A Study of Glass Surface Heterogeneity and Silylation by Inverse Gas Chromatography

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The method of obtaining energy and entropy of adsorption on homogeneous surfaces from retention time of a chromatographic peak is extended to heterogeneous surfaces. A heterogeneous surface is modeled as a collection of homogeneous patches (sites) and is characterized by a bidimensional distribution of these patches with respect to the energy and entropy of adsorption. This bidimensional distribution can be converted into a one-dimensional distribution of sites with respect to the free energy of adsorption. (The latter can be calculated from chromatographic elution profiles by known methods.) It is shown how to convert the free energy distribution of sites into the distributions of sites with respect to parameters similar to energy and entropy of adsorption. These are regressions of energy and entropy on the free energy of adsorption. Their meaning is elucidated by an example of the normal bidimensional distribution in {energy, entropy} pairs. The method is applied to the study of the silylation of glass fiber surfaces by trimethoxymethylsilane. The adsorption energy distributions of butanol on the silylated surfaces are obtained for different curing temperatures. At a fixed value of the distribution function in the interval of curing temperature from 180 to 350 °C, the adsorption activity of the surface is minimal at about 290 °C.

1. Introduction

Modification of silica and silicate glass surfaces by organosilanes is widely used in a variety of applications including coupling agents for fiber-reinforced composites, stationary phases in chromatography, and immobilization of biomolecules. An important question in these applications is the nature of the chemical bond between the coupling agent (organosilane) and the glass surface. The subject has been recently reviewed.[1−3]

In this paper, we study modification of a glass surface by trimethoxymethylsilane (TMMS, $MeSi(OMe)_3$, A1630). Reactions of TMMS vapor with a high surface area silica have been studied by IR spectroscopy in the range of 2700−4000 cm^{-1} (see refs 4 and 5) and low-frequency[6] (below 1300 cm^{-1}) regions. At room temperature, only physical adsorption of hydrogen-bonded molecules takes place.[4−6] At elevated temperatures (above 150 °C), about 40% of the physically adsorbed molecules react monofunctionally

$$\equiv SiOH + MeSi(OMe)_3 \rightarrow \equiv SiO-Si(OMe)_2Me + MeOH \quad (1)$$

and about 60% react difunctionally with the surface silanols ($\equiv$SiOH):[4,5]

$$2(\equiv SiOH) + MeSi(OMe)_3 \rightarrow (\equiv SiO)_2Si(OMe)Me + 2MeOH \quad (2)$$

Adsorption of TMMS (physical or chemical) leads to an intensity decrease of the sharp band at 3745 cm^{-1} assigned to nonhydrogen-bonded (free) surface silanols, which can be used for quantitative study of the kinetics of these reactions. The above conclusion was obtained from the kinetic equation describing the overall reaction of TMMS with the silica surface.[4,5]

A diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to investigate the reaction of TMMS (as well as $Me_2Si(OMe)_2$ and Me_3SiOMe) in toluene with Cab-O-Sil (high surface area silica).[7] Relative concentrations of TMMS on the suface of Cab-O-Sil were evaluated from the areas of specific IR bands. First, TMMS was adsorbed from toluene solution onto the Cab-O-Sil surface at room temperature. Then, samples were rinsed with toluene, dried, and treated (cured) at 80, 140, and 200 °C. When neither the toluene nor the Cab-O-Sil contained water, no chemical bonding between the TMMS and the silica surface could be found; curing only distilled TMMS from the Cab-O-Sil. However, when water was first adsorbed on the Cab-O-Sil, hydrolysis of TMMS

$$MeSi(OMe)_3 + 3H_2O \rightarrow MeSi(OH)_3 + 3MeOH \quad (3)$$

and condensation of organosilane silanols to silica silanols have been observed in the process of curing:

$$\equiv SiOH + MeSi(OH)_3 \rightarrow \equiv SiO-Si(OH)_2Me + H_2O \quad (4)$$

$$2(\equiv SiOH) + MeSi(OH)_3 \rightarrow (\equiv SiO)_2Si(OH)Me + 2H_2O \quad (5)$$

Another IR study of TMMS adsorption from heptane and carbon tetrachloride solution on silica deals primarily with physical adsorption (hydrogen bonding).[8] The multilayer silylation of a silica surface with vinyltrimethoxysilane (VTMS) from anhydrous solvents was also investigated to demonstrate and quantify the effects of surface water on multilayer silylation.[9] The reactions in this case are believed to be basically the same as for TMMS eqs 3−5; the only difference is that the methyl group is substituted by the vinyl one. The papers referred to above used IR spectroscopy and high surface area silicas. There was also an attempt to use DRIFTS for the study of silylation of 10 μm diameter glass fibers.[10] A silane coupling agent, in this case γ-methacryloxypropyltrimethoxysilane, was adsorbed on the glass fiber surfaces from aqueous solution. Because of a very

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low specific surface of glass fibers as compared to silica gels, the results of this study are less quantitative than those with silica gels mentioned above.

The IR spectroscopic studies described above give the first indications about heterogeneity of the silica surface. This means that there are different adsorption sites on the surface. In many cases, these sites are silanol groups and there are at least three types of them (free, vicinal, and geminal silanols).[3] The role of these silanols in the chemisorption of TMMS is different: in particular, the strongest chemisorption sites are free silanols.[4,5] Surface heterogeneity also plays a very important (usually negative) role in adsorption chromatography. It is the reason for the asymmetry (tailing) of chromatographic peaks, which prevents good analytical separations of gas or liquid mixtures. Thus, one of the important steps in adsorption chromatography is to make a surface homogeneous (usually by silylation). Inverse gas chromatography (IGC) pursues an opposite goal in comparison with conventional chromatography. It does not seek to analyze a gas mixture by separating it on a chromatographic column into nonoverlapping peaks but makes a conclusion about the adsorption properties of the column packing surface from the position and shape of (usually) one peak (elution profile).

