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Adsorption and Thermogravimetric Studies of Silica-Based Amide Bonded Phases

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A series of chemically modified porous silicas, which can be used in high-performance liquid chromatography (HPLC), were prepared by a two-step modification process. Aminopropyl groups were first attached to the silica surface and subsequently converted to amides via the reaction with appropriate acid chlorides. Changes in the surface properties of the silica caused by the chemical modification were monitored using elemental analysis and high-resolution thermogravimetry. In addition, complete nitrogen adsorption isotherms were measured at 77 K in the relative pressure range from 10^{-6} to 0.99. Standard adsorption characterization of the materials included the evaluation of the specific surface area, total pore volume, and pore size distribution. Moreover, adsorption energy distribution functions were calculated from submonolayer adsorption data using the regularization method. It was estimated that about 40% of the available surface silanols were converted to amine groups and about 60% of amines were converted to amides. It was shown that although the chemical modification of the surface does not significantly alter the porous properties of the starting silica, it significantly affects the interaction of nitrogen probe molecules with the surface. Moreover, it was demonstrated that nitrogen adsorption is quite sensitive to the presence or absence of various functional groups on the silica surface and that the information obtained from the adsorption measurements can be utilized for the characterization of silica-based materials used in chromatographic applications.

Introduction

Porous materials such as active carbons, zeolites, ordered mesoporous materials, and inorganic oxides are widely used in science and technology, especially in separation processes, extraction, purification, and catalysis.[1−5] The surface and structural properties of porous materials can be readily modified,[1,5−10] which makes them useful in a number of applications. In particular, chemically modified silica gels, otherwise known as chemically bonded phases (CBPs), are commonly used as column packing materials in high-performance liquid chromatography (HPLC) under hydroorganic conditions.[7−9] Silica surfaces modified with long alkyl chains are the most popular chromatographic packings. However, many applications require specially tailored bonded phases that range from phases containing specific functional groups to those with attached macromolecules, e.g., proteins. Among chromatographic packings, bonded phases containing amide functional groups possess several advantages.[11−13] These CBPs can interact with solutes via both dispersive and specific interactions and are suitable for use in HPLC even under fully aqueous conditions. The majority of the research on amide bonded phases to date has been performed on alkylamide CBPs prepared via a two-step modification procedure,[14,15] in which amine functional groups are first attached to the silica surface and subsequently converted to amides. It should be noted that the conversion of amine groups to amides in the second modification step is not quantitative, and the resulting bonded phase contains residual amine groups.

The behavior of a bonded phase under chromatographic conditions depends on its surface and porous properties. These properties can be evaluated by various physicochemical methods, which include elemental analysis, thermogravimetry, gas and liquid adsorption, and spectroscopic techniques.[16] In the current work, unmodified silica, an aminopropyl bonded phase and four amide CBPs were characterized by nitrogen adsorption at 77 K, high-resolution thermogravimetry (TGA), and elemental analysis. Three of the amide bonded phases studied contained unsubstituted or substituted aromatic rings and have not been investigated previously as potential chromatographic packings. The final amide CBP included for comparative purposes was a widely studied alkylamide phase.[14,15] Adsorption characterization included the evaluation of the specific surface area, total porosity, and pore size distribution of the materials. In addition, the low-pressure adsorption data were used to evaluate their energetic heterogeneity. Thermogravimetry provided a qualitative comparison of the surface properties of the bonded phases studied, and the surface coverages of ligands attached in the subsequent modification steps were estimated from elemental analysis. Additional information about the surface properties of the amide CBPs was obtained from the results of adsorption and thermogravimetric studies of polymeric and monomeric[17] *n*-octyl bonded phases.

Experimental Section

Materials. LiChrospher Si-100 silica (10 μm particle diameter) was purchased from EM Separations (Gibbstown, NJ). The γ-(aminopropyl)triethoxysilane, all acid chlorides (i.e., benzoyl, 4-cyanobenzoyl, phenylacetyl, and octanoyl), and isopropyl ether reaction solvent were from Aldrich Chemical Co. (Milwaukee, WI). The *n*-octyltriethoxysilane was from United Chemical Technologies, Inc. (Bristol, PA). Toluene reaction solvent was from Fisher Scientific (Pittsburgh, PA). All materials were used as received.

