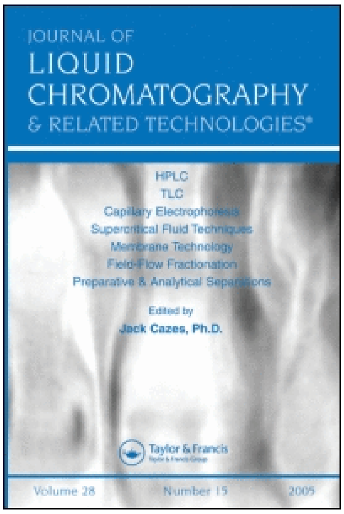

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Adsorption Characterization of Octyl Bonded Phases for High Performance Liquid Chromatography

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ADSORPTION CHARACTERIZATION OF OCTYL BONDED PHASES FOR HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Adsorption-desorption isotherms were measured for selected chromatographic silica gels with chemically bonded octyl groups. The standard sorption characterization of these packings provided the BET specific surface area, the total pore volume and the pore size distribution. Advanced numerical methods based on the density functional theory and the regularization method were used to calculate the pore volume and the adsorption energy distributions. The surface and structural properties of the silicas with chemically bonded octyl phases were compared to those of the original silica gels. The surface coverage of octyl groups occurred to be similar for all samples studied. After the octyl groups were bonded, the porous structure of the silica gels was not altered significantly, resulting in similar adsorption behavior of both unmodified and modified silica gels at pressures close to the saturation pressure. However, the adsorption properties in low pressure region were changed significantly. Namely, all modified silicas exhibited very low adsorption and similar shape of adsorption isotherms at low pressures. Therefore, their adsorption energy distributions resembled each other and did not feature the higher energy sites present on the surface of unmodified silicas. The low pressure adsorption behavior indicates that essentially all higher energy sites on the silica surface reacted in the course of the chemical modification.

INTRODUCTION

Porous silicas are widely applied in liquid chromatography due to their remarkable surface properties and high mechanical, thermal and chemical stability.[1-3] The surface of unmodified silica is polar and therefore bare silica is suitable for normal phase (NP) liquid chromatography (LC) separations. However, the presence of surface silanol groups allows us to chemically bond organic ligands, which change the polarity of the surface. Chemically bonded stationary phases (CBP) found wide application in reverse phase (RP) liquid chromatography.[2-4] The introduction of specific interaction sites in hydrophobic ligands allows us to obtain CBP useful in separations of polar compounds, such as drugs, antibiotics and peptides.[5-8] Chirally selective CBPs, for example immobilized cyclodextrines, proteins or Pirkle-type phases,[2, 9-11] were also applied. However, many RP LC separations can be performed using standard C_8 or C_{18} alkyl bonded stationary phases, which are much easier to synthesize and usually more thermally and chemically stable.

The chromatographic properties of CBPs depend not only on the type of ligands attached to the surface, but also on the properties of the silica used for their synthesis.[2] Hence, the surface and structural properties of the silica need to be known in order to obtain well-defined CBPs in a reproducible way. Our recent paper[12] reported extensive sorption studies of several commercially available chromatographic silica gels. Adsorption-desorption measurements in a wide pressure range were used to evaluate the specific surface area, the pore size distribution and the adsorption energy distribution for the silicas under study. The specific surface area is required to meaningfully compare different stationary phases with the same bonded groups on the basis of the surface coverage of the ligands.[4] The knowledge of the pore width and the pore size distribution for silica gels allows one to choose a brand of silica best suited for a given application as CBP support for chemically bonded phases.

Table 1

Surface Coverage of Octyl Groups

Silica	Manufacturer	Percentage of Carbon	Surface Coverage (μmol/m^2)
Hypersil	Alltech, IL, USA	2.52	3.9
LiChrospher	EM Science, NJ, USA	2.68	4.1
Partisphere	Whatman, Inc., NJ, USA	3.21	3.5
SG-7/G	Polymer Institute Bratislava, Slovakia	14.84	3.4
Silasorb	Lachema, Brno, Czech Republic	8.76	3.6
Vydac	Supelco, PA, USA	3.98	4.1

The current paper is a continuation of the previous work.[12] Several commercially available silica gels were modified by the chemical bonding of octyl (C_8) ligands. Subsequently, the properties of the octyl CBPs and the original silica gels were studied by means of nitrogen adsorption, elemental analysis and high resolution thermal gravimetry.

The obtained data were used to compare the surface and structural properties of the synthesized CBPs with one another and with the original silica gels.

