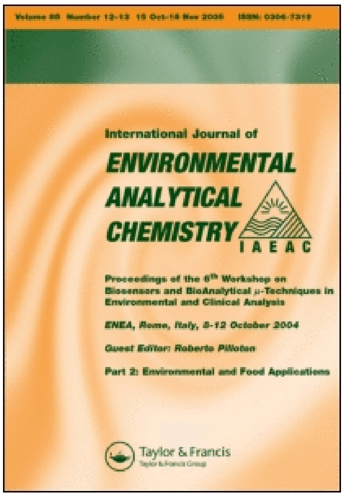

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Selectivity at the Solid-Liquid Interface on Bonded Sorbents[†]

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The rapid growth in the use of bonded phase silica adsorbents for reversed-phase liquid chromatography (RPLC) and solid-phase extraction (SPE) in recent years has sparked an interest in obtaining more than a working understanding of the surface chemistry of these systems. The difficulty in providing a descriptive model of the surface interactions on these materials lies in the complexity of the system. A structurally complex surface is presented by the highly porous silica support and the surface layer has contributions from solvents, the chemically bonded species, and the chemistry of the silica surface itself. All of these provide interactions with solutes of widely differing polarity and geometry in both chromatographic separations and selective adsorption experiments. The experimental investigations described in this work will address the three dimensional structure of the surface solvated layer, which acts as the stationary phase or extracting phase, in terms of a temperature and solvation dependent conformation change of the bonded hydrocarbon.

KEY WORDS: Bonded phase silica adsorbents, reversed-phase liquid chromatography (RPLC), solid-phase extraction (SPE), surface chemistry.

INTRODUCTION

The first use of bonded phase materials in separations was in gas chromatography, in which hydrocarbon species were chemically attached to particulate surfaces in an attempt to improve the

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selectivity of the separation.[1] Chemically modified materials gained acceptance in column liquid chromatography[2] and displaced coated phase liquid–liquid chromatographic materials because of their superior stability and improved efficiency. The first attempts to understand the retention mechanism with bonded phase materials made the obvious comparisons with established mechanisms in Liquid–Solid and Liquid–Liquid Chromatography (LSC and LLC). In LSC solutes are retained by adsorption onto the polar particulate surface with displacement of adsorbed solvent.[3] LLC relies on a retention process equivalent to the distribution of a solute between two immiscible liquids based upon differential solubility which occurs in liquid–liquid extraction. Neither mechanism suitably describes RPLC with bonded phase silica as pointed out by Kirkland,[4] but rather something intermediate between the two is appropriate. As discussed by Morel and Serpinet,[5] retention cannot be described as a purely adsorptive process because the surface bonded groups do not present a classical surface. Neither do these groups compose a liquid phase because of their surface anchoring and sparse population relative to a pure liquid hydrocarbon, thus eliminating the pure liquid–liquid partition description of retention interactions.

The current understanding of the composition of the bonded silica phase and its interaction with solute species is based upon three important parameters drawn from the work of many researchers. The stationary phase is a dynamic solvated layer whose structure is determined by: (i) the length and type of the bonded hydrocarbon moiety, (ii) the surface coverage of the bonded species and (iii) the types of intermolecular interactions provided by the organic solvent component of the mobile phase. Obviously, the intermolecular interactions will change as a function of the functional group on the bonded moiety (octyl, phenyl, propylcyano, propyldiol, propylamine, etc.), so that only the affect of changing the length of a saturated linear hydrocarbon chain bonded to the surface will be considered in this discussion. Berendsen and de Galan[6] observed a plateau in the increase in retention with increasing chain length as well as a dependence of the critical chain length on the size of the solute molecule. This indicates that solute molecules intercalate themselves between the hydrocarbon chains and that once the entire molecule can be "immersed" in the stationary phase, further increase in chain length does not affect retention. This is in agreement with recent work by Gouichon *et al.*[7] in which it was observed that linear hydrocarbon molecules showed inordinately low retention relative to shorter homologs once the length of the solute exceeds that of the bonded hydrocarbon chain. The observation of a plateau region in selectivity as a function of chain length was also observed by Lochmuller *et al.*[8] This data in comparison to the selectivity measured for liquid–liquid extraction experiments led them to postulate retention analogous to partitioning for long chain bonded groups, but not for short chain materials.

Surface coverage of the bonded hydrocarbon moieties has a twofold affect. As the number of hydrocarbon groups on the surface is increased to near monolayer coverage, the retentive capacity of the material through nonpolar interactions increases. However, past a certain point determined by the pore size of the material and the length of the bonded group, retention decreases because of the decrease in accessible surface area due to the physical blocking of pores. A major complementary consideration cannot be ignored in that as hydrocarbon groups are bonded to the silica surface through siloxane bonds, the amount of polar silica sites is decreased.[9] The effect of these sites is dramatically seen on lightly loaded silica in the asymmetric elution band shape of very polar solute species such as amines. The interactions at these polar sites are usually attributed to silanol groups,[10,11] although this has not been conclusively proven.