Bonded Phase Synthesis. The aminopropyl bonded phase (Silica-NH_2) was prepared by reacting LiChrospher Si-100 silica with γ-(aminopropyl)triethoxysilane as described by Engelhardt and Orth.[18] Prior to the reaction, approximately 5 g of silica was washed with deionized water and dried at 393 K for 20 h. Subsequently, the silica was dispersed in water-saturated toluene,

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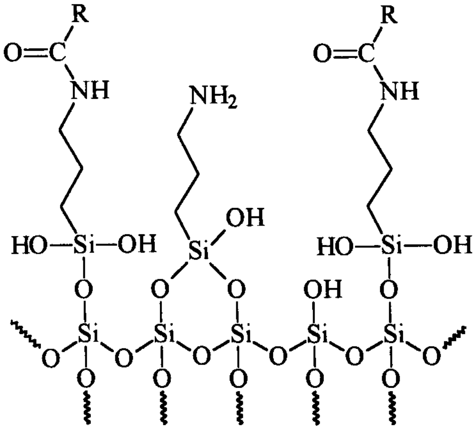
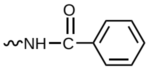
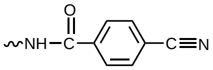
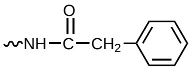
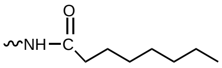


Figure 1. Schematic representation of amide bonded phases.

TABLE 1: Structures and Notation for the Amide Bonded Phases Studied

modified silica	notation	structure of amide group
phenylamide	silica-Ph	
cyanophenylamide	silica-CNPh	
phenylacetylamide	silica-PhAc	
octylamide	silica-AA$_8$	

reacted with 20 mL of γ-(aminopropyl)triethoxysilane under refluxing conditions for 17 h, washed with dry toluene and deionized water and dried at 393 K for 24 h. The water wash removes a substantial quantity of physically adsorbed γ-(aminopropyl)triethoxysilane and its hydrolysis products and is needed for the preparation of a well-defined aminopropyl bonded phase.[18,19]

The amine functional groups of the aminopropyl bonded phase were converted to amides by the reaction of (aminopropyl)silica with benzoyl, 4-cyanobenzoyl, phenylacetyl, or octanoyl chlorides. Approximately 1.5 g of aminopropyl silica was refluxed for 4 h with an isopropyl ether solution containing an excess of the appropriate acid chloride. The resulting amide phases were washed with isopropyl ether, 1:1 methanol/water mixture, and pure methanol and subsequently dried under vacuum at ambient temperature for 40 h. The schematic representation of an amide bonded phase is shown in Figure 1, and the structures and notation for the amide CBPs studied can be found in Table 1.

The polymeric *n*-octyl bonded phase (C_8-polymeric) was synthesized similarly to the aminopropyl-CBP, where *n*-octyltriethoxysilane was used instead of γ-(aminopropyl)triethoxysilane.

Characterization Methods. Nitrogen adsorption isotherms at 77 K were measured in the relative pressure range from 10^{-6} to 0.99 using a Micromeritics model ASAP 2010 (Norcross, GA) adsorption analyzer. The purity of nitrogen was 99.998%. Prior to the analysis, unmodified silica was degassed for 2.5 h in the degas port of the adsorption apparatus at 473 K under vacuum of about 10^{-3} Torr. The modified silicas were degassed for 2 h at 423 K. Appropriate degassing temperatures were chosen on the basis of TGA measurements. The percentages of carbon and nitrogen in the materials were obtained using a LECO Model CHNS-932 (St. Joseph, MI) elemental analyzer. At least two measurements were performed for each material with the relative error of about 3%. Thermogravimetric measurements were carried out using a TA Instruments Model TA 2950 (New Castle, DE) thermogravimetric analyzer, with an accuracy of 0.1% in the weight change. The materials were heated in dry nitrogen atmosphere from ambient temperature up to 1273 K using the maximum heating rate of 5 K/min.

