

Structure–Function Relationships in High-Density Octadecylsilane Stationary Phases by Raman Spectroscopy. 2. Effect of Common Mobile-Phase Solvents

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Raman spectroscopy is used to examine the effects of solvent, temperature, and surface grafting method (surface or solution polymerized) on alkyl chain rotational and conformational order in a series of high-density octadecylsilane stationary phases ranging in surface coverage from 3.09 to 6.45 $\mu\text{mol}/\text{m}^2$. Rotational and conformational order is assessed using the intensity ratio of the antisymmetric to symmetric $\nu(\text{CH}_2)$ modes as well as the frequency at which these Raman bands are observed. Solvents studied include perdeuterated hexane, toluene, chloroform, tetrahydrofuran, benzene, methanol, acetone, acetonitrile, and water. Stationary-phase order was investigated at temperatures between 258 and 323 K. Alkyl chain rotational and conformational order, and hence, solvation of the stationary phase, is dependent on solvent parameters (polarity, size, etc.), temperature, and stationary-phase properties (polymerization method and surface coverage). Information on stationary-phase conformational order allows solvent–stationary-phase interactions to be described in terms of a combination of adsorption and partitioning models for reversed-phase liquid chromatography. Finally, a distinct interplay between solvent- and temperature-induced ordering of these stationary phases is documented that is also a function of solvent and stationary-phase properties.

The use of alkyl-modified silica particles for the separation of molecules by reversed-phase liquid chromatography has evolved into a popular standard analytical technique. While the approach is common place, a molecular understanding of retention remains elusive despite the abundance of experimental and computational work. The least understood aspects of retention are intermolecular interactions between each chromatographic component (bonded alkyl chain, solvent, and solute) over the course of a separation. Such interactions include solvent–solute, solute–stationary phase,

solvent–stationary phase, and the intermolecular interactions of the alkyl chains within the stationary phase. The importance of each of these interactions is obvious in the context of solute retention. Recent efforts in this laboratory have focused on a systematic evaluation of the conformational order of the alkyl portion of alkylsilane stationary phases as an indicator of these interactions.^{1–5}

In the preceding paper in this journal,⁵ the effects of temperature, surface grafting procedure, surface coverage, and identity of the alkylsilane precursor on conformational order of five high-density alkylsilane stationary phases^{6–8} were examined. Here, the effect of mobile-phase solvent on conformational order of these same five phases is examined in an effort to clarify the role of solvent–stationary-phase interactions in solute retention in reversed-phase systems.

The effect of solvent on the intermolecular interactions of alkyl chains has been examined in numerous studies.^{4,9–30} While many

- (1) Thompson, W. R.; Pemberton, J. E. *Anal. Chem.* **1994**, *66*, 3362–3370.
- (2) Ho, M.; Cai, M.; Pemberton, J. E. *Anal. Chem.* **1997**, *69*, 2613–2616.
- (3) Ho, M.; Pemberton, J. E. *Anal. Chem.* **1998**, *70*, 4915–4920.
- (4) Pemberton, J. E.; Ho, M.; Orendorff, C. J.; Ducey, M. W. *J. Chromatogr., A* **2001**, *913*, 243–252.
- (5) Ducey, M. W.; Orendorff, C. J.; Sander, L. C.; Pemberton, J. E. *Anal. Chem.* **2002**, *74*, 5576–5584.
- (6) Sander, L. C.; Wise, S. A. *Anal. Chem.* **1995**, *67*, 3284–3292.
- (7) Pursch, M.; Sander, L. C.; Albert, K. *Anal. Chem.* **1996**, *68*, 4107–4113.
- (8) Pursch, M.; Vanderhart, D. L.; Sander, L. C.; Gu, X.; Nguyen, T.; Wise, S. A.; Gajewski, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 6997–7011.
- (9) Montgomery, M. E.; Green, M. A.; Wirth, M. J. *Anal. Chem.* **1992**, *64*, 1170–1175.
- (10) Burbage, J. D.; Wirth, M. J. *J. Phys. Chem.* **1992**, *96*, 5943–5948.
- (11) Montgomery, M. E.; Wirth, M. J. *Anal. Chem.* **1994**, *66*, 680–684.
- (12) Zulli, S. L.; Kovaleski, J. M.; Zhu, X. R.; Harris, J. M.; Wirth, M. J. *Anal. Chem.* **1994**, *66*, 1708–1712.
- (13) Kelusky, E. C.; Fyfe, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1746–1749.
- (14) Shah, P.; Rogers, L. B.; Fetzer, J. C. *J. Chromatogr.* **1987**, *388*, 411–419.
- (15) Bayer, E.; Paulus, A.; Peters, B.; Laupp, G.; Reiners, J.; Albert, K. *J. Chromatogr.* **1986**, *364*, 25–37.
- (16) Beauffils, J. P.; Hennion, M. C.; Rosset, R. *Anal. Chem.* **1985**, *57*, 2593–2596.
- (17) Sander, L. C.; Callis, J. B.; Field, L. R. *Anal. Chem.* **1983**, *55*, 1068–1075.
- (18) Doyle, C. A.; Vickers, T. J.; Mann, C. K.; Dorsey, J. G. *J. Chromatogr., A* **2000**, *877*, 25–39.
- (19) Sentell, K. B.; Bliesner, D. M.; Shearer, S. T. *Chem. Modif. Surf.* **1994**, *139*, 190–202.