MATERIALS

The silica gels used in the current study are listed in Table 1. The octyl phases were synthesized according to the following procedure. The silica gel was dried in a glass reactor for 12 hours under vacuum (0.01 Pa) at 458 K. Then, octyldimethylchlorosilane and dry morpholine were added and the reaction mixture was kept at 388 K for 12 hours.

Subsequently, the silica with bonded stationary phases was washed with toluene, methanol and hexane , and dried under vacuum at ambient temperature. The octyldimethylchlorosilane was purchased from Pertrach System (Levitton, PA, USA) and morpholine was obtained from E. Merck.

METHODS

Sorption and Thermogravimetric Measurements

Nitrogen adsorption-desorption isotherms were measured on an ASAP 2010 volumetric sorption instrument from Micromeritics (Norcross, GA, USA). The purity of nitrogen was 99.99 %. Before the measurements, samples were degassed for 2 hours in the degas port of the adsorption apparatus at 473 K under the vacuum of about 10^{-4} Torr. The measurements were performed for a wide range of relative pressures, usually from 10^{-5} in the case of bare silicas and 10^{-3} for octyl stationary phases.

Thermogravimetric measurements were performed under quasi-isothermal conditions in a nitrogen atmosphere on a high resolution thermogravimetric analyzer TGA 2950 from TA Instruments, Inc. (New Castle, DE, USA). The elemental analysis was carried out by Huffman Laboratories (Golden, CO, USA).

Characterization Methods

Most of the characterization methods used in the study were described in details elsewhere.[12] Several standard methods[13,14] were employed in order to calculate the specific surface area, the total pore volume and the pore size distribution for the samples studied. The specific surface area of the samples was evaluated from the standard BET method. The micropore volume was calculated from the t-plot method. The Barrett-Joynder-Halendra (BJH) method was employed to obtain the pore size distributions, total pore volumes and average pore sizes from adsorption and desorption data. Advanced numerical procedures based on the regularization method[15] were used to calculate the adsorption energy and the pore volume distributions. The local isotherms for pores of different sizes were obtained on the basis of the density functional theory.[16,17] In order to evaluate the adsorption energy distributions, the Fowler-Guggenheim adsorption isotherm was used as a local isotherm in the integral equation for the total amount adsorbed. The number of nearest neighbors and their interaction energy (divided by the Boltzmann constant) were set to 4 and 95 K, respectively. In most of our calculations, the regularization parameter γ was set to 0.1 for silicas and 0.01 for bonded stationary phases. Further details of the methods employed in the study can be found in our previous paper[12] and references therein.

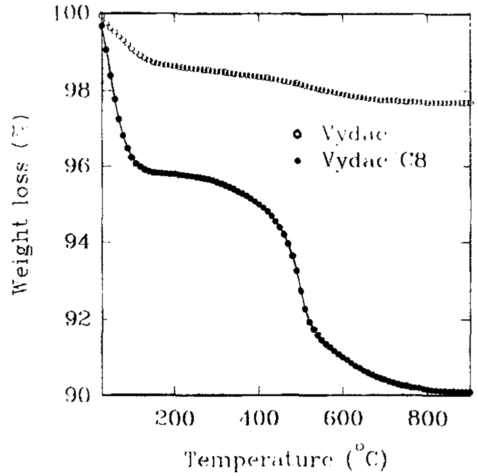

Figure 1. Thermogravimetric weight loss curves for unmodified Vydac and Vydac with chemically bonded octyl phase.

RESULTS AND DISCUSSION

Shown in Table 1, are percentages of carbon in octyl CBPs and the surface coverages of octyl groups. The latter were calculated on the basis of the BET specific surface area and the percentage of carbon in the samples[18] The octyl group surface coverage for the samples was in the range from 3.4 to 4.1 mmol/m^2 and tended to be higher for the samples of low surface areas. The above values of the surface coverage indicate that an appreciable amount of unreacted silanol groups is still present on the surface.[19]

In order to obtain information about thermal stability of the synthesized CBPs, high resolution thermoanalytical measurements were carried out. The samples were heated up to 1273 K in nitrogen atmosphere and the weight loss was recorded. As it is shown in Figure 1, after physically sorbed water was removed, there was a small step on the weight loss curves for unmodified silicas related to decomposition of surface silanols. In the case of silicas with bonded octyl groups, the physically adsorbed water and solvents left from the synthetic procedure were removed at the temperature below 373 K and the weight loss curve leveled. Then, in the temperature interval from 573 to 1023 K, there appeared a considerable weight loss, which can be attributed to the degradation of the chemically bonded stationary phase. The percentage of the weight loss for this step is in a good agreement with a weight percentage of the