Calculation Methods. The specific surface areas S_{BET} were calculated according to the standard Brunauer−Emmett−Teller (BET) method[20] using adsorption data in the relative pressure (p/p_0) range from 0.06 to 0.25, where p and p_0 denote the equilibrium pressure and the saturation pressure of nitrogen at 77 K, respectively. The total pore volumes V_{t} were evaluated by converting the volume adsorbed at p/p_0 of 0.98 to the volume of liquid adsorbate. The pore size distributions for the materials were evaluated from the desorption data using the Barrett−Joyner−Halenda (BJH) method,[21] which relies on the Kelvin equation[22] to relate the width of the pores to the condensation pressure. Note that according to the IUPAC recommendation[23,24] pores are classified as micropores (widths below 2 nm), mesopores (widths between 2 and 50 nm), and macropores (widths above 50 nm).

The adsorption energy distribution (AED) functions $F(\epsilon)$ for the materials studied were calculated from submonolayer adsorption data (i.e., $v < v^0$, where v and v^0 denote the volume adsorbed and the BET monolayer capacity, respectively) by inverting the integral equation of adsorption[25]

$$\Theta(p) = \int_{\epsilon_{\min}}^{\epsilon_{\max}} \theta(p,\epsilon)\, F(\epsilon)\, \mathrm{d}\epsilon \tag{1}$$

where $\Theta(p)$ is the total adsorption isotherm in the submonolayer range defined as the ratio of the volume adsorbed to the BET monolayer capacity, p is the equilibrium pressure, ϵ is the adsorption energy in the range from $\epsilon_{\min}$ to $\epsilon_{\max}$, $\theta(p,\epsilon)$ is the local adsorption isotherm as a function of the adsorption energy, and $F(\epsilon)\,\mathrm{d}\epsilon$ is the fraction of the surface sites with adsorption energies between ϵ and $\epsilon + \mathrm{d}\epsilon$. The Fowler−Guggenheim (FG) equation,[25,26] which describes localized monolayer adsorption with lateral interactions on adsorption sites of energy ϵ, was assumed to represent the local adsorption isotherm

$$\theta(p,\epsilon) = \frac{K_{\mathrm{L}} p \exp(z\omega\Theta/k_{\mathrm{B}}T)}{1 + K_{\mathrm{L}} p \exp(z\omega\Theta/k_{\mathrm{B}}T)} \tag{2}$$

where K_{L} is the Langmuir constant for adsorption on monoenergetic sites, z is the number of nearest neighbors to an adsorbate molecule in the monolayer, ω is the interaction energy between nearest neighbors, k_{B} is the Boltzmann constant, and T is the absolute temperature. The Langmuir constant K_{L} is defined as follows

$$K_{\mathrm{L}} = K_{\mathrm{L}}^{0}(T)\mathrm{e}^{\epsilon/k_{\mathrm{B}}T} \tag{3}$$

where $K_{\mathrm{L}}{}^{0}(T)$ is the preexponential factor which can be expressed in terms of the partition functions for an isolated adsorbate molecule in the gas and surface phases.[25,26] The FG equation (i.e., eq 2) implies a random distribution of adsorption sites, which appears to be a realistic model for unmodified and modified silicas because these materials are amorphous and contain different surface groups.[17,27] The AED functions for the materials studied were calculated using the INTEG program, which employs the regularization method[28] to invert the integral equation of adsorption (i.e., eq 1) with respect to $F(\epsilon)$. The

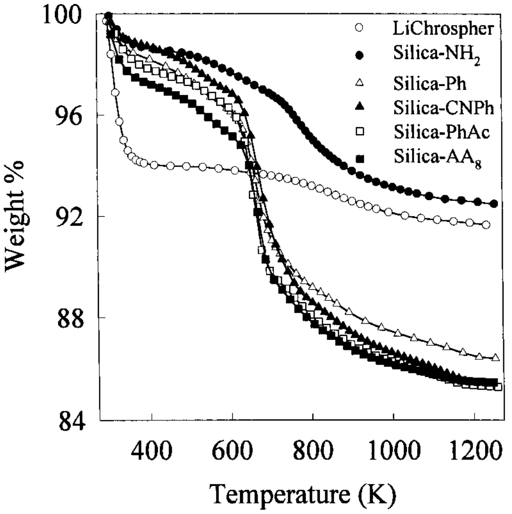


Figure 2. TGA curves for LiChrospher Si-100 silica gel, aminopropyl, and amide bonded phases.