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of these have been chromatographic,^{20–27} resulting in inferred solvent effects on the structure and order of the stationary phase, several have been spectroscopic,^{4,9–15,17,18,28,30} attempting to directly observe the effects of stationary-phase solvation. From these investigations, two models of solute retention have been proposed. The solvophobic (also called the hydrophobic) model^{31–34} treats the stationary phase as a passive entity. In this model, the stationary phase plays no role in the separation other than to provide a sorption site for the solute. The solvophobic model treats the separation as an adsorptive, rather than partitioning, process in which the solvation characteristics of the solvent for a particular solute dictate the extent of solute adsorption. In the partitioning model (also called the interphase model),^{35–38} the solute can become fully embedded within the chains of the stationary phase, thereby acting to compete with the mobile-phase solvent to “solvate” the solute. Thus, the stationary phase in this model plays an active role in retention with solute partitioning inducing changes in conformational order of the alkyl chains of the stationary phase. Although these models specifically address the interaction between solute and stationary phase, solvent–stationary-phase interactions should be similarly described.

These two models of solute retention represent clear pictures of the required intermolecular interactions during a separation; however, neither model may accurately describe the retention of every solute under all conditions. For example, several pieces of evidence suggest that solute retention cannot be completely described by either the solvophobic or partitioning models, including the following: (1) the observation that no single equation has been derived to account for the retention behavior of a solute,^{39–45} (2) observations^{35–38} that solute retention becomes increasingly entropic with increasing density of the alkyl component, and (3) wetting studies that suggest that solute or solvent

molecules are not always completely embedded within the stationary phase.^{9–11,30}

As previously demonstrated, Raman spectroscopy is an ideal technique for examining the intermolecular interactions of the alkyl chains in reversed-phase chromatographic materials^{1–5} due to its ability to provide a direct indication of the conformational order of the alkane component. Raman spectroscopy measurements are also free from spectral interferences from water and silanols that adversely affect IR measurements. Finally, Raman spectroscopy measurements can be carried out in the presence of solvent if care is taken to choose solvents that do not have interfering vibrational modes in spectral regions of interest. Thus, as part of an ongoing effort to elucidate retention mechanisms in reversed-phase liquid chromatography,^{1–5} our studies are expanded here to include the effects of solvent in addition to those parameters previously investigated.

When stationary-phase solvation is examined according to simple solvent classifications, including nonpolar solvents (possessing a weak dipole moment), polar solvents (possessing a strong dipole moment), and water, some trends are observed. In many cases, nonpolar solvents have been reported to disorder the alkyl chains of the stationary phase.^{4,13,14} Such disordering has been suggested to be the result of deep intercalation or partitioning of the solvent into the stationary-phase layer (fully solvating the alkyl chains). In contrast, polar solvents have been reported to have little to no effect on stationary-phase order,^{18,20,46} suggesting an adsorptive interaction of the solvent with the stationary-phase surface. In fact, several reports have indicated that polar solvents such as methanol increase alkyl component order relative to water.^{11,15–17} In water, the stationary phase has been described as collapsed in which the alkyl chains act to exclude water from the interior of the phase.^{9,30,47}

A few direct observations of alkyl chain conformation in the presence of solvent have been made by NMR,^{13–15,48,49} IR,¹⁷ and Raman spectroscopies.^{1–5,18} An early examination of octadecylsilane stationary phases in the presence of methanol and methanol/water mobile phases found that the alkyl chains of the stationary phase were ordered by these polar mobile-phase solvents.¹⁷ This was identified through the observation of a decrease in the number of carbon–carbon gauche bonds relative to the stationary-phase material in the absence of solvent. The molecular picture presented to explain these results was one in which the methanol molecules intercalate between the alkyl chains with the nonpolar methyl group embedded in the stationary-phase material and the polar hydroxyl group extending out of the surface.