A special advantage of using IGC for the study of the heterogeneity of the glass fiber surface is the following. Glass fibers have very small specific surfaces (orders of magnitude smaller than, for example, the silica gels used in conventional chromatography). Thus, conventional methods (such as FTIR or NMR spectroscopy) are not as effective for glass fibers as for silica gels. Even conventional chromatography on a column packed with glass fiber is ineffective due to the small number of adsorption sites in the column that causes the retention of adsorbed molecules. However, there is always a small number of very strong adsorption sites on glass surfaces due to the heterogeneity of these surfaces with respect to adsorption of some polar molecules. (In general, glass surfaces are heterogeneous with respect to adsorption of such polar molecules as butanol but can be homogeneous with respect to nonpolar molecules such as alkanes.) These strong sites hold special probe molecules for a very long time so that despite the small number of sites the total retention time of the column can be very long. In other words, the elution profile on such a column can have a very long tail for a tiny fraction of molecules such as butanol injected in the column. This phenomenon has been employed in our previous paper for the study of glass fiber surfaces by IGC with respect to adsorption of butanol used as a probe molecule.[12]

In this paper, we address two problems. On one hand, we try to promote a general understanding of surface heterogeneity and its analysis by the IGC. This part further develops our previous results[11,12] and is contained in Section 3 and in the discussion of Figures 1 and 2. We consider here our previous results[11,12] from a somewhat different point of view and further elucidate their meaning. In Section 3 of this paper as well as in our previous publications,[11,12] we develop a new approach to surface heterogeneity that allows one to rigorously separate the free energy distribution of adsorption sites into the energy and the entropy distributions. In the theory of adsorption on heterogeneous surfaces,[13,14] such a separation has been made on the basis of some approximations, which work well for small molecules such as nitrogen but can be inadequate for larger organic molecules (see ref 12 and references therein). Our approach can be considered as an extension to heterogeneous surfaces of the well-known method of separation of the free energy of adsorption on a homogeneous surface into the entropy and the energy of adsorption. It will be shown below (see discussion of Figure 1) that our approach helps to disclose some inconsistencies of the standard method of IGC when applied to heterogeneous surfaces and poses new problems. On the other hand, we try to apply the energy distribution function of adsorption sites on a heterogeneous surface to the study of the glass fiber silylation. This comprises the main experimental part of this work (Section 2 and Figures 3−6).

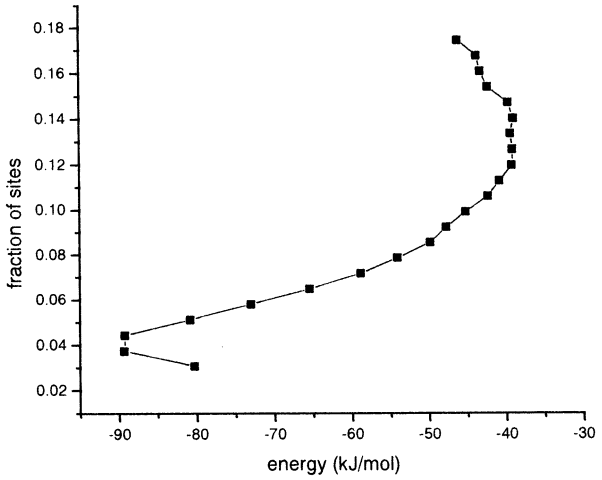

Figure 1. Energy distribution (cumulative) of sites for butanol on a glass surface as obtained from IGC. Fraction of sites = *N*.

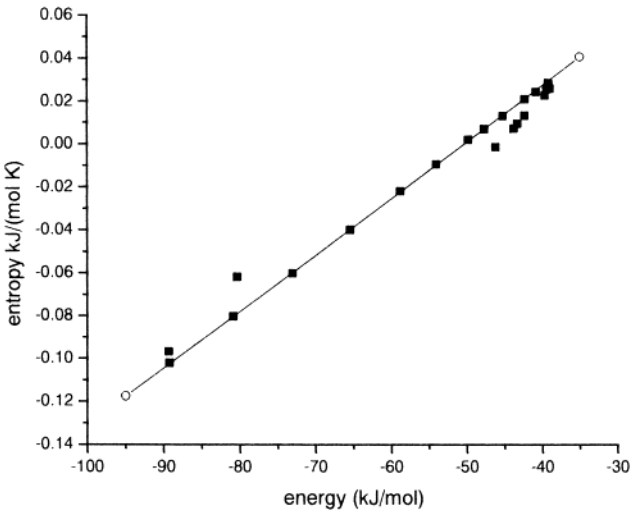

Figure 2. Adsorption entropy vs adsorption energy for butanol on glass at 46 °C. The straight line between circles corresponds to eq 30.

2. Experimental Section

The 1-butanol used in this study was from SIGMA-Aldrich, high-performance liquid chromatography (HPLC) grade (99.8%). TMMS was from Gelest Inc. Both reagents were used as obtained. Methane from the Methane Cylinder Kit (Restek Corporation) was used as the nonadsorbing gas. E-glass fibers were freshly drawn and sealed in a vacuum until their silylation; the fiber diameter was 13.2 μm.

Silylation of the glass fibers was accomplished by immersing about 5 g of fiber in 200 mL of 1 w% aqueous solution of A1630 brought to pH 4 by acetic acid. The fiber was held in the solution (without stirring) for 17 h at the ambient temperature. Afterward, the solution was decanted and one of the samples (sample B) was slightly rinsed three times in a small amount of deionized (DI) water (about 20 mL). The second sample (sample A) was

thoroughly rinsed with water by immersing in 200 mL of DI water (without stirring), and in 15 min, the water was decanted. This procedure was repeated five times. Then, both samples were dried in air at 90 °C for an hour.