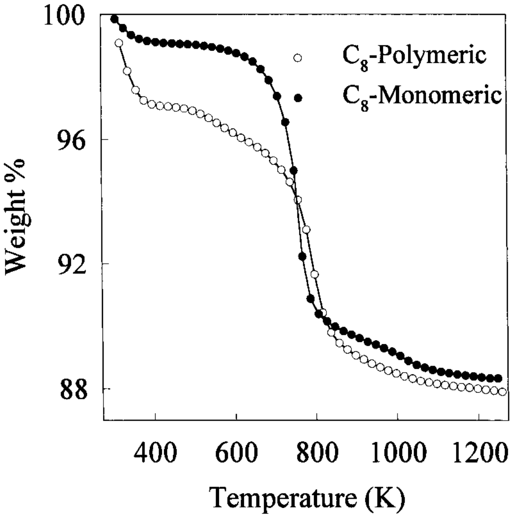


Figure 3. TGA curves for polymeric and monomeric *n*-octyl bonded phases.

interaction parameters $z = 4$, $\omega/k_B = 95$ K, and the regularization parameter $\gamma = 0.01$ were assumed in all calculations.[17,28]

Results and Discussion

High-resolution thermogravimetric analysis (TGA) was used to estimate the silanol concentration in the starting silica and to qualitatively compare the changes induced by surface modification. Figure 2 shows the TGA curves for unmodified silica, aminopropyl, and amide bonded phases. The TGA curve for unmodified silica has two distinct weight-loss regions. The first of these occurs in the 298−473 K range (maximum rate of weight loss at approximately 313 K) and corresponds to the thermodesorption of physically adsorbed water molecules from the silica surface. In the temperature range from 473 to 573 K, the weight loss is negligible and the TGA curve is relatively flat. The second weight loss region occurs between 573 and 1073 K (maximum rate of weight loss at approximately 873 K) and corresponds to silanol condensation.[29] Using the weight-loss in the 573−1073 K range, the silanol concentration for unmodified silica was estimated as 7.0 ± 0.2 μmol/m^2 on the basis of two replicate measurements, which is in good agreement with values generally observed (6−8 μmol/m^2) for different native silicas.[30,31]

The TGA curve for the aminopropyl bonded phase differs significantly from that for the unmodified silica. The weight loss in the temperature range from 298 to 473 K is substantially decreased, which indicates a smaller amount of physically adsorbed water on the (aminopropyl)silica surface. This can be attributed to the increasing hydrophobic character of the material and indicates a decrease in the effective silanol concentration. It should be noted that the aminopropyl CBP is a so-called polymeric phase, i.e., prepared from a trifunctional silane. Therefore, the absolute silanol concentration of this material may actually exceed the silanol concentration of unmodified silica,[18,32,33] because the majority of the attached aminopropyl ligands possess one or two silanol groups. The weight loss at temperatures exceeding 473 K can be divided into two regions. The first weight-loss region occurs in the 473−673 K range and can be attributed to the condensation of silanol groups between neighboring aminopropyl ligands and between ligands and residual surface silanols, often referred to as cross-linking.[8,9] This is supported by the comparison of the TGA curves for polymeric and monomeric *n*-octyl bonded phases (see Figure 3). The weight loss between 673 and 873 K (maximum rate of weight loss at approximately 773 K) can be attributed to the thermal decomposition of the chemically bonded aminopropyl ligands. The TGA curves for amide CBPs have very similar weight-loss profiles, which indicates similar surface coverages of amide ligands for these materials. The weight loss in the temperature range from 573 to 773 K (maximum rate of weight loss at approximately 673 K) corresponds to the decomposition of the bonded phase, i.e., aminopropyl and amide ligands. The comparison of the TGA curves for amide bonded phases and the aminopropyl CBP reveals a much greater weight loss corresponding to the bonded phase decomposition for the amide materials, which indicates the attachment of additional ligands to surface.