The third factor controlling the behavior of the stationary phase, as mentioned above, is the type of organic solvent used as the mobile phase modifier. The intermolecular interactions of van der Waals forces (1–3 kcal/mole), dipole-induced dipole (1–4 kcal/mole), dipole–dipole (3–8 kcal/mole), and specific hydrogen bonding (5–10 kcal/mole) are the forces controlling the solvation of hydrocarbon bonded silica with the organic solvent/water mobile phases most commonly used in RPLC. Because of the nonpolar nature of hydrocarbon moieties as bonded species, the solvation interactions between the organic solvent and these groups are the relatively weak van der Waals and dipole-induced dipole forces. All of the forces may play a role in the solvent–solvent, solvent–solute and solvent–silica surface interactions. Because of the strength of the specific hydrogen bonding interactions between the silica surface and water, as evidenced by the difficulty in drying the silica by thermal means,[12] it is expected that any unreacted silica surface is covered by

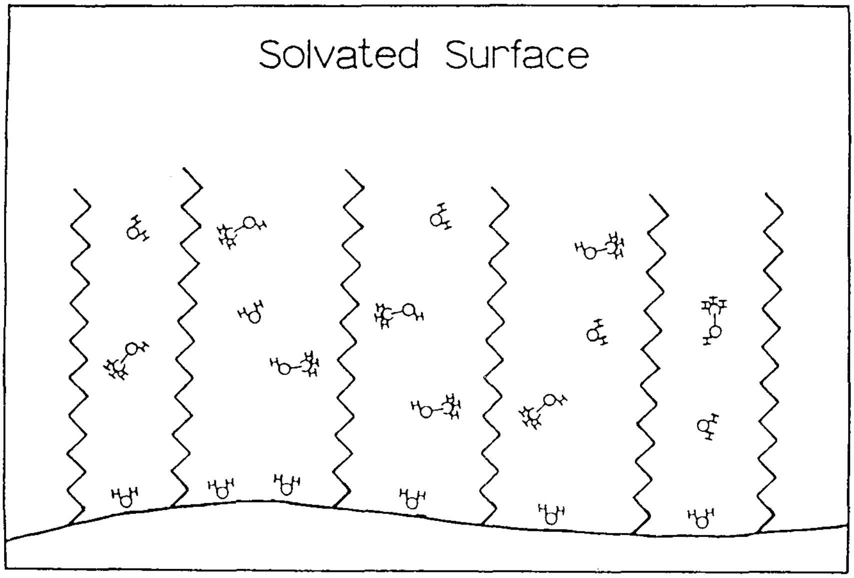

FIGURE 1 Schematic representation of RPLC stationary phase showing bonded octadecyl chains and solvent molecules.

at least one monolayer of adsorbed water.[13–15] In addition, several workers have investigated the solvation of chemically modified silica by the organic solvent/water solutions used as mobile phases. Poppe *et al.*[16] found that a positive surface excess of organic solvent exists on alkyl modified materials. This is in agreement with the results of Yonker, Zwier and Burke,[17,18] who attempted to measure the composition of the stationary phase solvation layer by flushing an equilibrated column with a strong solvent and quantitating the collected components. They found that the stationary phase is enriched in the organic solvent component of the mobile phase and that this enrichment increases as the chromatographic strength of the solvent increases ($CH_3OH < CH_3CN < THF$).

Thus, the current view of the stationary phase describes a dynamic multicomponent mixture of silica surface and bonded hydrocarbon, solvated by an organic enriched solvent mixture. Retention of at least nonpolar solute species is accompanied by intercalation of the solute molecule into this mixture. At this point it is necessary to add a fourth consideration to the structure and behavior of the stationary phase. Namely, the conformational shape and mobility of the bonded hydrocarbon chains. Halász *et al.*,[19] suggested that the bonded hydrocarbon chaims be described as bristles sticking out from the silica surface like a brush. Further research added refinements to this model when Kovats *et al.*[20] showed a phase transition in hydrocarbon bonded to acid etched silica as detected by a sharp change in wetting angle as a function of temperature and chain length. In comparing liquid–liquid extraction data with RPLC bonded phase selectivity, Lochmuller and Wilder[8] proposed that the hydrocarbon moieties preferentially associate with one another to collapse and form pseudo-liquid droplets on the surface. Gilpin[21–23] further showed that for intermediate length (C8–C10) bonded hydrocarbon materials with pure water mobile phases, an irreversible transition involving the release of surface organic solvent could be affected as a function of temperature. This transition was shown to be a function of the bonded alkyl chain length and the type of organic conditioning solvent. Based upon this data he proposed that collapsed hydrocarbon chains held trapped organic solvent until sufficient thermal energy was supplied to extend the chains in pure water and release the trapped solvent. Another type of surface transition was observed by Morel and Serpinet[5,24] using both GC and LC retention data in which they found a nonlinear change in retention as a function of temperature. They interpreted their data in terms of a change from a high temperature partition to a low temperature adsorption retention mechanism for long chain bonded phase materials (C18, C22).

The molecular mobility of bonded hydrocarbon chains has also been investigated spectroscopically. Using ^{13}C NMR Zwier and Burke[18] showed that the liquid-like mobility of the chains increased as a function of chain length and solvation, but only minor changes occurred as a function of temperature over the range studied. By selective positional ^{13}C enrichment of hydrocarbon bonding reagents, Gilpin and Gangoda[25] showed with NMR that mobility increases rapidly as one moves up the carbon chain away from the anchoring bond at the surface. FTIR spectrometry has been employed by Callis *et al.*[26] to show that for dry bonded phase silica a phase transition similar to that of a pure liquid hydrocarbon can be thermally induced on long chain bonded phases (C18–C22). For very well solvated materials (70% to 100% d4-methanol) FTIR measurements indicated an increase in the straightness of the bonded hydrocarbon relative to unsolvated conditions. Taken all together, the work of these researchers seems to indicate that two conformations of saturated hydrocarbon chains bonded to silica contribute to chromatographic response. One conformation is associated with stiffened chains of little mobility and the other with bent chains of higher mobility, Figure 2. In addition, the average conformation can