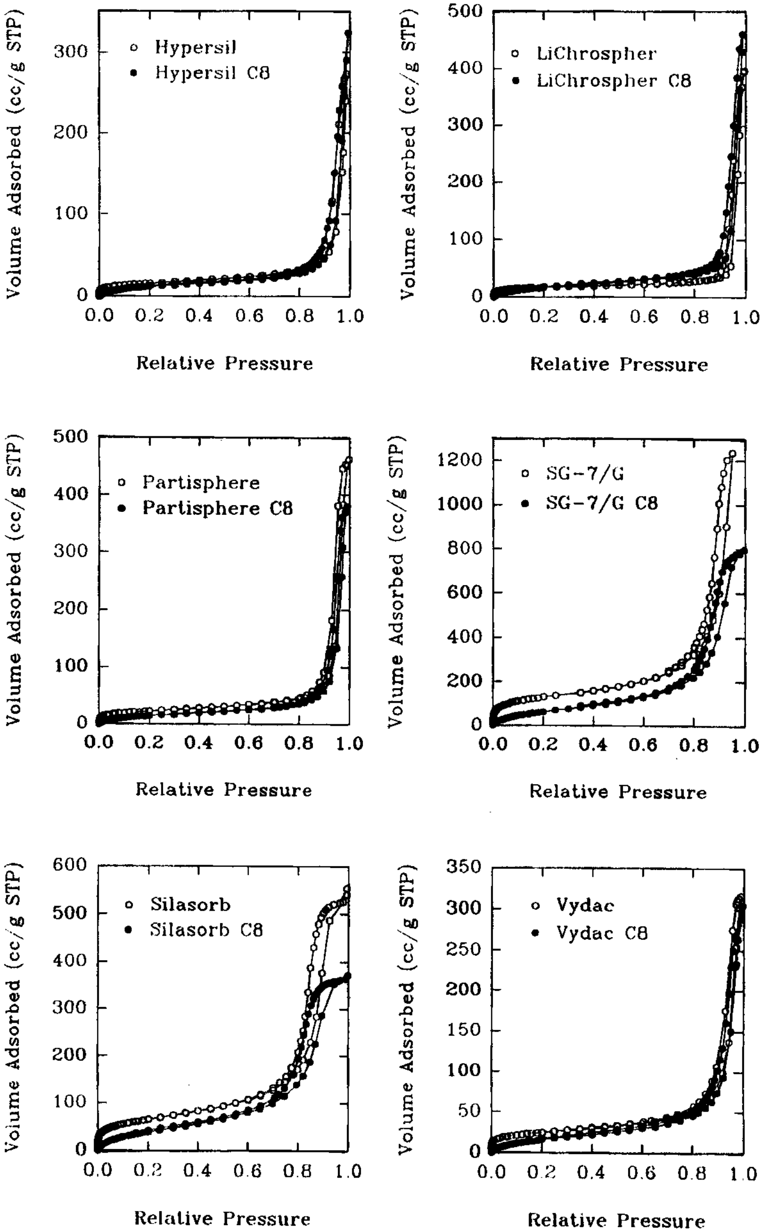

Figure 2. Adsorption-desorption isotherms for the chemically bonded phases and unmodified silicas.