The treated fibers were pulled through a glass tube (ca. 23 cm long, ca. 4 mm i.d.) to make chromatographic columns so that the weight of the column packing was about 3 g. With the E-glass density of about 2.5 g/cm^3, the surface area of the column packing was evaluated as 0.36 m^2. The area of a butanol molecule was evaluated[15] as 0.28 nm^2; that gives 2.1 μmol for the capacity of monolayer in the column. The injected amount of butanol was in almost all cases 0.02 μL (except when indicated otherwise). This corresponds to 0.22 μmol and about 10% loading. Such a small amount of butanol was injected by a 1 μL syringe (Hamilton Company, 7000 series); so, the accuracy of injection was not high (about 20%). The accurate amount of injected butanol was determined by the area of the elution profile obtained as described earlier.[12]

The gas chromatograph (GC) used in this study was a Hewlett-Packard HP5890 monitored by HP ChemStation (Rev. A.06.04) software (under Windows NT, PC) and equipped with a DP95 digital RTD thermometer (OMEGA Engineering, Inc.). The stability of the temperature in the GC oven as measured by the thermometer was 0.01 °C. A flame ionization detector (FID) was used, the temperatures of the detector and the injector being 250 and 170 °C, respectively. The carrier gas was helium; the flow rate of He was about 15 mL/min under the head pressure of about 5 psi. All of the calculations were performed with the help of VBA (Visual Basic for Applications) modules in EXCEL developed specially for this study.

3. Gas Chromatography on a Heterogeneous Surface

The conventional method for determination of adsorption thermodynamic functions in linear chromatography is based on the equations (see, e.g., ref 16, p 231):

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -RT\ln K = -RT\ln V_S \qquad (6)$$

where $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$ are the standard molar Gibbs free energy, enthalpy, and entropy of adsorption, respectively; K is the Henry constant; and V_S is the net retention volume divided by the total surface area of the column packing. The values of $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$ are the differences between the values of the corresponding molar thermodynamic functions in the standard adsorption state and those in the standard gas state (see definition of these standard states below). To simplify the notations, we will designate them below as G, H, and S, respectively. It is usually assumed that H and S do not depend on temperature (at least in a relatively narrow temperature interval of a conventional chromatographic experiment) and can be obtained from the temperature dependence of G or $RT\ln V_S$.

$$dG/dT = -S \qquad (7)$$

Thus, eq 6 describes a surface with respect to its interaction with a given probe molecule by two constants H and S. This means that the surface is homogeneous. Thus, in linear chromatography on homogeneous surfaces, one determines directly from experiment (from V_S in eq 6) the standard Gibbs free energy of adsorption G that strongly depends on temperature and separates it into two approximately temperature-independent pair of constants $\{H,S\}$.

As a first approximation, a heterogeneous surface can be considered as a collection of patches (sites) of homogeneous surfaces, each patch being described by a unique pair of constants $\{H,S\}$. Thus, in distinction from a homogeneous surface that is described by only one pair of constants, a heterogeneous surface is described by a collection of pairs, which gives rise to the problem of finding a bidimensional distribution of the number of patches (sites) with respect to these pairs. Let $n(H,S)$ be a bidimensional density of patches ($n(H,S)\,dH\,dS$ is the number of patches in the rectangle of area $dH\,dS$ around the point (H,S) on the H,S parameter plane) and $\chi(x)$ is the unit step-function:

$$\chi(x) = 1 \text{ if } x < 0;\ \chi(x) = 0 \text{ if } x > 0 \qquad (8)$$

Consider the function $N(G,T)$ defined by the following equation

$$N(G,T) = \int\int \chi(H - TS - G)n(H,S)\,dH\,dS \qquad (9)$$

Integration in eq 9 is over all the domain of definition of H and S, but the step function of eq 8 in the integrand of eq 9 selects only those values of H and S that satisfy the inequality

$$H - TS < G \qquad (10)$$

Therefore, $N(G)$ (T is a parameter) in eq 9 is a distribution function of sites with respect to the standard Gibbs free energy of adsorption (we call it free energy distribution function below) since it gives the number of sites for which the value of this thermodynamics function is less than G. The derivative of $N(G)$ with respect to G is the density of sites at a given value of G. (In adsorption literature, the density of sites is sometimes called the distribution function. In this case, one should call $N(G)$ the cumulative distribution function.)

Consider now a change of $N(G,T)$ from eq 9 that is so small that it can be considered as a sum of changes ΔG at constant T and $S\Delta T$ at constant G

$$\begin{aligned}\Delta N = N(G + \Delta G, T + \Delta T) - N(G,T) = [N(G + \Delta G, T + \Delta T) - N(G, T + \Delta T)] + [N(G, T + \Delta T) - N(G,T)] \approx \\ [N(G + \Delta G, T) - N(G,T)] + [N(G, T + \Delta T) - N(G,T)] = \\ \Delta G \int\int \Delta_G(H - TS - G)n(H,S)\,dH\,dS + \\ \Delta T \int\int S\Delta_{TS}(H - TS - G)n(H,S)\,dH\,dS \qquad (11)\end{aligned}$$

where $\Delta_y(x)$ is an impulse function with $\chi(x)$ from eq 8:

$$\Delta_y(x) = [\chi(x - y - \Delta y) - \chi(x - y)]/\Delta y \qquad (12)$$

This function is a rectangular pulse that is zero when x is outside of the interval $[y, y + \Delta y]$ and has unit area under the pulse. (In the limit $\Delta y \to 0$, $\Delta_y(x)$ is the Dirac δ-function $\delta(x - y)$.) The approximate part of eq 11 is due to the neglect of the values proportional to $\Delta G\Delta T$ in comparison to those proportional to ΔG or ΔT and becomes accurate when $\Delta T \to 0$ and $\Delta G \to 0$. At $\Delta N = 0$, one obtains from eq 11

$$\begin{aligned}(\Delta G/\Delta T)_N = -\int\int S\Delta_{TS}(H - TS - G)n \\ (H,S)\,dH\,dS/\int\int \Delta_G(H - TS - G)n(H,S)\,dH\,dS \qquad (13)\end{aligned}$$