While the effect of solvent on intermolecular interactions of the stationary phase is not yet clearly defined, the additional effect of temperature may be even less understood. Temperature effects on solute retention have generally been investigated using a van't Hoff analysis of the dependence of the capacity factor on temperature. While this approach has been useful in identifying temperatures at which a change in the retention mechanism is observed (presumably resulting from a phase change within the

- (20) Scott, R. P. W.; Simpson, C. F. *J. Chromatogr.* **1980**, *197*, 11–20.
- (21) Morel, D.; Serpinet, J. J. *J. Chromatogr.* **1981**, *214*, 202–208.
- (22) Hennion, M. C.; Picard, C.; Combellas, C.; Caude, M.; Rosset, R. J. *J. Chromatogr.* **1981**, *210*, 211–228.
- (23) Morel, D.; Serpinet, J. J. *J. Chromatogr.* **1982**, *248*, 231–240.
- (24) Gilpin, R. K.; Gangoda, M. E.; Krishen, A. E. *J. Chromatogr. Sci.* **1982**, *20*, 345–348.
- (25) Morel, D.; Serpinet, J.; Letoffe, J. M.; Claudy, P. *Chromatographia* **1986**, *22*, 103–108.
- (26) Cole, L. A.; Dorsey, J. G.; Dill, K. A. *Anal. Chem.* **1992**, *64*, 1324–1327.
- (27) Tchapla, A.; Heron, S. J. *J. Chromatogr., A* **1994**, *684*, 175–188.
- (28) Bliesner, D. M.; Sentell, K. B. *Anal. Chem.* **1993**, *65*, 1819–1826.
- (29) Klatte, S. J.; Beck, T. L. *J. Phys. Chem.* **1996**, *100*, 5931–5934.
- (30) Wong, A. L.; Hunnicutt, M. L.; Harris, J. M. *Anal. Chem.* **1991**, *63*, 1076–1081.
- (31) Horvath, C.; Melander, W.; Molnar, I. *J. Chromatogr.* **1976**, *125*, 129–156.
- (32) Karger, B. L.; Gant, J. R.; Hartkopf, A.; Weiner, P. H. *J. Chromatogr.* **1976**, *128*, 65–78.
- (33) Vailaya, A.; Horvath, C. *J. Phys. Chem. B* **1997**, *101*, 5875–5888.
- (34) Vailaya, A.; Horvath, C. *J. Phys. Chem. B* **1998**, *102*, 701–718.
- (35) Marqusee, J. A.; Dill, K. A. *J. Chem. Phys.* **1986**, *85*, 434.
- (36) Dill, K. A. *J. Phys. Chem.* **1987**, *91*, 1980–1988.
- (37) Dill, K. A.; Naghizadeh, J.; Marqusee, J. A. *Annu. Rev. Phys. Chem.* **1988**, *39*, 425–461.
- (38) Dorsey, J. G.; Dill, K. A. *Chem. Rev.* **1989**, *89*, 331–346.
- (39) Lochmuller, C. H.; Reese, C.; Aschman, A. J.; Breiner, S. J. *J. Chromatogr.* **1993**, *656*, 3–18.
- (40) Snyder, L. R.; Kirkland, J. J.; Glajch, J. L. *Practical HPLC Method Development*; Wiley: New York, 1997.
- (41) Snyder, L. R.; Dolan, J. W.; Rigney, M. P. *LC-GC* **1986**, *4*, 921–929.
- (42) Snyder, L. R.; Quarry, M. A. *J. Liq. Chromatogr.* **1987**, *10*, 1789–1820.
- (43) Stuart, J. D.; Lisi, D. D.; Snyder, L. R. *J. Chromatogr.* **1989**, *485*, 657–672.
- (44) Abraham, M. H.; Roses, M.; Poole, C. F.; Poole, S. K. *J. Phys. Org. Chem.* **1997**, *10*, 358–368.
- (45) Wang, A.; Tan, L. C.; Carr, P. W. *J. Chromatogr., A* **1999**, *848*, 21–37.

- (46) Gilpin, R. K.; Gangoda, M. E.; Krishen, A. E. *J. Chromatogr. Sci.* **1982**, *20*, 345–348.
- (47) Carr, J. W.; Harris, J. M. *Anal. Chem.* **1987**, *59*, 2546–2550.
- (48) Albert, K.; Bayer, E. *J. Chromatogr.* **1991**, *544*, 345–370.
- (49) Albert, K.; Brindle, R.; Martin, P.; Wilson, I. D. *J. Chromatogr., A* **1994**, *665*, 253–258.