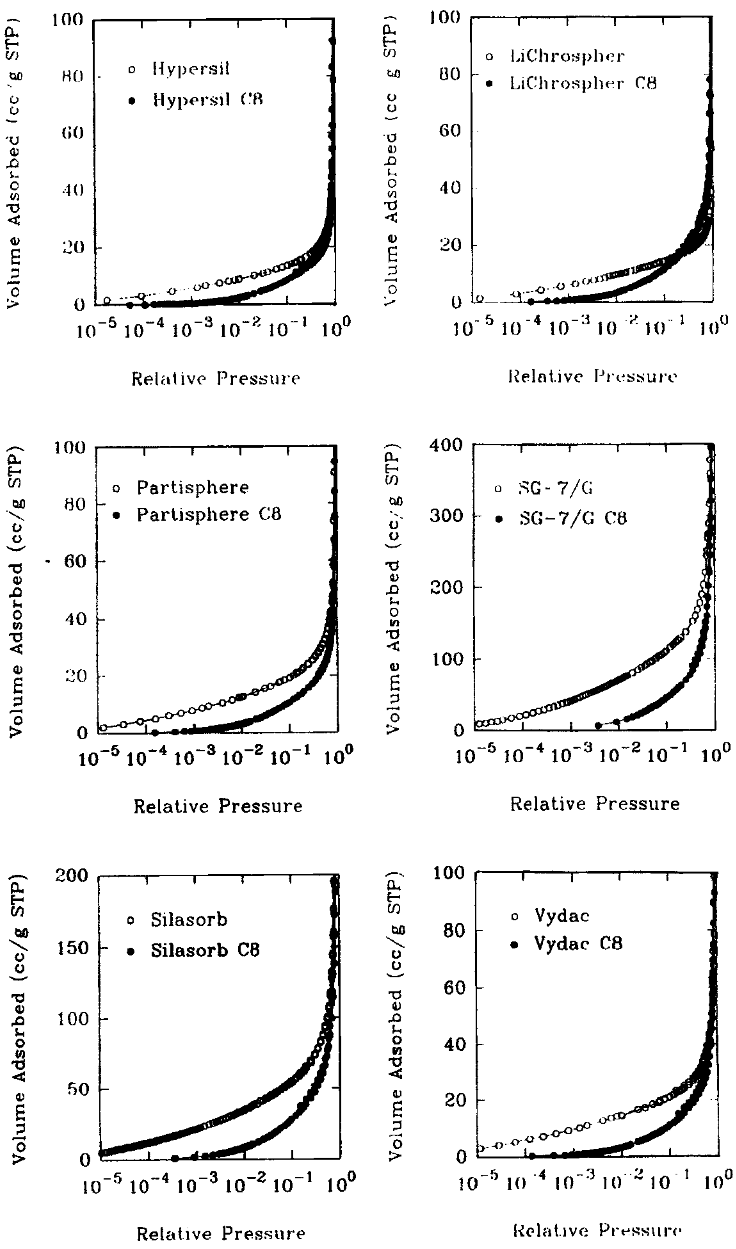

Figure 3. Low pressure parts of adsorption isotherms for the chemically bonded phases and unmodified silicas.

Table 2

BET Specific Surface Area and BJH Desorption Total Pore Volume (1.7 to 300 nm)

Silica	BET Surface Area (m^2/g)		BJH Total Pore Volume (cc/g)	
	Original	C_8 Phase	Original	C_8 Phase
Hypersil	56	47	0.42	0.50
LiChrospher	57	67	0.61	0.71
Partisphere	81	58	0.72	0.59
SG-7/G	464	268	1.86	1.24
Silasorb	234	162	0.86	0.57
Vydac	86	64	0.49	0.47

bonded octyl groups in the samples. It can be seen in Figure 1, that the temperature of 473 K is suitable for the outgassing procedure before adsorption measurements, since it is high enough to remove physically adsorbed species, but yet below the temperature of the degradation of the CBP.

Shown in Figures 2 and 3, are adsorption isotherms for the silicas with CBP and the unmodified silicas. It can be noticed that the adsorption behavior at high relative pressure (in the range from about 0.5 to 1 p/p_0) does not change significantly after the octyl groups were introduced, which indicates that the porous structures of the samples were not altered appreciably in the course of the modification. All isotherms are of the type IV (or intermediate between II and IV) according to the IUPAC classification[20,21] and exhibit adsorption-desorption hysteresis loops . In the case of Hypersil, LiChrospher, Partisphere and Vydac (both modified and unmodified), the hysteresis loop occurs at relative pressures from about 0.85 to 0.95 and most closely resembles type H1 according to the IUPAC classification.[20, 21] SG-7/G and Silasorb exhibit hysteresis loops intermediate between type H1 and H2 for pressures from 0.75 to 0.95. The low pressure parts of the adsorption isotherms are shown in Figure 3. For all C_8 bonded phases, the adsorption at relative pressures up to about 0.002 was very small, which was not the case for the original silica samples. Moreover, the shape of low pressure parts of the isotherms for CBPs was almost identical, which indicates, that their surface properties are similar. The values of the BET specific surface area and the BJH pore volume (calculated from the desorption data) are listed in Table 2. The average pore size data obtained from the BJH method (adsorption and desorption) are shown

Table 3

BJH Adsorption and Desorption Pore Diameter

Silica	BJH Adsorption Average Pore Diameter (nm)		BJH Desorption Average Pore Diameter (nm)	
	Original	C_8 Phase	Original	C_8 Phase
Hypersil	33	38	29	32
LiChrospher	57	36	39	32
Partisphere	37	34	30	31
SG-7/G	16	14	16	13
Silasorb	14	11	12	9
Vydac	26	23	23	21

in Table 3. It needs to be remarked, that the samples of the CBPs used for the sorption measurements were very small and one might expect an error in weighing the samples. Moreover, in the range of pressures very close to the saturation pressure (above 0.95 relative pressure), the adsorption on the walls of the glass tube with adsorbent may noticeably increase the gas uptake, which introduces some error, especially for very small samples. However, the errors are not expected to influence the shape of the isotherms (except for pressures very close to the saturation pressure), the pore size distribution functions and the adsorption energy distribution functions.