Here, the denominator is the total number of patches that have the values of H and S such that $H - TS$ is in the interval $[G, G + \Delta G]$ and the numerator is the total standard entropy of adsorption on these patches. Thus, the fraction on the right-hand side of eq 13 is the mean entropy of adsorption averaged

over patches that have the Gibbs free energy of adsorption in the small interval $[G,G + \Delta G]$.

$$(\Delta G/\Delta T)_N = -\langle S\rangle_G \tag{14}$$

Although eq 14 is similar to eq 7, there are two differences between them. First, the full derivative on the left-hand side of eq 7 is substituted by the partial derivative at constant value of the (cumulative) distribution of sites in eq 14. Second, the meanings of the right-hand sides in eqs 7 and 14 are different.

To explain the meaning of $\langle S\rangle_G$ in eq 14, consider as an example the normal bidimensional distribution of sites with respect to H and S:[17]

$$\varphi(H,S) = \frac{1}{2\pi\sigma_1\sigma_2\sqrt{1-\rho_{12}^2}}\exp\left[-\frac{u_1^2 - 2\rho_{12}u_1u_2 + u_2^2}{2(1-\rho_{12}^2)}\right] \tag{15}$$

where

$$u_1 = (H - \langle H\rangle)/\sigma_1;\ u_2 = (S - \langle S\rangle)/\sigma_2 \tag{16}$$

and $\langle H\rangle$, $\langle S\rangle$, σ_1, σ_2, and ρ_{12} are five constants independent of temperature ($\langle H\rangle$, σ_1 and $\langle S\rangle$, σ_2 are the unconditional means and the standard deviations of H and S, respectively, and ρ_{12} is the correlation coefficient between H and S).

One may also consider a regression of S on H:[17]

$$\langle S\rangle_H = \langle S\rangle + \rho_{12}(\sigma_2/\sigma_1)(H - \langle H\rangle) \tag{17}$$

that is the mean value of S averaged over the distribution of eq 15 subject to the condition that H is kept constant. The meaning of $\langle S\rangle_G$ in eq 14 is similar to $\langle S\rangle_H$ on the left-hand side of eq 17; the only difference between them is that the value that is kept constant on the right-hand side of eq 14 is not H as in eq 17 but

$$G = H - TS \tag{18}$$

Thus, $\langle S\rangle_G$ in eq 14 can be called regression of S on G.

In variables of eq 16, eq 18 takes the form

$$u_1 = au_2 + b;\ a = T\sigma_2/\sigma_1;\ b = (G - \langle G\rangle)/\sigma_1;\ \langle G\rangle = \langle H\rangle - T\langle S\rangle \tag{19}$$

Use u_1 from these equations to eliminate u_1 from the argument of the exponent in eq 15 and bring that argument to the following form

$$\frac{u_1^2 - 2\rho_{12}u_1u_2 + u_2^2}{2(1-\rho_{12}^2)} = A[(u_2 - \langle u_2\rangle)^2 + B] \text{ with } \langle u_2\rangle = \frac{b(\rho_{12} - a)}{1 - 2\rho_{12}a + a^2} \tag{20}$$

where a and b are constants from eqs 19 and A and B are also constants that can be expressed through a and b (A and B are not used below). The value of $\langle u_2\rangle$ in eq 20 is the mean value of u_2 subject to the first of eqs 19. The latter is equivalent to eq 18. Thus, insert b and a from eq 19 into $\langle u_2\rangle$ from eq 20 and use eq 16 to obtain

$$\langle S\rangle_G = \langle S\rangle + \frac{\sigma_2}{\sigma_1}\frac{(G - \langle G\rangle)(\rho_{12} - a)}{1 - 2\rho_{12}a + a^2} \tag{21}$$

(now, S in eq 16 becomes $\langle S\rangle_G$ because eq 18 is observed.) The values of $\langle H\rangle_G$ and $\langle S\rangle_G$ are connected by the equation

$$\langle H\rangle_G - T\langle H\rangle_G = G \tag{22}$$

obtained from eq 18. Substitute eq 21 into eq 22 to obtain

$$\langle H\rangle_G = \langle H\rangle + \frac{(G - \langle G\rangle)(1 - \rho_{12}a)}{1 - 2\rho_{12}a + a^2} \tag{23}$$

It is clear from eqs 21 and 23 that $\langle H\rangle_G$ and $\langle S\rangle_G$ depend on temperature (through a in eq 19). This is in contrast with H and S in eqs 6 and 7 for homogeneous surfaces that are assumed to be independent of temperature. Consider, however, the limit case of $\rho_{12} = 1$ when the correlation between H and S is so strong that they are, in fact, functions of one another. In this case, eq 15 is a very narrow distribution (δ-function) so that in eq 16 $u_1 = u_2$ and

$$G - \langle G\rangle = (S - \langle S\rangle)(\sigma_1/\sigma_2)(1 - a) \tag{24}$$

Substitute eq 24 into eq 23 with $\rho_{12} = 1$ to obtain

$$\langle H\rangle_G = \langle H\rangle + (\sigma_1/\sigma_2)(S - \langle S\rangle) \tag{25}$$

At $\rho_{12} = 1$, the distribution of eq 15 is, in fact, the δ-function, which means that the surface is homogenous and S is, by the above assumption, independent of temperature. Thus, $\langle H\rangle_G$ in eq 25 is also independent of temperature and will approximately stay so when ρ_{12} is close to 1.