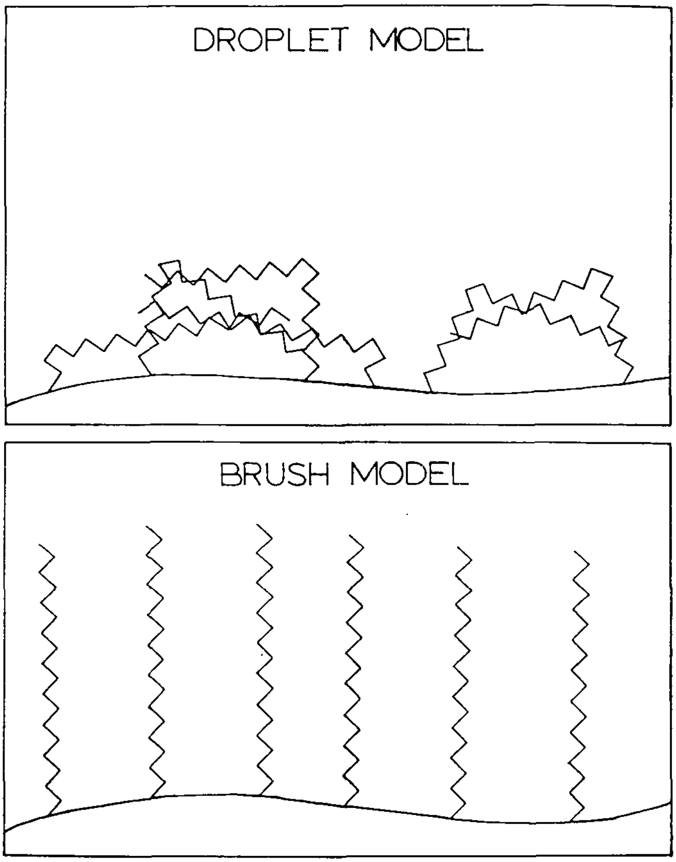

FIGURE 2 Schematic representation of proposed bonded hydrocarbon molecular conformations on the silica surface.

be altered by solvation and/or temperature changes, but the relative conditions required for these conformations is not without ambiguity.

The experimental work presented in this paper will address the nature of this conformation change on the most commonly used bonded phase chromatographic system, octadecylsilane bonded silica (C18) with methanol/water mobile phases. Under equilibrium mobile phase conditions a solvation dependent thermal transition is detected by the changing retention of a variety of solutes. Investigation of the thermodynamics of this transition and the response of solutes of differing polarity and geometry allows not only the determination of the nature of this rearrangement, but also the three dimensional structure of the stationary phase in terms of the location of the retention interactions of various solute types.

EXPERIMENTAL

Apparatus

An IBM Instruments Inc. (Danbury, CT) Model LC/9533 ternary gradient liquid chromatograph equipped with a Rheodyne (Cotati, CA) injection valve with a 20 μl sample loop was used. Sample detection was done with an IBM Instruments Inc. LC/9522 fixed wavelength UV absorbance detector at 254 nm or a Micromeritics Instruments Corp. (Norcross, GA) refractive index detector or a Waters (Milford, MA) Model R-400 differential refractive index detector. Retention data was measured manually from data recorded on a Linear Instruments Inc. (Irvine, CA) Model 261/MM chart recorder. Column temperature was regulated within a column jacket above ambient by circulating water from a 20 L reservoir with a Haake (Saddle Brook, NJ) Model E52 constant temperature circulator. Below ambient temperatures were regulated by circulating isopropanol with a Neslab Instruments Inc. (Portsmouth, NH) Models CF-D and CC60FII circulating cooling bath. Column temperatures were monitored with a precision thermometer (Van, Waters and Rogers Inc. $-1°$ to 101°C @ 1/10°) inserted into the thermostated liquid flow stream during operation and were controlled to ± 0.2°C. Data reduction and calculations were performed with an IBM Instruments Inc. Model 9000 laboratory computer.

Chemicals

All chemicals used in these experiments were reagent grade or better and were used without further purification except as specified. Normal alcohols from 1-propanol to 1-heptanol were obtained from Aldrich Chemical Co. Inc. (Milwaukee, WI). Absolute ethanol, USP reagent quality, was obtained from U.S. Industrial Chemical Co. (N.Y., NY). Phenol, benzene, potassium hydroxide and potassium permanganate were obtained from Fisher Scientific Co. (Fair Lawn, NJ). Toluene was obtained from Burdick and Jackson Inc. (Muskegon, MI). Methanol was obtained from EM Scientific (Gibbstown, NJ). Aniline and methoxybenzene were obtained from Mallinckrodt Chemical Works (St. Louis, MO). Water was double distilled, the second distillation being from potassium hydroxide and potassium permanganate solution.

Chromatographic procedures

All mobile phase solvents were filtered through 0.45 μm membrane filters (Millipore Corp. Bedford, MA) prior to mixing. Mobile phase solutions for temperature studies were prepared volumetrically in quantities of at least 6 L so that an entire temperature study could be completed with one batch of mobile phase. Solvents were degassed with helium purge during use.

The HPLC column used in these experiments was packed in our laboratory by a balanced density slurry packing technique described elsewhere.[27] A 100×4.6 mm stainless steel column was used, packed with 10 μm LiChrosorb RP-18 obtained from E. Merck Inc. (Cherry Hill, NJ) batch number 9633245VV1282. Elemental analysis of this material showed 19.1% carbon wt/wt. This material is stated to be derivatized with octadecyldimethylsilane.

