1240–1320 cm⁻¹ region, ● corresponds to spectra in part c, and ▲ corresponds to the 2950–3800 cm⁻¹ region.

specific differences in the adsorption response to surface heterogeneity.

On the basis of results for adsorption of the individual solutes onto silica from *n*-heptane, spectroscopic isotherms for the displacement of ethyl acetate from the silica surface by 2-propanol were also measured; this study was designed to investigate the mechanism of normal-phase chromatographic elution by addition of a strongly adsorbed component to the mobile phase. These experiments were carried out at a fixed ethyl acetate solution concentration of 80 mM (initial mole fraction = 0.012), which corresponds to initial coverages of $\theta_{AS}^S = 0.95$ for the stronger, silanol, site and $\theta_{AS}^W = 0.73$ for the weaker, adsorbed water, site. As the 2-propanol concentration was varied from 0 to 0.055 mole fraction, bands corresponding to adsorbed ethyl acetate diminished while those for adsorbed 2-propanol appeared in the spectra. This behavior could be captured by a single-displacement equilibrium used to model the concentration dependence (correcting for changes in X_M due to the difference in the molar volumes of *n*-heptane and 2-propanol). The results are plotted in Figure 10 for an average isotherm with a selectivity coefficient of $K_S = 4.7 \pm 0.2$, corresponding to a free energy difference for ethyl acetate displacement by 2-propanol of -3.8 ± 0.1 kJ/mol.

The concentration variations projected from the data $\hat{\mathbf{C}}$ for four spectral regions (3800–2950, 1800–1600, 1320–1240, and 990–920 cm⁻¹) are also plotted in Figure 10, along with representative bands from $\hat{\mathbf{A}}$, for the adsorbed 2-propanol and displaced ethyl acetate from two of those regions (see spectra in Figure 10b,c). The spectra extracted from these data show adsorbate peaks that match the bands obtained for pure 2-propanol adsorbed onto the sol–gel surface. We were unsuccessful in resolving two distinct isotherms from the data, however, which was unexpected, since the difference in the free energies of adsorption for ethyl acetate at the two sites is large, ≈ 5.6 kJ/mol. Some lack of fit was noted with this simple model, especially in the 1700 cm⁻¹ region, where

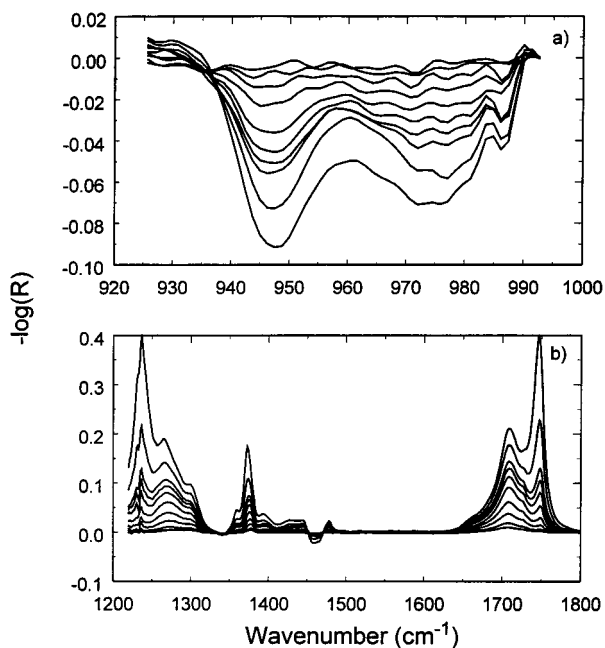


Figure 11. ATR-FT-IR difference spectra for the displacement of 2-propanol from the silica surface by ethyl acetate, with the ethyl acetate concentration ranging from 10 mM to 1.64 M: (a) spectra showing the decrease in the C—C—C backbone stretching band of 2-propanol with increasing ethyl acetate concentration; (b) Spectra showing ethyl acetate accumulating at the silica surface as 2-propanol is displaced.

the ethyl acetate spectrum is sensitive to a hydrogen-bonding environment; a two-component model, however, could not resolve two adsorbed components from the data, so the simpler isotherm was used. One possible explanation for the inability to extract two isotherms is that the water/*n*-heptane interface changes in the presence of 2-propanol. As mentioned above, the coverage of ethyl acetate on the water layer is initially only 73% for these experiments, so when displacement of ethyl acetate is detected from the water layer, one-fourth of this surface is already interacting with 2-propanol. This amount of 2-propanol could change both the structure and the polarity of the interface and influence the nature of the ethyl acetate–water interaction.