Table 1. Raman Peak Frequencies and Assignments at 293 K

peak frequency (cm ⁻¹) ^a					assignmt
TFC18SF	TFC18SL	DFC18SF	DFC18SL	MFC18	
2954	2954	2954	2955	2954	$\nu_a(\text{CH}_3)$
2932	2929	2925	2926	2920	$\nu_s(\text{CH}_3)_{\text{FR}}$
2895	2897	2898 sh	2896	2900	$\nu_s(\text{CH}_3)$
2880	2880	2882	2884	2884	$\nu_a(\text{CH}_2)$
2846	2851	2851	2851	2853	$\nu_s(\text{CH}_2)$

^a sh, shoulder.

stationary phase), the resulting changes in alkyl chain architecture must be inferred from the data.

Here, we examine the role of solvent and temperature as well as the interplay between them in dictating the conformational order of five previously described^{6–8} octadecylsilane stationary phases. In addition, the effect of surface grafting method, silane precursor identity, and surface coverage is also examined as a function of solvent and temperature.

EXPERIMENTAL SECTION

Materials. Octadecylsilane-modified silica-based stationary phases were prepared and characterized as previously described;^{5–8} the specifications of these stationary phases, including surface coverage, are listed in Table 1 in the preceding paper in this journal. Perdeuterated solvents used in these experiments (water, methanol, acetonitrile, acetone, tetrahydrofuran (THF), chloroform, benzene, toluene, hexane) were obtained from Cambridge Isotope Laboratories, Inc. and used as received.

Procedures. Samples were prepared by placing between 25 and 100 mg of stationary-phase material into a 5-mm-diameter NMR tube; 200 μL of solvent was then added. Samples were sonicated for 10 min and equilibrated at 293 K for a minimum of 12 h prior to spectral acquisition. Raman spectra were collected and analyzed using the same instrument parameters and conditions described in the preceding paper in this journal.⁵

RESULTS AND DISCUSSION

Raman Spectroscopy of High-Density Alkylsilane Stationary Phases. Raman spectroscopy is a powerful tool for the investigation of alkylsilane stationary-phase structure due to the plethora of spectral indicators of conformational order, especially in the $\nu(\text{C-H})$ region between 2750 and 3050 cm^{-1} . Spectral interrogation of conformational order in this region is achieved in the presence of solvent without significant spectral interference from the silica substrate and surface-bound water. Although the spectral region between approximately 900 and 1500 cm^{-1} in which the $\nu(\text{C-C})$ and $\delta(\text{C-H})$ modes are observed also contains a number of significant conformational order indicators for alkane systems, these high-density stationary-phase materials were prepared on silica particles that possess considerable inherent fluorescence that interferes with acquisition of Raman vibrational information in this region. Therefore, for these systems, conformational order assessment is restricted to the high-quality spectral data that can be obtained in the $\nu(\text{C-H})$ region.

Typical spectra for each of the stationary-phase materials at room temperature in two solvents that are representative of the

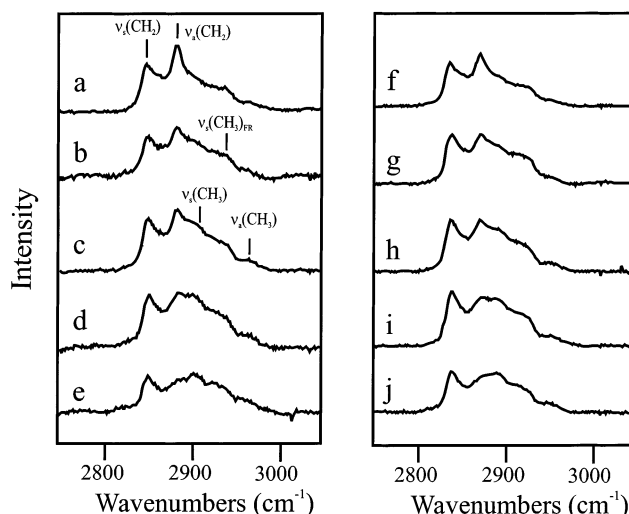


Figure 1. Raman spectra in the $\nu(\text{CH})$ region at 293 K in methanol for (a) TFC18SF, (b) TFC18SL, (c) DFC18SF, (d) DFC18SL, and (e) MFC18 and in CHCl_3 for (f) TFC18SF, (g) TFC18SL, (h) DFC18SF, (i) DFC18SL, and (j) MFC18. Spectral acquisition times for TFC18SF, TFC18SL, DFC18SF, and DFC18SL in both solvents are 2 min. Spectral acquisition times for MFC18 in both solvents are 5 min.

extremes of stationary-phase conformational order, methanol and CHCl_3 , are shown in Figure 1 with the corresponding peak frequencies and vibrational mode assignments provided in Table 1. Spectra for the five stationary phases studied here in all solvents are available in the Supporting Information.