It can be expected, that the introduction of the octyl groups on the silica surface would decrease the total pore volume, the average pore diameter and the specific surface area of the samples, provided the only process in the course of the modification is just chemical bonding between the surface silanol groups and ligands. The reason is that the bonded groups would occupy some space in the porous structure, decreasing the pore diameter and hence the volume of pores, or maybe even block some of them and make them inaccessible to nitrogen adsorption. Moreover, the presence of CBP increases the mass of the sample, so even if the surface area or the pore volume are not altered, the specific surface area and the specific pore volume will decrease. Our measurements show that indeed such trends can be observed, especially for samples of higher surface area (SG-7/G, Silasorb), where the decrease in the specific surface area and the pore volume was quite pronounced. However, in the case of the samples of the lowest surface area, the opposite tendency could be noticed. The specific surface, the average pore diameter, the pore volume of Hypersil and the pore volume of LiChrospher increased after the octyl groups

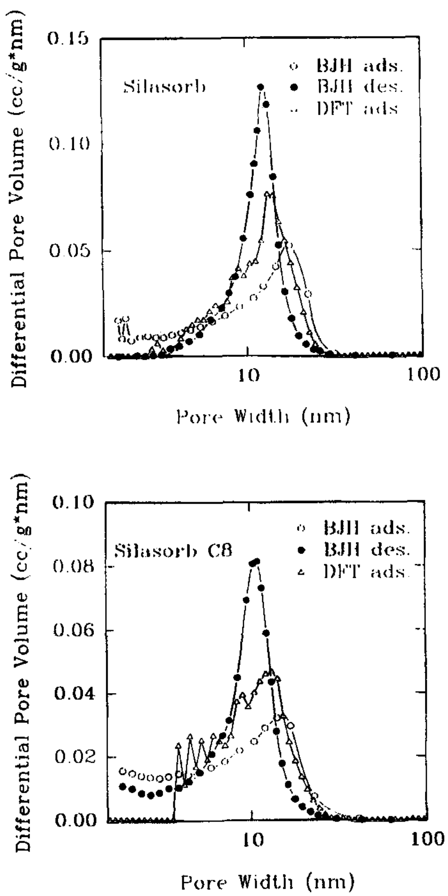

Figure 4. Comparison of the differential pore volume distributions obtained by means of the BJH method (from adsorption and desorption data) and the DFT software.

were bonded. It is not clear if these results arise from the experimental error or they are caused by minor structural changes of the silica samples in the course of their modification. Further studies are required in order to find out the reason of these unexpected findings.

The pore size distributions (PSD) for the samples under study were calculated by using BJH method (adsorption and desorption) and the DFT software supplied by Micromeritics, Inc. Shown in Figure 4, are differential PSD for Silasorb and Silasorb-based octyl stationary phase obtained by means of these methods. The overall shape of the PSD functions for a given sample is similar, but there is a difference in the location of the peak corresponding to the maximum on PSDs. Namely, the peaks from the DFT calculations lie between these from the BJH adsorption and the BJH desorption. However, all three methods consistently show no considerable differences between PSDs for the original silica gel and the octyl CBP. It can be seen that in order to trace the changes of porous structures of the samples, the results from one of these methods need to be compared between one another.

In the current paper, the DFT software was used to provide the PSDs for the samples under study. The DFT program is best suited to slitlike pores with graphite type surfaces. The pores in silica gels are rather irregular in shape and their surface has different properties than the surface of graphite. However, PSDs are calculated from high pressure parts of isotherms, for which the surface is covered by at least a monolayer of the adsorbate and the surface properties are not that important, as in the submonolayer region. Secondly, the studied silicas have fairly wide pores, for which the effect of the geometry should be somewhat smaller. Finally, the comparative analysis of the unmodified and the modified samples is performed. Therefore, the DFT software was used to carry out the required PSD calculations, since it is numerically the most advanced method available now.

The incremental pore size distribution functions are shown in Figure 5. The PSDs for both octyl CBPs and the corresponding original silicas are of the same shape and lie in the same pore size range, which indicates that the porous structures of the samples were essentially unchanged in the course of the modification. All samples are mostly mesoporous (mesopores are pores with the widths between 2 and 50 nm according to the IUPAC recommendations[20,21]), but some of them (Hypersil, LiChrospher, Partisphere and Vydac) also possess appreciable fractions of small macropores (the widths above 50 nm). The PSDs show little or no evidence of the presence of micropores, which is in agreement with the micropore volumes obtained from the t-plot method.