The TGA curves for a polymeric *n*-octyl CBP (C$_8$-polymeric) and a monomeric *n*-octyl phase[17] (C$_8$-monomeric) are compared in Figure 3. The surface coverages of octyl ligands were 2.2 and 3.6 μmol/m^2 for the polymeric and monomeric phases, respectively. These bonded phases were prepared on different types of silica via different modification procedures, and so they are expected to have different surface coverages of octyl ligands. However, the silicas from which these CBPs were prepared had nearly identical weight-loss profiles up to about 700 K. Moreover, significant differences in the weight-loss profile are not expected to occur for a monomeric *n*-octyl bonded phase synthesized using a chlorosilane and the same type of CBP prepared from an alkoxysilane. The only significant difference between the two *n*-octyl phases (for the comparison of their TGA curves) appears to be that the polymeric bonded phase has a higher effective concentration of silanol groups. The weight loss between 673 and 873 K for both polymeric and monomeric *n*-octyl CBPs can be attributed to the thermal decomposition of the bonded phase. However, the polymeric *n*-octyl phase also exhibits a significant weight loss in the 473−673 K range, which is not observed for the monomeric material. Moreover, the weight loss for the polymeric material in the above-mentioned temperature range is too large to correspond entirely to the condensation of the surface silanols originally present in unmodified silica. (See TGA curve for unmodified silica in Figure 2.) Therefore, it appears that the weight loss between 473 and 673 K involves the condensation of silanol groups on the ligands of the polymeric bonded phase, i.e., cross-linking. It should also be noted that the weight-loss profiles for the polymeric *n*-octyl phase and the aminopropyl CBP (also polymeric-type phase) from ambient temperature up to 673 K are nearly identical.

TABLE 2: Surface Properties of Unmodified and Modified Silicas

material	% carbon	% nitrogen	α_{amide} (μmol/m^2)	α_{NH_2} (μmol/m^2)
LiChrospher Si-100	0.06	0.01		
silica-NH$_2$	3.17	1.22		2.90
silica-Ph	7.59	1.13	1.94	0.96
silica-CNPh	8.45	1.81	2.07	0.83
silica-PhAc	8.17	1.08	1.93	0.97
silica-AA$_8$	7.36	1.11	1.61	1.29

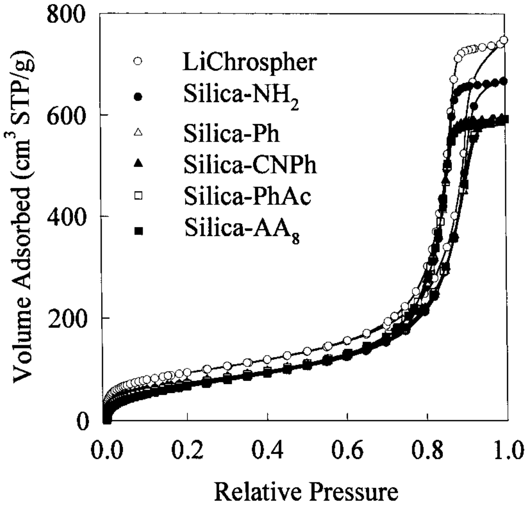


Figure 4. Adsorption isotherms for LiChrospher Si-100 silica gel, aminopropyl, and amide bonded phases.

TABLE 3: Structural Properties of Unmodified and Modified Silicas

material	BET specific surf. area (m^2/g)	total pore vol (cm^3/g)	BJH av pore width (nm)
LiChrospher Si-100	336	1.15	12.9
silica-NH$_2$	271 (303)	1.03 (1.15)	12.5
silica-Ph	263 (311)	0.92 (1.09)	11.9
silica-CNPh	269 (324)	0.92 (1.11)	11.8
silica-PhAc	267 (319)	0.91 (1.09)	11.6
silica-AA$_8$	257 (304)	0.91 (1.08)	11.5

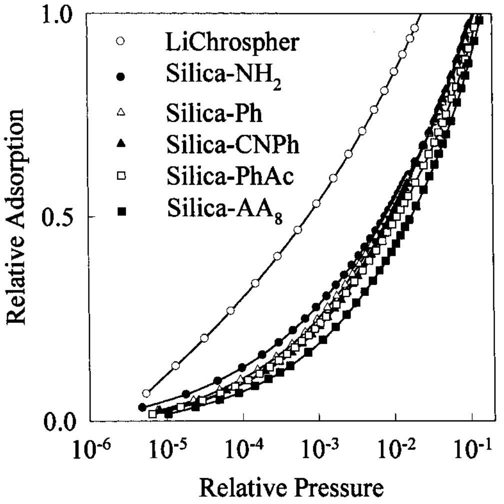


Figure 5. Relative adsorption curves for LiChrospher Si-100 silica gel, aminopropyl, and amide bonded phases.