It follows from eqs 21 and 23 that the normal bidimensional distribution of sites leads to the linear regressions of entropy $\langle S\rangle_G$ and enthalpy $\langle H\rangle_G$ on G and correspondingly linear relation between them. That is what is usually observed experimentally (see ref 12 and references threrin). The physical meaning of the correlation between entropy and energy has been discussed in the literature for a long time (see ref 12 and references therein). In this particular case, it simply means that the stronger the adsorption site is, the more it restricts the freedom of an adsorbed molecule, that is, diminishes the entropy of adsorption.

To determine the standard states mentioned in connection with eq 6, consider the Langmuir model of adsorption on a heterogeneous surface that assumes a patch to be a site that can adsorb only one molecule, adsorption states of different sites being independent of each other. In the Langmuir model, the entropy of adsorption is[18]

$$S = R\ln(\nu\tau_0 C_0) \tag{26}$$

where νC_0 is the number of impacts per unit of time of ideal gas molecules on a site at the standard gas concentration C_0 and τ_0 is some characteristic time (preexponential factor in the Frenkel equation for the time of adsorption[12,18]). The value of ν in eq 26 is

$$\nu = [RT/(2\pi M)]^{1/2}\sigma\alpha N_A \tag{27}$$

where σ is the area of a site; M is the molecular weight of a molecule; α is the accommodation coefficient; and N_A is the Avogadro's number. The value of S in eq 26 is similar to $\Delta S^\ominus$ in eq 6. The difference is that S in eq 26 has a natural dimensionality of entropy since the argument of the logarithm is dimensionless in contrast with $\Delta S^\ominus$ in eq 6 that has unnatural dimensionality due to the dimensionality of V_S. To give the

standard entropy of adsorption in eq 6 the natural dimensionality of entropy, one can modify eq 6 as follows:

$$G = H - TS = -RT \ln(V_S C_0/N_S) \tag{28}$$

where N_S is the number of sites per unit area of the surface.

The value of S in eq 26 is the difference between the molar entropy of adsorbed molecules in the standard adsorption state and that of gas molecules in the standard gas state. The standard state of adsorbed molecules in eq 26 (for the Langmuir model) is the state when the number of adsorbed molecules is half of the number of sites (coverage is 0.5). In this state, the configurational (collective) entropy of adsorbed molecules is zero and their entropy is determined by the partition functions of individual molecules adsorbed on sites. The standard state of the gas molecules is the state of the ideal gas at concentration C_0. If one chooses in eq 26

$$C_0 = 1/\nu\tau_0 \tag{29}$$

then, the entropy of adsorption is zero ($S = 0$). The problem is that on a heterogeneous surface the values of ν and τ_0 are different for different sites. Thus, as in our previous paper, we choose here a standard value of $\tau_0 = 10^{-12}$ s, a standard value of accommodation coefficient $\alpha = 0.1$, and the value of σ equal to the molecular area (0.28 nm^2 for butanol).[12] With these values of parameters in eqs 27 and 29, the value of C_0 at 300 K equals about 800 mol/L corresponding to a pressure of the ideal gas of about 2 GPa.

Because the gas phase in its standard state is ideal by definition, its molar enthalpy does not depend on concentration or pressure and is always a molar energy (that also does not depend on pressure) plus RT. In the adsorption state, enthalpy and energy coincide. For that reason, we call below H adsorption energy although its designation usually corresponds to enthalpy. For simplicity, we will also call $\langle H\rangle_G$ adsorption energy and $\langle S\rangle_G$ adsorption entropy although, as explained above, these are, in fact, regressions of these thermodynamic functions on free energy of adsorption.

4. Results and Discussion

First, we discuss using eqs 14 and 22 to obtain the distribution of sites in adsorption energy. To this end, we have chosen a silylated glass fiber that has been cured at the highest temperature of 350 °C (see below). Elution profiles of butanol were obtained at 35.81 (three profiles) and 55.81 °C (four profiles). In all of these experiments, 0.04 μL of butanol was injected (loading about 20%) and an elution profile was recorded for 30 min. After this, the temperature of the column was raised to 200 °C and the quantity of residual butanol was evaluated from the area under the thermodesorption peak. These data allow one to determine a portion of the (cumulative) distribution function of sites on the glass surface with respect to the molar Gibbs free energy of butanol adsorption $N(G)$ (N is normalized as a fraction of all the sites).[12] Thus, we obtained three such functions for 35.81 °C and four functions for 55.81 °C. These data were averaged to obtain one averaged distribution $N(G)$ for 35.81 °C and another for 55.81 °C. (We found minimal and maximal values of N common to all seven plots, divided the interval between them into 30 parts, and interpolated these data to 30 fixed values of N. For each value of N, nine nearest neighbors from experimental data points corresponding to each temperature were selected and the values of G corresponding to this N were obtained by the linear least-squares interpolation.) This allows one to use eq 14 with $\Delta T = 20$ °C to obtain $\langle S\rangle_G$ for each of these values of N. Then, we use eq 22 to obtain $\langle H\rangle_G$ for 30 values of N corresponding to the intermediate temperature of 45.81 °C . The plot N vs $\langle H\rangle_G$ is presented in Figure 1. We conditionally call it a (cumulative) distribution function of adsorption sites (patches) in energy. In fact, the abscissa of a point in Figure 1 corresponding to a fixed value of N (fraction of sites) is not exactly the adsorption energy of a site (homogeneous patch), but rather, a regression of enthalpies of adsorption of a group of sites having the same value of G corresponding to this value of N. This was explained at the end of Section 3 as well as why we assume no difference between enthalpy and energy of the adsorbed species.