It is not surprising to see a strong adsorbate such as 2-propanol displace a weaker adsorbate such as ethyl acetate from the surface. It has been postulated from chromatographic studies, however, that strongly hydrogen-bonding adsorbents form surface phases that are not displaced by weaker adsorbates.⁵ To test this hypothesis, a silica film was equilibrated with a fixed concentration (25 mM) of 2-propanol, corresponding to an initial surface coverage of 91%, while the concentration of ethyl acetate was varied from 0 to 0.2 mole fraction. Evidence of displacement of 2-propanol by ethyl acetate is clearly observed in the 950 cm⁻¹ region plotted in Figure 11a. The adsorbate band that disappears is the C—C—C backbone stretch of 2-propanol, also shown in Figures 7a and 9a. Comparison with the solution-phase spectrum isolated in Figure 9a (which is identical to that of solution-phase 2-propanol on a bare germanium IRE element with a single peak around 950 cm⁻¹) shows that the spectrum in Figure 11a is indeed due to adsorption of 2-propanol. The reason for the presence of two peaks in the adsorbate spectra could be different conformational forms of the molecule that are present on the surface; band separation of different conformations of normal alcohols in solution

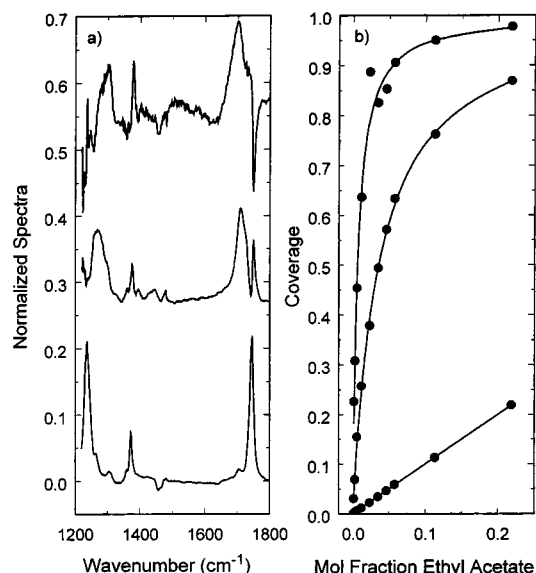


Figure 12. Modeling the displacement of 2-propanol by ethyl acetate: (a) component spectra \hat{A} resolved with two Langmuir displacement isotherms (top, middle), and a solution-phase solute component (bottom); (b) model concentration dependence (lines) and the projections of the spectra \hat{A} onto the data (\hat{C} , points).

has been reported.⁵² Because of the lack of bands that are sensitive to the adsorption environment in this region, only a single Langmuir isotherm was used to model the data. The selectivity coefficient obtained from fitting the 950 cm⁻¹ region was 0.12 ± 0.01 , which corresponds to an average free energy change for displacement of 2-propanol by ethyl acetate of $5.3 (\pm 0.1)$ kJ/mol. This value is similar in magnitude (40% larger; opposite sign) to that obtained for the displacement of ethyl acetate by 2-propanol; see discussion below.

Growth of the ethyl acetate bands in the 1220–1800 cm⁻¹ region during the displacement of 2-propanol is shown in Figure 11b. These data clearly show differential growth of two adsorbed components, similar to the results for adsorption of ethyl acetate in the absence of 2-propanol in Figure 3a. The displacement results in this spectral region were successfully fit to two Langmuir displacement isotherms, plus a linear component to account for the change in the solution-phase concentration of ethyl acetate; the *F*-ratio for a two-isotherm model compared to a single-isotherm fit is significant, $F = 2.2$. The selectivity coefficients for ethyl acetate adsorption found from the modeling are 0.58 ± 0.25 and 0.10 ± 0.01 . Pure-component spectra and isotherms resolved from the data are plotted in Figure 12. The spectra resolved from these data are nearly identical to the pure-component spectra from ethyl acetate adsorption in Figure 4; frequency-shifting of the solution bands at the high concentrations (>1.6 M) required for 2-propanol displacement (also observed in solution spectra measured against a bare IRE) has caused some of solution intensity to be captured by the adsorbate spectra. The consistency of the ethyl acetate adsorbate bands indicates that displacement occurs from both sites on the silica surface. The weaker selectivity coefficient corresponds to the spectrum that was previously assigned to ethyl acetate interacting with the surface-bound water, while the

(52) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: New York, 1991; Chapter 4.

stronger selectivity coefficient produces a spectrum assigned to ethyl acetate adsorbed on silanols.

In the analysis of the adsorption data for 2-propanol (Figures 5 and 6), it was concluded that interactions with the surface were more homogeneous, so that a dispersion in adsorption equilibria could not be detected for this solute. If the adsorption equilibrium constants for preadsorbed 2-propanol are indeed the same for both sites, then K_a^M for both sites would be identical. This would predict that the selectivity coefficients for displacement of 2-propanol from these sites would be governed solely by differences in the adsorption equilibrium constants for ethyl acetate, K_a^A in eq 10. If this were true, then the ratio of the selectivity coefficients for the two sites would be 10, the same as the ratio of the strong and weak adsorption equilibrium constants for ethyl acetate (see above). The actual ratio of the selectivity coefficients that is observed is 5.8, which corresponds to 2-propanol having a slightly (1.7 times) greater affinity for silanol sites than for surface-adsorbed water. This difference would be too small to be resolved from the 2-propanol adsorption data but can be detected in the smaller selectivity coefficient for displacement by ethyl acetate than is predicted from differences in K_a^A for the two sites.