Elemental analysis provided the percentages of nitrogen and carbon in the materials. The surface coverage of aminopropyl ligands (α_{NH_2}) could be calculated from both nitrogen and carbon contents, and the coverages of amide ligands (α_{amide}) were estimated from the carbon content of the materials using equations reported previously.[34] The surface properties of unmodified silica and bonded phases are found in Table 2. As can be seen, about 40% of the available silanol groups are converted to aminopropyl ligands in the first modification step. Moreover, the experimental molar carbon-to-nitrogen ratio of 3.02 for the aminopropyl bonded phase, compared with the theoretical one of 3.00, indicates a nearly complete hydrolysis of all ethoxy groups originally present in the silane used for the surface modification. Therefore, on the basis of TGA and elemental analysis, it can be concluded that the aminopropyl CBP contains only chemically bonded aminopropyl ligands with no residual ethoxy groups. In the second modification step, approximately 60% of the amine groups are converted to amides for all amide CBPs studied. Therefore, the resulting bonded phases are mixed amine−amide phases.

According to the common classification of adsorption isotherms,[23,24] the isotherms for unmodified silica and bonded phases (see Figure 4) can be considered type IV. The hysteresis loops observed during desorption are typical for mesoporous materials and closely resemble the loops of type H1 and H2 according to the IUPAC classification.[23,24] The general profiles of adsorption and desorption are similar at high relative pressures (i.e., $p/p_0 > 0.2$) for all materials studied, which indicates that no significant changes were introduced in the porous structure of the silica during chemical modification. The structural properties of unmodified and modified silicas evaluated from nitrogen adsorption are shown in Table 3. As can be seen, the specific surface area and total pore volume expressed per 1 gram of the bonded phases decrease with the increasing degree of modification. This decrease became much smaller when the above noted quantities are expressed per gram of pure silica. (See the corresponding values in parentheses in Table 3.) This result can be expected for the relatively low surface coverages of small ligands obtained on silica of approximately 10 nm pore width via the chemical modification process. However, it should be noted that quite significant changes in the structural properties related to the blockage of pores can be observed for the modification of mesoporous molecular sieves with small ligands (e.g., trimethylsilyl)[6] and the modification of mesoporous silica with large ligands.[35]

Low-pressure adsorption isotherms (i.e., in the relative pressure range from 10^{-6} to 10^{-1}) can be used to obtain information about the interaction of nitrogen probe molecules with the surfaces of the materials studied. The isotherms, presented in terms of relative adsorption (i.e., volume adsorbed divided by the BET monolayer capacity), for unmodified silica and bonded phases are shown in Figure 5. For the aminopropyl CBP there is a substantial decrease in low-pressure adsorption, and a change can be observed in the shape of the isotherm compared to the unmodified silica. The change in the adsorption profile indicates the removal of a fraction of high-energy adsorption sites upon silanization. It is shown later that the high-energy adsorption sites correspond to surface silanols. The subsequent conversion of amine groups to amides has a smaller effect on the low-pressure adsorption properties of the materials studied. However, a few interesting observations regarding the use of nitrogen probe molecules to study the surface properties of materials can be made based on the comparison of the relative adsorption curves for the amide bonded phases. It appears that nitrogen molecules are not suitable probes for detecting the presence of nitrile functional groups on the silica surface because the adsorption isotherms for the phenylamide and cyanophenylamide CBPs are nearly identical. The failure of nitrogen adsorption to detect nitrile groups on the silica surface has been reported recently for silica surfaces modified with liquid crystals containing such functional groups,[35] and it implied similar interaction energies of nitrile groups and aromatic rings with

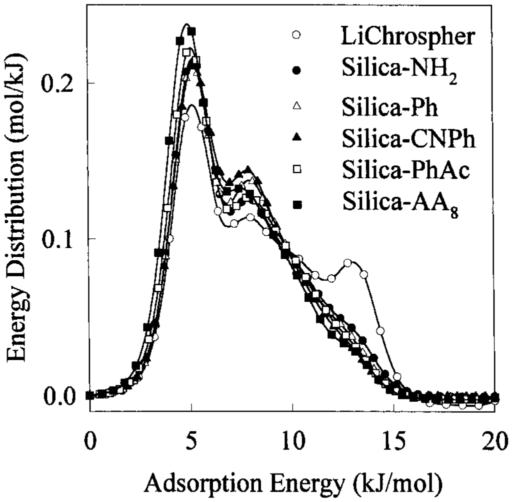


Figure 6. Adsorption energy distribution functions for LiChrospher Si-100 silica gel, aminopropyl, and amide bonded phases.