Another peculiarity of the plot in Figure 1 is that it has a physical meaning only in the interval $0.04 < N < 0.12$. Without this restriction, the function presented in Figure 1 can have two values of N corresponding to one value of energy, and this is not what one would expect from a distribution function. A possible explanation of this inconsistency is that we have obtained the distribution of sites in free energy $N(G)$ by the standard method of IGC (elution of characteristic point, ECP), which is based on the ideal equilibrium chromatography that totally ignores the kinetics of adsorption as well as molecular and eddy diffusion of the solute in the carrier gas.[12,16] This condition can be violated for very strong adsorption sites. The stronger the adsorption site, the longer is the time it holds an adsorbed molecule, and the slower is the kinetics of adsorption/desorption on such a site. This property of adsorption sites can be employed to obtain the energy distribution of sites in linear chromatography.[18] For very strong sites, their number usually decreases with strength. Thus, one would expect the portion of the plot in Figure 1 below the level of 0.04 to refer to the sites, which have energies less than −90 kJ/mol. The reason for which they were assigned higher energies might be explained by the slow kinetics of adsorption on these sites that has not been taken into account. A similar explanation can be given to the portion of the plot in Figure 1 above the level of 0.12. (In Figure 1, only half of this portion is presented.) One would expect the sites in the range $N > 0.12$ of Figure 1 to have higher energy than those in the range $N < 0.12$. The fact that this is not the case can be explained by molecular and eddy diffusion of the solute in the carrier gas, which is not taken into account in the ECP method but might influence the very sharp portion of the elution profile that gives this portion of the distribution function. In principle, given the values of corresponding parameters, all of these effects can be taken into account by numerical simulation of the chromatography process on a homogeneous surface.[19] The problem is to extend these numerical simulations to heterogeneous surfaces with a given free energy distribution function and especially to solve the inverse problem, that is, to find the free energy distribution function from numerical simulations of a chromatographic process.

Rather, we use the following approach. For each value of N in Figure 1, we have not only the energy but also the entropy or rather $\langle S\rangle_G$—a regression of adsorption entropy on G. The plot of $\langle S\rangle_G$ vs $\langle H\rangle_G$ is presented in Figure 2. In the middle part of this plot, there is a linear portion that corresponds to the physically meaningful portion of the distribution function in Figure 1. This portion was least-squares fitted by a straight line

$$\langle S\rangle_G = S_0 + \langle H\rangle_G/T_i \tag{30}$$

with $S_0 = 132$ J mol^{-1} K^{-1} and $T_i = 380$ K. We have obtained a similar linear portion of the entropy/energy relation in our previous work, albeit, with somewhat different parameters: $S_0 = 95$ J mol^{-1} K^{-1} and $T_i = 480$ K.[12] One possible explanation

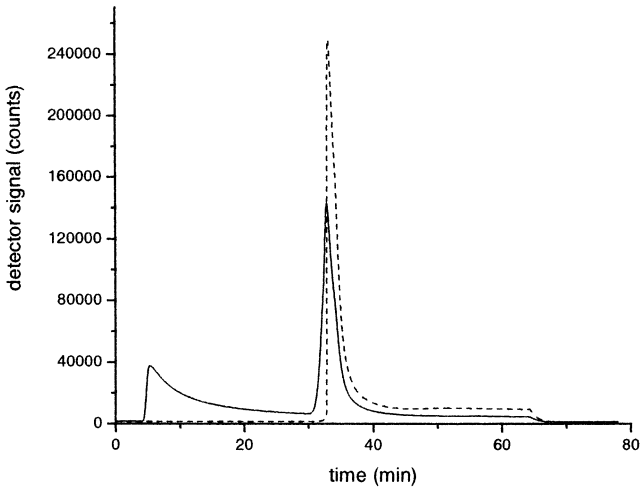

Figure 3. Influence on elution profiles of rinsing silylated fibers by water. Dashed line, thoroughly rinsed sample A; solid line, slightly rinsed sample B (see Section 2). The elution profiles were obtained at 41 (the 1st 30 min) and 120 °C (next 30 min) by injection of about 0.02 μL of butanol.

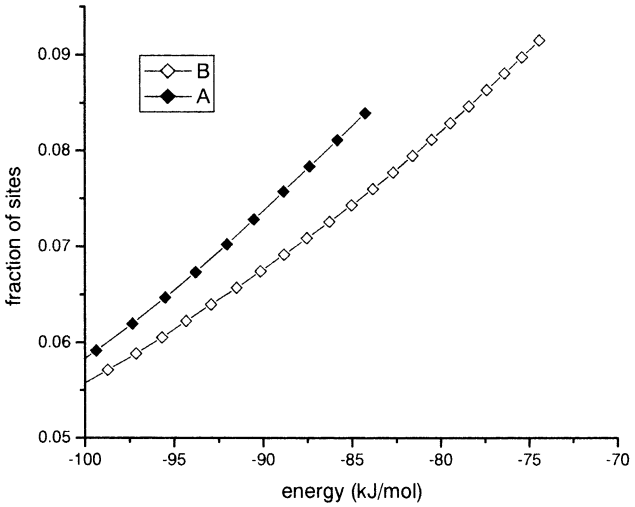

Figure 4. Energy distributions of sites corresponding to the elution profiles in Figure 3. A and B in the labels correspond to samples A and B in Section 2.

for the difference in the values of the parameters of eq 30 obtained here and in ref 12 is that parameters obtained in ref 12 refer to 95 °C and those of the straight line in Figure 2 refer to 46 °C. As shown in Section 3, values of $\langle S\rangle_G$ and $\langle H\rangle_G$ explicitly depend on temperature. Besides, the column in ref 12 was 8.7 times longer than that used in this work, and the surface of the fiber in the column used there was 16 times larger than in the present case. Moreover, the nature of the surfaces was different: unmodified E-glass fiber was used in ref 12. (Longer columns are more effective for IGC but complicate considerably the experimental part of the IGC studies of glass fiber surfaces.)