For chromatographic measurements the column was equilibrated at the desired temperature with at least 100 column volumes of mobile phase solvent prior to use. Chromatographic measurements were made from 60.0° to −15.0°C with the range depending upon the mobile phase concentration. Upper temperature limits were established at least 5°C below the boiling point of the organic solvent and lower limits at least 3°C above the freezing point of the mixed solvent as determined experimentally. Samples were made up in the mobile phase at concentrations for the UV chromophores which gave a full scale response at 0.002 AUFS and for the *n*-alcohols of 1 to 4 mg/ml depending upon detectability and solubility. For every solute the retention volume was measured at least three times. Mobile phase volumes, V_m, were determined by the method of linearization of the retention of an homologous series of *n*-alcohols by minimization of the chi squared function. V_m values were determined under all conditions and it was found that no determinate variation in V_m with temperature was detectable. Based upon this, average V_m values and their variances were calculated as the mean and variance of all values at a given mobile phase concentration. These values were used to calculate k' and the standard deviation in $\ln k'$ by

$$S_{\ln k'} = \frac{\sqrt{S_{V_r}^2 + S_{V_m}^2(1+k'^2)}}{k' V_m}.$$

Retention volumes were corrected for flow rate deviations from the nominal instrument setting of 1.00 ml/min by volumetrically determining the flow rate under every set of conditions. Flow rates were measured by collecting 10.00 ml of solvent after the detector in a 50 ml buret for a measured period of time. Retention volumes were also corrected for extra column volume contributed by the valve, connecting tubing and detector by replacing the column with a zero dead volume union and measuring the elution volume of an injected solute.

RESULTS AND DISCUSSION

Thermodynamics and chromatography

The basis of separation in all forms of chromatography including solid phase extraction is the distribution of solute molecules between the flowing mobile phase and the stationary phase on the support particle surfaces. The total energy difference in the solvation energies when a solute molecule moves from the mobile to the stationary phase or *vice versa* is described by the free energy change ΔG. The free energy change is related to the equilibrium constant (K) of the distribution process by

$$\Delta G = -RT \ln K \tag{1}$$

where R is the gas constant and T the absolute temperature. If the retention of solutes for a particular set of conditions can be attributed to a single retention mechanism, then the equation of Martin and Synge[29] applies

$$V_r = V_m + KV_s \tag{2}$$

where the volume of solvent required to elute a solute from the sorbent is called the retention volume V_r and is related to the mobile phase volume V_m, the equilibrium constant K, and the stationary phase volume V_s.

Rearrangement of Eq. (2) gives the relationship between the capacity factor k' and the equilibrium constant K

$$\begin{aligned} k' &= \frac{\text{amount of solute in stationary phase}}{\text{amount of solute in mobile phase}} \\ k' &= \frac{V_r - V_m}{V_m} = KV_s/V_m = K\phi \end{aligned} \tag{3}$$

the proportionality constant is the phase ratio ϕ. The change in free energy (ΔG) can be related to the change in enthalpy (ΔH) and the change in entropy (ΔS) of the retention process by

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

where T is the absolute temperature of the system.

By combining Eqs (1), (3) and (4) the thermodynamic quantities can be related to experimentally measured quantities in the van't Hoff equation

$$\ln k' = \frac{-\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} + \ln \phi \tag{5}$$

Thus the slope of the linear function gives a measure of the enthalpy of the retention process.

$$-R\frac{d\ln k'}{(d1/T)}=\Delta H \tag{6}$$

Unfortunately, the important quantity of the entropy change of the retention process is convolved with a quantity whose value is difficult to determine accurately, namely the volume of the stationary phase, V_s.

In order to make use of the chromatographic retention data to determine thermodynamic values, an accurate measure of the mobile phase volume must be obtained. The method of this measurement has received much discussion and for thermodynamic calculation the method of choice is the value obtained from linearization of an homologous series.[28]

As Eq. (5) states, if the retention interactions are constant over a given temperature range, then a linear plot of $\ln k'$ versus $1/T$ will be obtained. However, if a change in retention interactions occurs in this temperature range, such as a phase transition in the stationary phase, then nonlinearity will be observed. This nonlinearity may range from smooth curvature to a discontinuity between two linear segments. This type of behavior has been used extensively in gas chromatography to study phase transitions in organic compounds, polymers, liquid crystals, metal complexes, etc.[30]

Solvation interactions

When a solute molecule is solvated by a bulk liquid solvent, a solvation sphere of solvent molecules forms around the solute molecule.[31,32] That is, the molecules arrange themselves in an order which provides a minimum in the total potential energy of the system. The degree of organization and long range order of this solvation sphere is dependent upon both the strength and the directionality of the intermolecular interactions. Since molecules in a liquid solution have a great deal of freedom of motion, these solvation structures are very dynamic and are continuously changing in size and composition. Very loosely organized solvation spheres that do not extend more than one molecular layer may form under the influence of van der Waals or weak dipole-induced dipole forces. However, highly organized solvation layers which extend several molecular units from the solute molecule may form when strong directional dipole–dipole forces, such as hydrogen bonding interactions, are responsible for solvation. This latter type of behavior is observed for the solvation of very polar or ionic solutes in aqueous solutions.

In RPLC or SPE relatively nonpolar solutes are studied in aqueous solutions of organic solvents, such as methanol. In this type of solution it would be expected that the organic solvent molecules will arrange themselves around the solute molecule in an orientation providing the most favorable interaction with both the solute and water as shown in Figure 3A. When the solute moves from the mobile phase solvent to the stationary phase, the formation of a classical solvation sphere, as has been described, is no longer possible because the surface solvated layer is not a classical liquid