The bonding of octyl groups to the silica surface is likely to decrease the pore size diameter. However, taking into account the size of the bonded ligand, the decrease is not expected to exceed 1 nm. The sizes of most pores present in the samples are above 10 nm, which is much higher than the expected decrease. Therefore, the latter decrease may be difficult to infer from the pore size distribution functions. This actually seems to be the case, since the distributions for some of the CBPs (Hypersil, LiChrospher, Silasorb) are slightly shifted towards small pore sizes with respect to the distributions for the unmodified silica gels, but this tendency is not well pronounced.

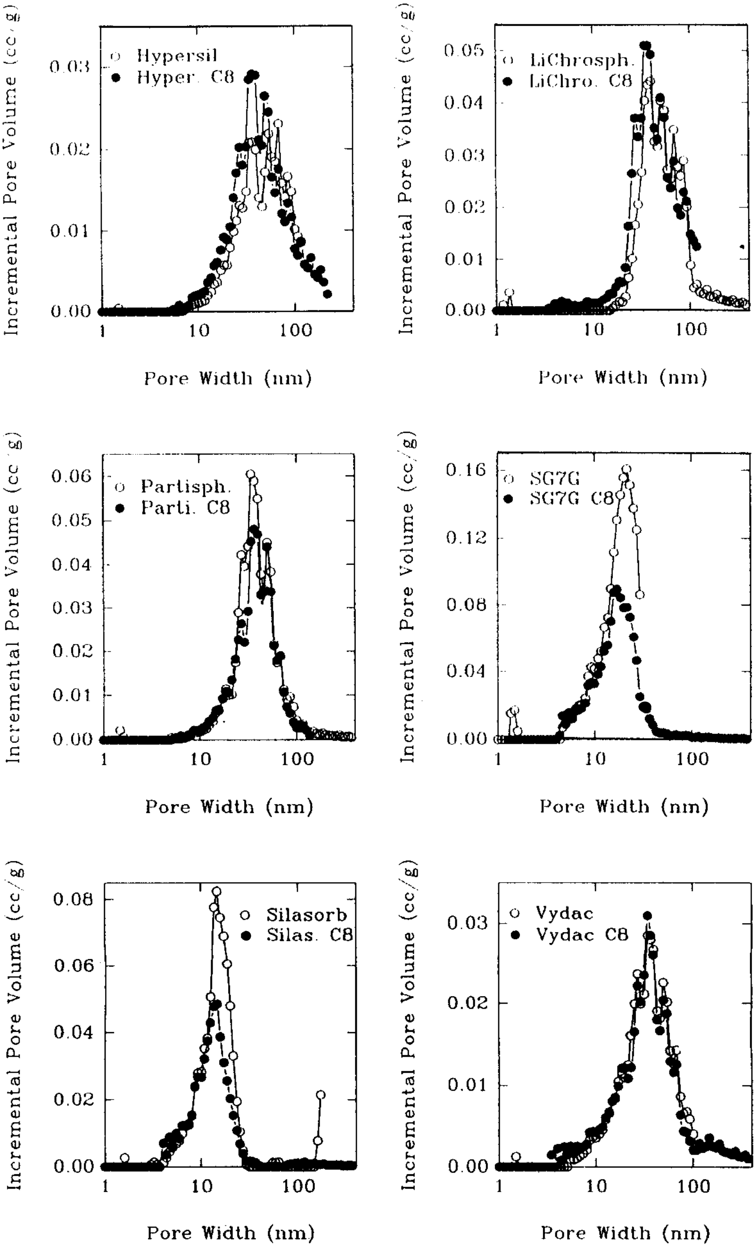

Figure 5. Incremental pore volume distributions for the chemically bonded phases and unmodified silicas.