the nitrogen molecules. However, nitrogen adsorption can be used to detect a difference between amide bonded phases of the aliphatic and aromatic types because the low-pressure adsorption isotherm for the octylamide bonded phase is slightly different from the isotherms for the amide CBPs containing aromatic rings. This difference in the isotherms can be attributed to a small difference in the interaction energies of alkyl chains and aromatic rings with nitrogen probe molecules.

The adsorption energy distribution functions (see Figure 6) were calculated from low-pressure adsorption data for unmodified silica and bonded phases. The AED function for unmodified silica has the shape typically observed for chromatographic grade silica gels.[36] The distribution function consists of three overlapping peaks with maxima located at approximately 5, 8, and 13 kJ/mol, where the peaks centered at 5 and 13 kJ/mol appear to be most significant. This suggests at least two to three main types of adsorption sites on the silica surface. Following the first surface modification step, a fraction of the high-energy adsorption sites is removed, which is exhibited in the decrease in the height of the peak at 13 kJ/mol. The AED functions for the amide CBPs are very similar to one another and to the distribution function for the aminopropyl bonded phase. The presence of a nitrile group does not differentiate the AED curves for the phenylamide and cyanophenylamide CBPs. However, a small difference is observed in the interaction energy of nitrogen with alkyl chains and aromatic rings as shown by the comparison of the AED functions for the octylamide phase and the amide bonded phases containing aromatic rings. This difference is consistent with that observed previously in the low-pressure adsorption isotherms for the amide bonded phases (see Figure 5).

The AED functions for unmodified silica and polymeric and monomeric[17] *n*-octyl bonded phases are compared in Figure 7. The polymeric and monomeric *n*-octyl CBPs have been prepared using different starting silicas. However, it was shown previously[17] that monomeric *n*-octyl bonded phases based on different starting silicas exhibit nearly identical AED profiles. Assuming that the only significant difference between the polymeric and monomeric *n*-octyl CBPs is that the polymeric phase has a higher silanol concentration, the comparison of the AED functions clearly identifies the difference between these CBPs. The peak at 13 kJ/mol decreases for the polymeric *n*-octyl CBP compared to the unmodified silica and disappears completely for the monomeric phase. Therefore, the peak at 13 kJ/mol can be attributed to the presence of silanol groups on the surface of the materials studied.

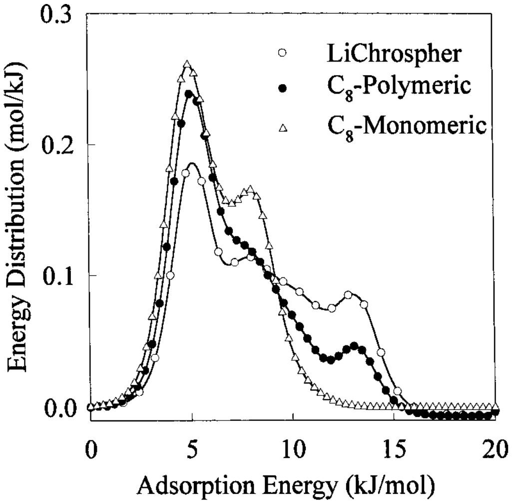


Figure 7. Adsorption energy distribution functions for LiChrospher Si-100 silica gel and polymeric and monomeric *n*-octyl bonded phases.

Conclusions

It was shown that nitrogen adsorption and high-resolution thermogravimetry in conjunction with quantitative data obtained from elemental analysis are useful for the detailed characterization of chemically modified silicas. In particular, the two-step modification process employed for the preparation of the amide bonded phases allowed for a systematic and comparative study of the changes in the surface area, pore size distribution, and adsorption energy distribution of silica induced by the stepwise chemical modification. This comparative study demonstrated that the adsorption energy distributions evaluated from low-pressure nitrogen adsorption data are particularly attractive for monitoring the changes in the energetic heterogeneity of silica caused by its silanization.

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