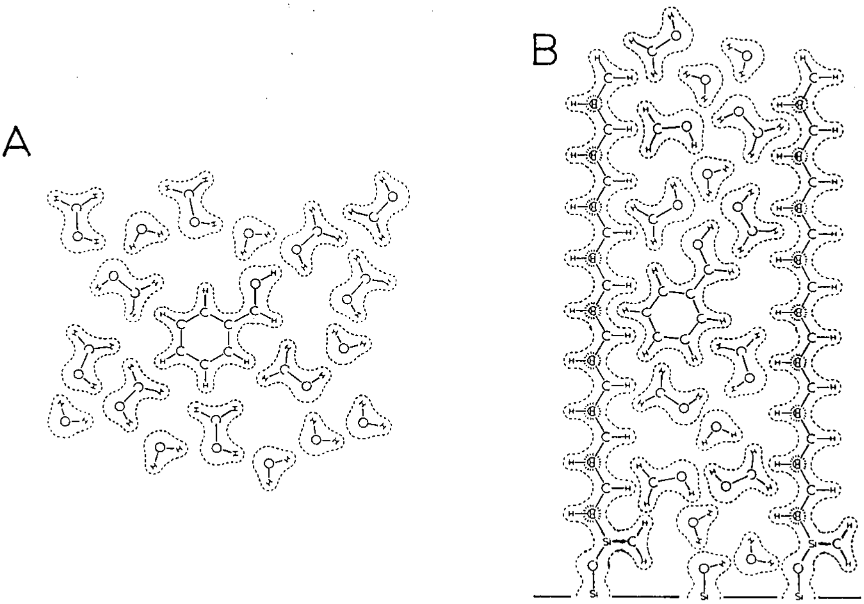

FIGURE 3 (A) Two-dimensional diagrammatic representation of the solvation sphere of a solute in mixed methanol and water solvent. (B) The interrupted solvation sphere of a solute in the RPLC stationary phase.

with all three degrees of freedom. The formation of a different arrangement of solvent molecules induced by the presence of the solute molecule (Figure 3B) would none-the-less occur because of the change in the position of the minimum in the potential energy surface describing the collective molecular interactions.

Conformation change of the bonded octadecylsilane groups

Because of the difference in molecular polarity and geometry from one solute to another, the solvation interactions available to a given solute in a chromatographic system must also vary. Therefore, different molecular probes would provide different sensitivity to a change in the stationary phase depending upon their ability to participate in the solvation interactions associated with the change. In these experiments, an understanding of the effects of altering the conformation and mobility of the octadecyl bonded groups on the retention interactions of various solutes is sought.

Under conditions of poor solvation on a silica material with high surface coverage (4.3 μmole/m^2) a nonpolar probe would be expected to provide the best sensitivity to any change in the stationary phase. Therefore, the chromatographic response of benzene is considered first, as shown in Figure 4A. At high temperature the linear behavior predicted by the van't Hoff equation is observed, but as the thermal energy of the system is decreased, a deviation in the response to lower than expected retention is observed. In an attempt to characterize this thermal behavior, a deviation onset temperature is assigned to the nonlinear van't Hoff plots by calculating the best two linear segments for the high and low temperature branches. As the concentration of organic solvent in the mobile phase is increased, two effects on the nonlinear behavior are observed. The temperature of the deviation onset decreases, indicating a dependence upon the composition of the surface solvation layer. And the magnitude of the deviation as measured by the change in slope ($\Delta\Delta H$) decreases (Table I), indicating that better solvation attenuates the effect of the surface change with respect to solute interactions. In order to confirm that the retention response of the probe solute benzene is not an anomalous observation, the retention of toluene in the same system was also considered, Figure 4B. Similar deviations from linear

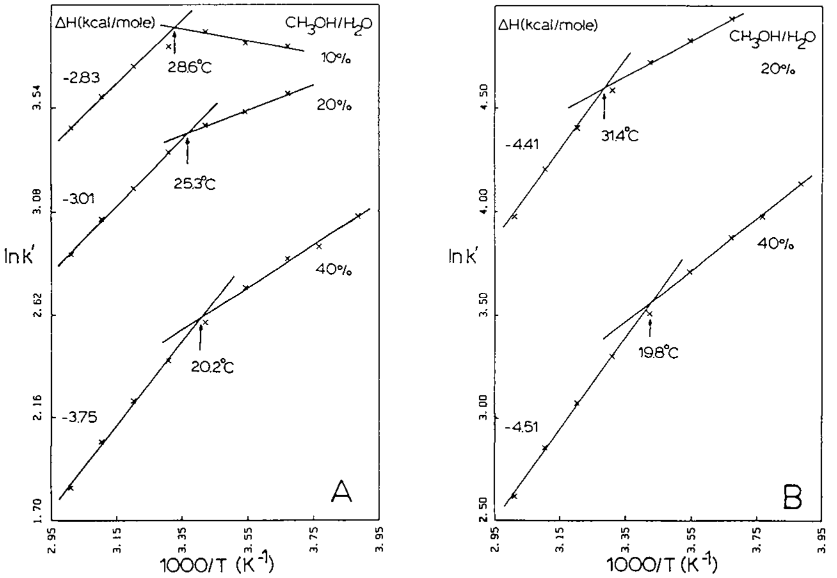

FIGURE 4 Chromatographic retention of (A) benzene and (B) toluene as a function of temperature in 10%, 20% and 40% v/v methanol/water mobile phases with LiChrosorb RP18 packing material.

TABLE I

Van't Hoff plot parameters for solutes in methanol/water mobile phases

Mobile phase		Solutes				
% v/v	Parameter	Benzene	Toluene	Methoxy-benzene	Phenol	Aniline
10	Deviation *T*	28.6	—	32.8	22.1	—
	High *T* Δ*H*	−2.83	—	−4.15	−3.78	−3.72
	ΔΔ*H*	−3.35	—	−1.84	−1.71	+0.11
20	*T*	25.3	31.4	26.3	16.8	none
	Δ*H*	−3.01	−4.41	−4.36	−3.65	−3.96
	ΔΔ*H*	−1.88	−2.71	−1.15	−1.19	0.0
40	*T*	20.2	19.8	15.6	10.3	—
	Δ*H*	−3.75	−4.51	−4.46	−3.78	−4.82
	ΔΔ*H*	−1.96	−2.08	−0.64	−0.89	+0.42

Deviation temperature in *K*, high temperature Δ*H* of retention and deviation magnitude in kcal/mole.

response are indeed observed in 20% and 40% methanol/water, but a greater rate of change of deviation temperature with mobile phase concentration is noted.