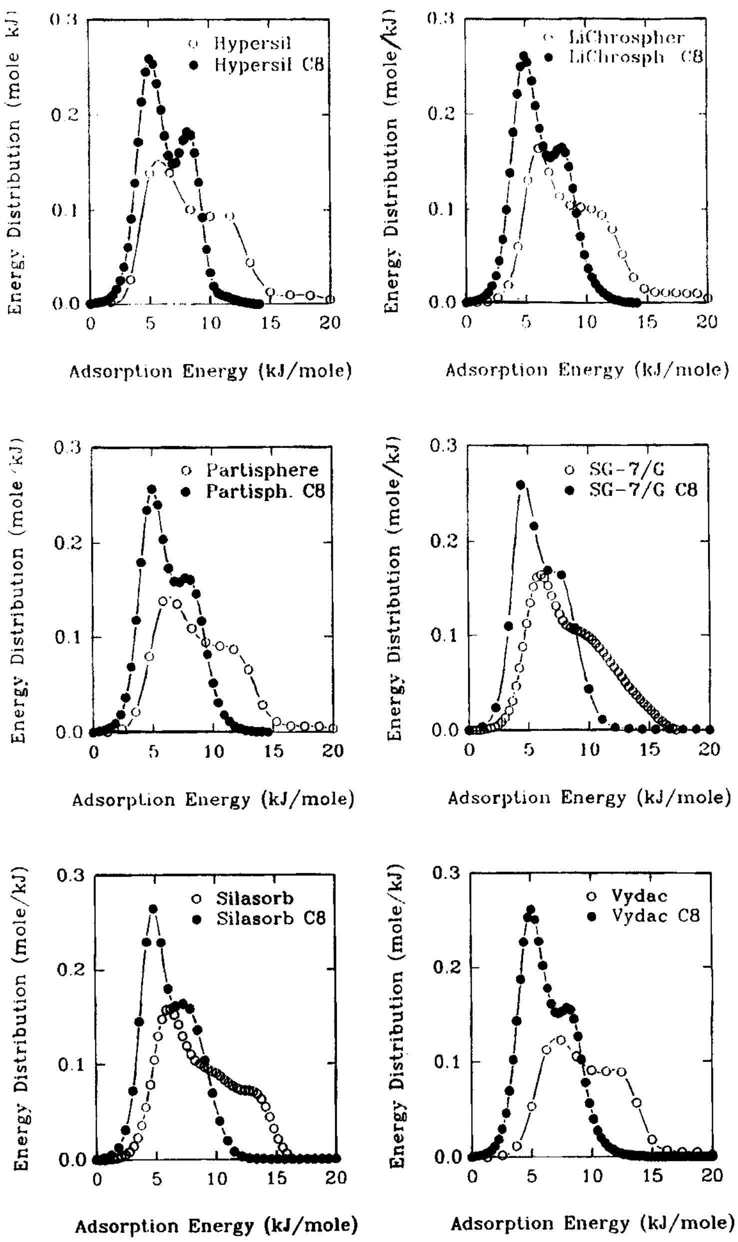

Figure 6. Adsorption energy distributions for the chemically bonded phases and unmodified silicas.

The adsorption energy distributions (AEDs) for both the CBPs and the unmodified silicas are shown in Figure 6. In order to obtain the AED functions, the inversion of the integral equation for the total amount adsorbed needs to be performed.[12] In the case of the CBPs, the inversion procedure occurred to be stable even for small values of the regularization parameter (γ). The latter parameter indicates the degree of smoothing of the input data, which is introduced in order to obtain numerically stable solution for the AED. In Figure 7, shown are adsorption energy distributions for Silasorb and Silasorb-based CBP, calculated for different values of γ. The distribution for the CBP does not exhibit negative (nonphysical) solutions for γ as low as 10^{-4}. In the case of the silica gel, the negative solutions are present to some extent even for the regularization parameter equal to 10^{-1}. The numerical stability of the solutions for the octyl CBPs allows obtaining physically meaningful adsorption energy distribution functions, with several (two to four; three in case of the Silasorb-based CBP) coalesced but yet distinct peaks, appearing for similar adsorption energy values for most CBP under study. However, their presence or absence seems to be dependent on the number of points on the isotherms in the submonolayer range of pressures. Further studies are needed to assess, if these peaks correspond to some adsorption sites on the surface of CBPs or are just the computational artefact. Because of the reasons mentioned above, the values of the regularization parameter used in the current study were chosen to be rather high and equal to 0.1 for the unmodified silicas and 0.01 for the octyl CBPs. For some unmodified silicas, their AEDs exhibit small negative parts (see Figure 7), which are nonphysical and therefore not shown in Figure 6.

The AED functions for unmodified silica gels cover the range from about 4 to 15 kJ/mol. The presence of small populations of higher energy sites (15-20 kJ/mol) is evidenced for Hypersil and LiChrospher. Previous thermogravimetric studies[22] showed that these gels contain relatively high amount of physically adsorbed water. The latter finding can be caused by the presence of these higher adsorption energy sites. However, these high energy tails may just be artefacts arising from the fact that too few isotherm data points were available for the calculations. Hence, the definite solution of that problem requires further studies. The distributions for bare silicas show the presence of two or more broad peaks. One of them is well pronounced and appears for about 6 kJ/mol, whereas the other peak, which corresponds to the adsorption energy of about 11-13 kJ/mol, is broader and maybe coalesced with other peaks. Because of that, the distributions show no considerable decrease in the range of 10-12 kJ/mol and then decline rapidly in the energy interval of about 13 to 15 kJ/mol. The adsorption energy distribution for SG-7/G is somewhat distinct from the others, as it exhibits a rather steep decrease in population of the adsorption energy sites in the range from 10 to 16 kJ/ mol.