One can use eq 30 to convert the distribution of sites in free energy G that is originally obtained from an elution profile into the energy distribution function; i.e., substitute eq 30 into eq 22 to obtain

$$\langle H\rangle_G = (G + TS_0)/(1 - T/T_i) \qquad (31)$$

To convert the free energy distribution function of sites into the energy distribution function (both are cumulative distributions), one has just to substitute G in $N(G)$ by $\langle H\rangle_G$ from eq 31.

Now, we consider application of this method to the analysis of the glass fiber silylation. First, consider elution profiles (the source experimental data for our analysis) of the samples A and B (see Section 2) preconditioned (cured) in situ (in flow of He) progressively at 90, 120, and 150 °C (1 h at each temperature) as presented in Figure 3. These are responses of the chromatographic columns to the pulse (fraction of a second) injection of 0.02 μL of liquid butanol. There is no detector signal (only a background signal of about 1000 counts) for the column filled with fiber A for the first 30 min when the temperature of the column is maintained at 40.81 °C. After 30 min, the temperature of the column is raised at the rate of 20 °C/min up to 120 °C, is maintained at this level for another 30 min, and then is returned to the initial temperature. The sharp peak for column A in Figure 3 is a thermodesorption peak of butanol, which was adsorbed on the surface of the sample A and was not eluted from the column by the carrier gas at the lower column temperature. The retention capacity of sample B is much lower than that of sample A since the first portions of butanol already have reached the detector in about 5 min after injection. The thermodesorption peak for column B is lower than for column A because a considerable part of butanol was eluted from column B in the first 30 min at about 41 °C. Notice also that after 45 min when the thermodesorption peaks in Figure 3 decrease to a plateau, the detector signal of column A is still greater than that of column B. This means that the thermodesorption temperature of 120 °C is not high enough to remove all of the butanol from the surface of sample A. (We always maintain the thermodesorption temperature somewhat lower than the highest curing temperature of a sample (150 °C in this case) lest thermodesorption influence curing.) The higher thermodesorption plateau for column A in Figure 3 is due to butanol that is adsorbed on the stronger sites of sample A and is slowly eluted by the carrier gas at 120 °C. Thus, the repeated rinsing of sample A at ambient temperature removed some of the TTMS from its surface and made it considerably more active with respect to the adsorption of butanol.

The same conclusion, in a more quantitative form, can be made from the energy distributions obtained from the source data in Figure 3. These are presented in Figure 4. The energy distribution B in Figure 4 is calculated on the basis of the corresponding elution profile in Figure 3 with parameters of eq 30 corresponding to 46 °C, which have been obtained in this work. However, the energy distribution A in Figure 4 cannot be obtained in this way since the elution profile A in Figure 3 has only a thermodesorption peak that gives only one initial point of a distribution function. Thus, the energy distribution A in Figure 4 was obtained from an elution profile for a higher temperature (90.8 °C) and with parameters of eq 30 obtained in ref 12 for 95 °C (see above). Both of the distributions in Figure 4 have portions extending below −100 kJ/mol, which appear if one uses eq 31 beyond the limits of its applicability. As shown in the discussion of Figure 1, eq 30 can be applied only above energies of −90 kJ/mol. Thus, we truncated distributions in Figure 4.

Now, we consider the influence of curing temperature on the surface properties of sample A. Some of the energy distribution functions for sample A, cured at various temperatures, are presented in Figure 5. The column A was initially treated (cured) as explained above (see discussion of Figure 3 and Section 2). Then, it was cured for 2.5 h at 180 °C and after that the energy distribution of sites with respect to butanol was determined as described in Section 3 and presented in Figure 5. This was repeated seven times in a sequence of increasing curing temperatures: 180, 200, 230, 260, 290, 320, and 350 °C (the

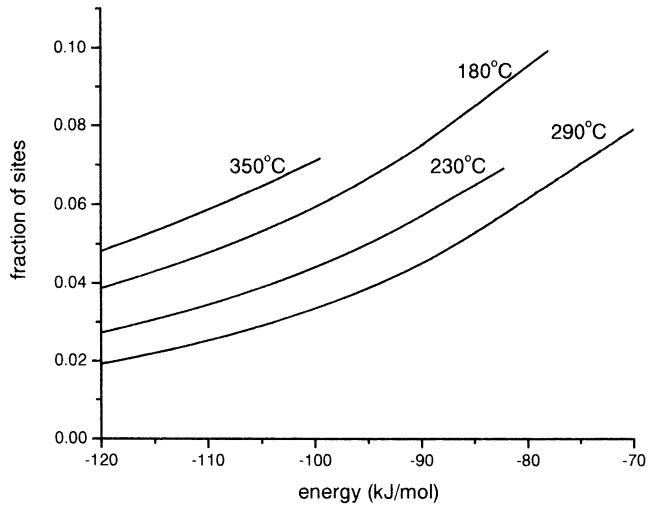

Figure 5. Influence of curing temperature on the energy distributions of sites. The distribution marked by the indicated temperature was obtained after treatment of the column in situ at this temperature for more than 2 h.