Probing the surface with a slightly more polar methyl ether solute, methoxybenzene, gives similar behavior to benzene in that negative deviations are observed (Figure 5A). The magnitude of the deviation, $\Delta\Delta H$, is less than was observed for benzene, as would be expected for a more polar probe sensing a change in the nonpolar interactions of the stationary phase. The deviation temperature also decreases with increasing percentage organic solvent, but at a greater rate than for benzene. A still more polar solute, phenol, which is acidic and a hydrogen bond donor, gives slightly different results (Figure 5B). Again the $\Delta\Delta H$ of the deviation is less than for benzene, but similar to methoxybenzene. The deviation temperature is shifted to lower values than benzene by 7° to 10°C, but the rate of change with mobile phase concentration is similar to benzene.

The response of these solute probes in terms of previously

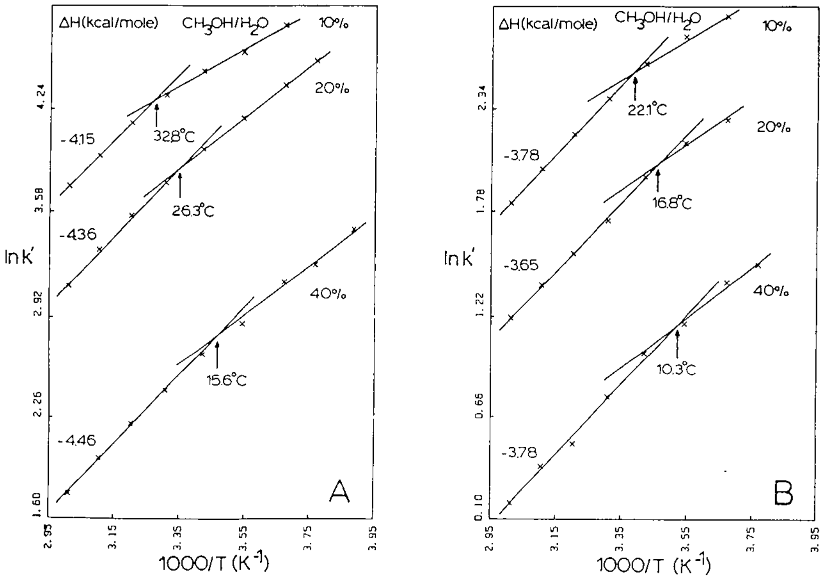

FIGURE 5 Chromatographic retention of (A) methoxybenzene and (B) phenol as a function of temperature under the same conditions as Figure 4.

established models of a solvated surface can now be considered. As the temperature is decreased, the molecular flexibility of long chain hydrocarbons decreases, such that the molecules become elongated and rigid, having fewer bends and kinks.[26] Also, the carbon atoms with the least mobility are those close to the anchoring site at the silica surface.[18,33] As the solute molecules intercalate themselves between the bonded hydrocarbon chains in the retention process,[6,7] they reside, on the average, in the region of the solvated layer which provides the most favorable interactions. Figure 6 shows the retention location of the three solutes discussed in a very simplified

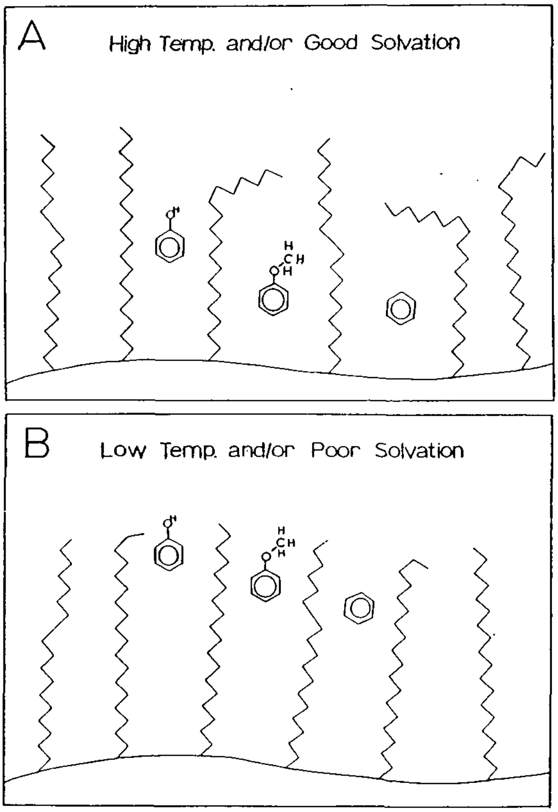

FIGURE 6 Schematic representation of the location of solute retention and bonded hydrocarbon conformation in the solvated stationary phase at (A) high and (B) low temperatures.

picture of the stationary phase. For simplicity, the imbibed solvent molecules are not shown. Consider first the behavior of the system at high temperature. Benzene finds its most favorable interactions through van der Waals and dipole-induced dipole forces near the central region of the solvated layer where a minimum in polarity exists. Further penetration to near the silica surface would be less favorable because of the increase in polarity near the adsorbed water layer. Methoxybenzene resides in nearly the same region as benzene, but will be oriented to keep its polar ether group nearer a higher polarity region. The location of phenol molecules will be on the average in the higher regions of the solvated layer, with the hydroxyl group oriented toward the mobile phase. In this location, they can find both nonpolar interactions with the solvated hydrocarbon chains and more favorable hydrogen bonding interactions with either methanol or water in a less restricted environment than near the silica surface. Although, better hydrogen bonding interactions may be available nearer the adsorbed water layer deep in the stationary phase, competition with the methanol solvent molecules, which are in much higher concentration, would restrict the availability of these interactions.