Comparing the relative amplitudes of the unnormalized pure-component spectra shows that the ratio of surface water to silanol sites is about 4.5:1 for ethyl acetate displacement of 2-propanol, a significant change from the ethyl acetate adsorption data, which gave a ratio of about 1:1. This result lends support to the idea, discussed above, that 2-propanol may change the interfacial water layer, perhaps causing it to spread over a greater fraction of the silica surface. Using the 4.5:1 ratio of surface sites in a weighted average of the adsorption free energies for ethyl acetate predicts a site-weighted average energy of -13.8 kJ/mol for the adsorption of ethyl acetate onto a 2-propanol-wetted surface. From this result, one can subtract the adsorption energy of 2-propanol, -19.7 kJ/mol, to predict a free energy change of 5.9 kJ/mol for the displacement of 2-propanol by ethyl acetate. This prediction compares very favorably with the average displacement energy, 5.3 kJ/mol, determined from the data in Figure 11a. When displacing ethyl acetate by 2-propanol, one would expect the site ratio to be closer to unity on the basis of the quantitative analysis of the spectra in Figure 4. Under these conditions, the site-weighted average free energy for ethyl acetate adsorption would increase to -15.7 kJ/mol; subtracting the free energy for 2-propanol adsorption predicts a free energy change of -4.0 kJ/mol for the displacement of ethyl acetate by 2-propanol. This result agrees with the free energy change determined from the measured displacement equilibrium, $-3.8 (\pm 0.1)$ kJ/mol. Therefore, the discrepancy between the displacement energies could be due to the preadsorbed 2-propanol increasing the fraction of available water sites on the silica surface.

The clearest conclusions that we can derive from these displacement data are that a less polar molecule like ethyl acetate can indeed displace a strongly hydrogen-bonded adsorbate such as 2-propanol from a silica surface and that the loss of the preadsorbed monolayer coincides with the accumulation of the displacing adsorbate on the surface. A displacement model that includes delocalization of the preadsorbed monolayer is not consistent with these results, since such a model would predict

that the first ethyl acetate to be adsorbed would displace the most delocalized 2-propanol and would exhibit a weak interaction with the surface. If this were the case, the pure-component spectrum, which would dominate at low concentrations of ethyl acetate on the surface, would exhibit weak hydrogen-bonding interactions; this is not the case, since the initially adsorbed ethyl acetate corresponds to the spectrum of ethyl acetate interacting with free silanols. In addition, two distinct displacement isotherms and their corresponding adsorbate spectra are evident over the entire range of solute concentration, which differs from the predictions of a delocalization model, where the spectra would shift as the coverage changes.

CONCLUSIONS

Adsorptions of ethyl acetate and 2-propanol from *n*-heptane solution onto silica sol-gel thin films have been characterized using ATR-FT-IR. The films have been shown to have high surface areas for adsorption and in combination with a germanium IRE substrate provide high sensitivity and broad spectral coverage for studying normal-phase chromatographic interfaces. Spectra of ethyl acetate adsorption were detected at concentrations as low as $200 \mu\text{M}$ in solution, which corresponds to fractional coverages of 5% and 0.7% of a monolayer for the two adsorption sites on the surface. Obtaining structural information at such low adsorbate coverages is unusual for in situ solid/liquid interface measurements.

Least-squares modeling of ethyl acetate adsorption onto the silica surface was able to extract isotherms and component spectra of two distinct forms for ethyl acetate on the surface, showing that site heterogeneity can account for nonlinear adsorption behavior in this system. From an examination of the behavior in the OH stretching and water bending regions of the spectrum, it appears that the two adsorption sites are isolated silanols and surface water adsorbed on vicinal silanols. Adsorption of 2-propanol onto the silica surface was also studied and exhibited single-isotherm behavior, indicating comparable interactions with silanols and surface water due to stronger hydrogen bonding and miscibility with the latter sites. Competition between these two molecules for adsorption at the *n*-heptane/silica interface was also studied. It was found that 2-propanol can be displaced by ethyl acetate from the surface with a displacement free energy gain that can be predicted from the free energies of adsorption of each compound. It was also determined that displacement of 2-propanol by ethyl acetate is characterized by two isotherms, similar to the direct adsorption of ethyl acetate. The ratio of surface water to free silanol sites appears to increase when 2-propanol is preadsorbed on the surface, possibly indicating that 2-propanol causes water to spread over a larger area of the silica surface.

ACKNOWLEDGMENT

This work was supported in part by grants from the U.S. Department of Energy (DE-FG03-93ER14333) and the National Science Foundation (CHE98-17534).

Received for review August 24, 1999. Accepted December 14, 1999.

AC990968H