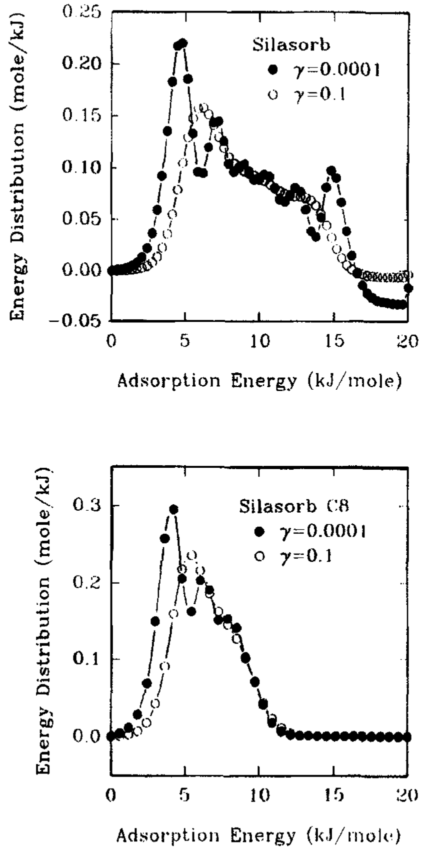

Figure 7. Comparison of the adsorption energy distributions calculated for different values of the regularization parameter.

The adsorption energy distributions for the octyl CBPs differ significantly from those for the unmodified silicas. The former are essentially the same for all CBPs samples studied and lie in the adsorption energy range from 3 to 10 kJ/mol. They exhibit two more or less distinct peaks corresponding to energies of 5 and about 8 kJ/mol. There is no evidence of the high energy sites (10-15 kJ/mol), which are present on the surface of the unmodified silicas. The distributions for both unmodified and modified samples show low energy peaks for very similar values of adsorption energies, that is 5-6 kJ/mol. It can be best seen in Figure 7, where the same regularization parameters were applied for both compared samples.

In Figure 6, the lowest energy peaks for silicas and the corresponding CBPs are somewhat shifted with respect to one another, most likely because of the different values of the regularization parameter used in the calculations.

As it was mentioned before, the surface coverages of octyl groups indicate that a considerable amount of unreacted silanol groups is still present on the surface of the CBPs. It is not likely that the octyl groups are able to shield the remaining silanols so effectively that the latter are not exposed to the nitrogen adsorption. Moreover, the similar shape of the low energy parts of the AEDs for both modified and unmodified silicas suggests that the low energy peaks may correspond to the adsorption sites on the unshielded silica surface. Therefore, the absence of the high energy sites on the surface of the CBPs arises presumably from the fact that these sites reacted in the course of the derivatization. The high energy sites can probably be identified with isolated silanols, as other silanols can be involved with hydrogen bonding between one another or with water molecules, which is likely to lower their accessibility and/or their interaction energy with nitrogen molecules used for the adsorption study. Other groups present on the surface of silica , such as siloxanes, are not expected to interact strongly with the adsorbate.

Since low energy peaks on the adsorption energy distributions for the CBPs seem to correspond to the peaks present on the AEDs for the unmodified silicas, the same groups on the silica surface may be responsible for their presence. But, adsorption energies of interactions of nitrogen molecules with octyl ligands are still unidentified. However, they may just be similar to the energy of one or even both of the low energy peaks, which seem to have their counterparts in the distribution functions for unmodified silicas. This is another problem, which would need to be addressed in further studies.

CONCLUSIONS

Samples of silicas with octyl bonded phases were analyzed by sorption measurements, high resolution thermogravimetry and elemental analysis. The latter technique allowed us to obtain the percentage of carbon in octyl bonded phases. High resolution thermogravimetry was employed to assess the thermal stability of the silicas and the CBPs studied. Nitrogen adsorption measurements provided the specific surface area, the pore volume distribution and the adsorption energy distribution for the samples. The surface and structural properties of octyl CBPs were compared with each other and with properties of corresponding unmodified silica gels. It was shown that although the coverage of C_8 groups varied by about 15% from one sample to another, the surface properties of the octyl CBPs were quite similar, which can be seen from the low pressure adsorption behavior and the adsorption energy distributions. Unmodified silicas possess considerable fraction of adsorption sites of the adsorption energy between 10 and 15 kJ/mol. After octyl groups were bonded, these sites were no longer evidenced, which can be explained by assuming that most of them reacted in the course of the octyl group bonding. Owing to the absence of high energy adsorption sites, the adsorbed amount for octyl CBPs in low pressure region is much lower than in the case of unmodified silicas. However, the high pressure behavior of both modified and unmodified gels of the same type is similar, which indicates, that the porous structure of gels is not altered significantly in the course of the chemical bonding of octyl ligands.

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