Upon reducing the thermal energy of the bonded hydrocarbon groups, the chains lose mobility and become more rigid. This restricted motion is expected to move up from the anchored end of the molecule as the temperature decreases. Thus, as the restricted region extends into the location of retention of a particular solute, the retention behavior of that solute changes (Figure 6B). As the temperature of the system is reduced and restriction in chain mobility moves up from the silica surface, the retention of solutes retained deep in the stationary phase, such as benzene, are affected first. It is not until more thermal energy is removed and nearly the entire length of the hydrocarbon chain is restricted that the retention of solutes retained higher in the solvated layer, such as phenol, are affected. Therefore, as Figures 4 and 5 show, regardless of the mobile phase concentration the retention of phenol is not affected by the change in hydrocarbon chain conformation until lower temperatures are reached.

In the same manner that solute access is restricted by the reduced mobility of the hydrocarbon chains, solvent access and mobility between the chains must also be restricted. The polarity gradient between the chains, i.e. the solvation layer composition, is therefore altered by this restriction. It is this change in interchain polarity gradient that is associated with the concentration dependence of the deviation temperature. This polarity gradient is also responsible for the difference in the rate of change of the deviation temperature with solvent concentration for two solutes which are retained in similar regions of the stationary phase, as is observed for benzene, toluene and methoxybenzene.

Retention behavior of a polar basic solute

In order to determine the effect on the accessibility of the silica surface by the conformational change in the bonded hydrocarbon and the accompanying change in the solvation layer, a basic hydrogen bonding solute, aniline, was used as a surface probe. It has been proposed that the retention of this type of solute is greatly affected by the availability of the silica surface, because of "acid-base" interactions with the acidic silica sites.[11] Unusual behavior is observed for all conditions in the van't Hoff plots for the retention of this solute, Figure 7. At 10% methanol a sharp deviation between two lines of nearly equal slope (ΔH) is observed between 30° and 40°C. Since this indicates only a change in intercept ($\Delta S/R+\ln\phi$), the effect of the surface change on the retention of this solute is purely entropic under these conditions. Linear behavior is observed at 20% methanol with a good deal of scatter in the data due to the difficulty in accurately measuring the V_r of a tailing peak. Under these conditions, aniline is unaffected by the surface change detected by other solutes.

The most interesting behavior occurs at 40% methanol. Linear high temperature response is followed by a sharp positive deviation to a second line, unlike all of the previous data. This indicates that more favorable interactions are available to aniline at low temperature. This data can be used to improve the detail in the three dimensional retention model presented in Figure 6. If the strong hydrogen bonding "acid-base" interaction of aniline with the silica surface dominates the retention interactions, then this solute would be retained deep in the stationary phase near the silica surface (Figure 8). Upon lowering the temperature and inducing a change in the conformation of the bonded hydrocarbon chains, the interchain

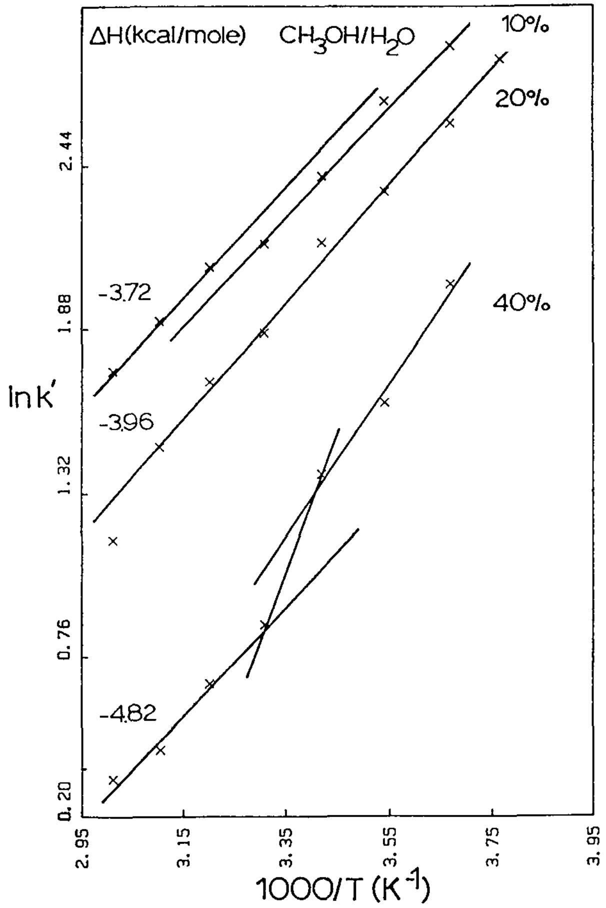

FIGURE 7 Chromatographic retention of aniline as a function of temperature under the same conditions as Figure 4.

polarity gradient decreases. Since the aniline solute is still attracted to the silica surface by the strong surface interactions, the local solvation environment is enthalpically more favorable for solvation of the phenyl ring. That is, unlike the previous solutes, the interaction location does not change with the surface conformation change. However, because of the restricted motion near the silica surface, the entropic contribution is less favorable. Thus at 10%