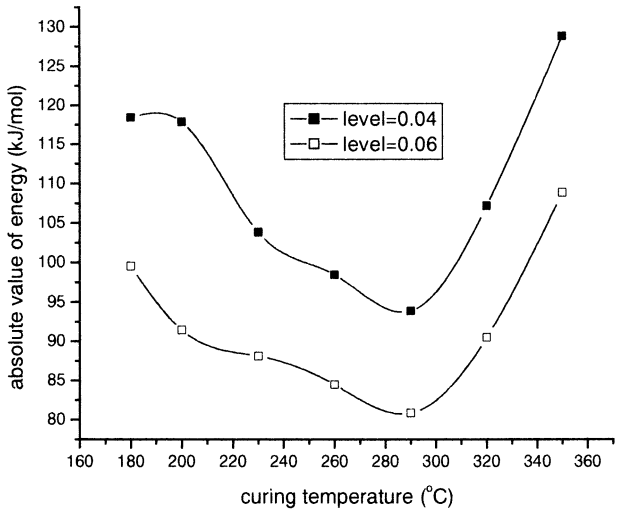

Figure 6. Cross-sections of all of the energy distributions (some of which are in Figure 5). Each point is an intersection of a horizontal line corresponding to a fixed value of the fraction of sites (level) with an energy distribution such as those in Figure 5.

highest temperature in our GC). The time of curing at each of these temperatures was 2.5−4 h, since we checked that curing for more than 1 h negligibly changes the final results. After each curing, the energy distribution function with respect to butanol was determined. Some of them are presented in Figure 5. Cross-sections of all of the distributions at the levels of 0.04 and 0.06 are presented in Figure 6. Points in Figure 6 are the intersections of the horizontal lines corresponding to the fixed values of fraction of sites (levels) with distributions such as those in Figure 5. The abscissa of a point in Figure 6 is a curing temperature that marks the corresponding curve in Figure 5, and the ordinate of the point in Figure 6 is the absolute value of the energy corresponding to the abscissa of the intersection of the horizontal line with the corresponding distribution. It is clear that curing up to about 290 °C decreases the adsorption energy of sites with respect to adsorption of butanol and above this temperature increases this energy.

A possible explanation of this effect might be as follows. As explained in Section 1, TMMS hydrolyzes in aqueous solution according to eq 3, and one should expect adsorption not of TMMS but of $MeSi(OH)_3$ molecules on the glass surface. The silanol groups of these molecules condense with those of the glass surface and between themselves to form siloxane bonds (cf. eqs 4 and 5). After curing at lower temperatures, there are still many noncondensed silanols either on the glass surface or on adsorbed molecules, which interact with OH− groups of butanol. The curing at elevated temperatures removes those residual silanols and makes the silylated glass surface more hydrophobic. However, siloxane bonds rupture at temperatures around 350 °C, which is the reason for increased adsorption activity of the surface after such a high-temperature treatment. It has been reported long ago that $(Me)_3Si-O-Si\equiv$ coverage of the glass surface is destructed in a vacuum at 350 °C.[20] This is an estimate of the stability limit of a siloxane bond $\equiv Si-O-Si\equiv$. In our case, breaking of some bonds that attach chemisorbed molecules TMMS to the glass surface begins at lower temperature (around 290 °C), but basically, our results agree with the estimate of the stability of the siloxane bonds on the silylated surface mentioned above.

5. Conclusion

The standard method of surface characterization by IGC, assuming a homogeneous surface, is to determine a retention volume at different temperatures and find from these data the adsorption enthalpy (energy) and the adsorption entropy (for a chosen probe molecule), which are usually assumed to be approximately independent of temperature. This method can be extended to heterogeneous surfaces modeled as collections of homogeneous patches (sites). Such a surface is characterized by a bidimensional distribution of homogeneous patches with respect to {energy, entropy} pairs. From this bidimensional distribution, which is practically independent of temperature, one can calculate a one-dimensional distribution with respect to the free energy of adsorption. The latter explicitly depends on temperature and can be obtained from adsorption and chromatographic experimental data by various methods well-documented in the literature.

In this and our previous papers, we show how to separate the distribution of sites in free energy of adsorption into two distributions with respect to parameters similar to the energy and entropy of adsorption.[11,12] The method is similar to that widely used for IGC on homogeneous surfaces. The main difference is that instead of energy of adsorption on a homogeneous surface one obtains a regression of energy on the free energy of adsorption on a heterogeneous surface. The same is true for entropy. Even if the energy and entropy of adsorption on homogeneous patches are independent of temperature, their regressions on the free energy of adsorption on a heterogeneous surface explicitly depend on temperature (although this temperature dependence is not so strong as that of free energy). For simplicity, we call here these regressions simply energy and entropy.

The entropy/energy relation is linear in some interval of energies, which allows one to obtain the energy distribution of sites from the free energy distribution at one temperature. However, this procedure cannot be applied to very strong adsorption sites because the method of calculation of the adsorption free energy distribution from chromatographic data that is known at present (nonlinear ideal equilibrium chromatography) neglects kinetics of adsorption that might be important for the strongest adsorption sites. Possibly, one can resolve the problem by numerical simulation of a chromatographic process, but this method is yet to be developed.

The energy distribution of sites is a useful characteristic of glass fiber surfaces. We used it to study the silylation of E-glass

fibers with TMMS from aqueous solution. At ambient temperature, a considerable portion of the TMMS is weakly bonded to the glass surface and can be removed by a thorough rinsing with water. The rinsing increases the interaction of the modified glass surface with butanol (in fact, with the OH group of butanol probing hydrophilicity of the surface). This interaction can again be decreased by curing the glass fiber; i.e., treating it at elevated temperature. The curing experiments reveal that there is a curing temperature where the adsorption energy reaches a minimum (cf. Figure 6). We explain this phenomenon by assuming that molecules of TMMS physically adsorb on the glass surface from an aqueous solution as $MeSi(OH)_3$ (cf. eq 3), and their silanol groups partly condense with those of the glass surface according to eqs 4 and 5. Initially, an increase of the curing temperature leads to a decrease of silanol groups belonging both to the glass surface and to the adsorbed molecules as a result of the condensation reaction. This makes the surface more hydrophobic. However, when the curing temperature exceeds 290 °C (minimum in Figure 6), the siloxane bonds between the glass surface and the chemisorbed molecules of TMMS begin to rupture and the hydrophilicity of the surface increases again.

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