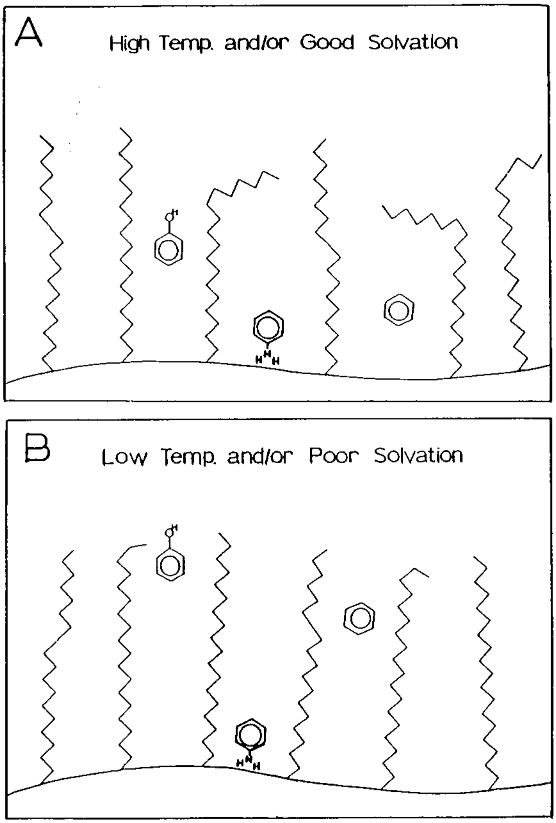

FIGURE 8 Schematic representation of the location of solute retention in the solvated stationary phase.

methanol the data indicates little solvent polarity change, but a restriction in surface availability. At 20% no change is detectable and at 40% both a decrease in interchain solvent polarity and a restriction in access occurs.

It is noted at this point that the behavior of aniline should be associated with a change in column efficiency, i.e. phase transfer kinetics, as a function of temperature. However, both because of the asymmetric non-gaussian peak shape of aniline and the relatively low efficiency of the column used in these experiments (28% of theoretical maximum), this effect could not be observed.

CONCLUSIONS

The chromatographic investigation of the bonded octadecylsilane conformation change with methanol/water mobile phases has led to a refinement in the model of the solvated layer stationary phase in bonded sorbents. A significant improvement in the understanding of the three dimensional character of the solvated layer has been determined, as well as the average location of retention interactions of solutes of differing polarity. For organic solvents with hydrogen bonding capability (such as methanol) effective competition occurs with acidic hydrogen bonding solutes, causing these solutes to be retained in the upper portion of the stationary phase. Hydrogen bonding solutes with basic character (such as aniline) find their major interactions deep in the stationary phase near the silica surface regardless of the solvent interactions. Low polarity and nonpolar solutes (e.g. benzene and methoxybenzene) whose retention interactions are primarily van der Waals and dipole-induced dipole forces, are on the average retained in the central region of the stationary phase where a minimum in polarity exists and the most favorable nonpolar solvation interactions occur.

When thermal energy is removed from the system, the bonded octadecyl groups become elongated and stiffened, the onset of which is in the region between 25°C and 35°C. This conformation change is accompanied by an alteration in the composition of the solvated layer and a restriction in the interchain access of both solvent and solute molecules. In general a net decrease in retention occurs with this surface reorganization. This restricted access can be overcome only by a solute with strong hydrogen bonding ability for the near surface region (like aniline). The polarity profile of a methanol solvated layer is shown in Figure 9 as a function of distance from the silica surface and interchain distance. When the bonded octadecyl groups are reduced in mobility, a change in the interchain polarity of the solvent occurs as shown.

It must be stressed that the detailed models of the solvated stationary phase layer on octadecylsilane bonded silica which have been developed are an attempt to represent the average interactions which are available and may occur. While these refinements of the stationary phase model provide a more accurate description of the intermolecular interactions responsible for retention and selectivity

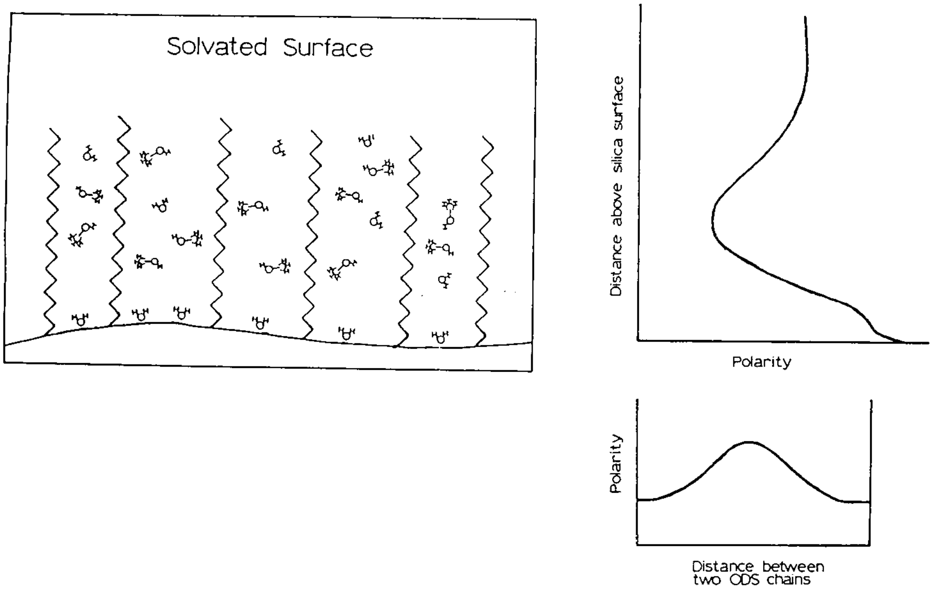

FIGURE 9 Schematic representation of the stationary phase solvated layer and solvent polarity gradients.

than was previously available, it must be remembered that when a highly porous silica surface is chemically modified with an alkyl silane, a surface which is heterogeneous in both physical structure and chemical activity is obtained, so that any average picture of the system is not complete in itself. Variables such as the surface coverage of the bonded alkyl moieties, the addition of functional groups to the bonded species and specific solvation interactions from the organic solvent will alter the detail of the structure and interactions of the stationary phase.

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