The basis for interpretation of the Raman spectral results for surface-confined alkylsilanes in the $\nu(\text{C-H})$ region using the intensity ratio of the $\nu_a(\text{CH}_2)$ mode to the $\nu_s(\text{CH}_2)$ mode $\{I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]\}$, the $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ peak frequencies, and the intensity ratio of the $\nu_s(\text{CH}_3)_{\text{FR}}$ to the $\nu_s(\text{CH}_2)$ $\{I[\nu_s(\text{CH}_3)_{\text{FR}}]/I[\nu_s(\text{CH}_2)]\}$ is discussed in the preceding paper in this journal.⁵

Effect of Solvent on Conformational Order. To examine solvation effects on conformational order of alkyl moieties relevant to chromatographic separations, each stationary phase was exposed to a range of common chromatographic solvents. The solvents examined include water, methanol, acetonitrile, acetone, THF, CHCl_3 , benzene, toluene, and hexane. These solvents exhibit wide variability in their characteristics including polarity, dipole moment, polarizability, hydrogen bond accepting/donating ability, hydrophobicity, shape, and size that have been quantified according to the solvatochromic parameter, π^* , developed by Kamlet et al.⁵⁰ These parameters are listed in Table 2. This parameter separates solvents by their dipole moment normalized to the solvent polarizability (i.e., a measure of electron mobility within the molecule). It is important to note throughout this discussion the close relationship between π^* and other solvatochromic parameters including hydrogen bond-donating and -accepting ability (α and β , respectively), the Hildebrand solubility parameter (δ_{H}), and the solvent self-association parameter (δ_{SA}).^{50–53}

(50) Kamlet, M. J.; Abboud, J. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877–2887.

(51) Kamlet, M. J.; Carr, P. W.; Taft, R. W.; Abraham, M. H. *J. Am. Chem. Soc.* **1981**, *103*, 6062–6066.

(52) Kamlet, M. J.; Doherty, R.; Taft, R. W.; Abraham, M. H. *J. Am. Chem. Soc.* **1983**, *105*, 6741–6743.

Table 2. Solvatochromic Parameters^a π^* , α , and β for Solvents

solvent	π^*	β	α
water	1.09	0.18	1.17
acetonitrile	0.75	0.31	0.19
acetone	0.71	0.48	0.06
methanol	0.60	0.62	0.93
benzene	0.59	0.10	0
THF	0.58	0.55	0
CHCl ₃	0.58 ^b	0	0.44
hexane	0.54	0	0
toluene	-0.08	0.11	0

^a As described by Kamlet et al.⁵⁰ ^b Actual value of π^* for CHCl₃, but plotted at 0.57 in the figures to discriminate it from THF.

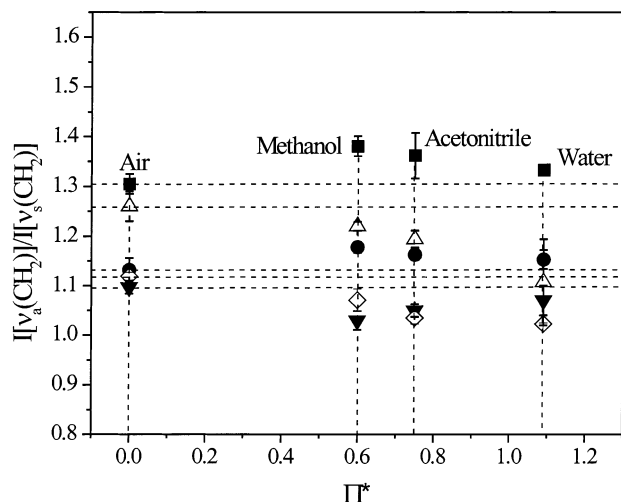


Figure 2. $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ as a function of solvent solvatochromic parameter, π^* , for TFC18SF (■), TFC18SL (△), DFC18SF (●), DFC18SL (◇), and MFC18 (▼) in the polar solvents methanol, acetonitrile, and water at 293 K. The error bars represent one standard deviation.

Figures 2 and 3 show $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ for all five stationary phases as a function of the solvatochromic parameter, π^* , for polar (Figure 2) and nonpolar (Figure 3a and b) solvents at room temperature (293 K). The horizontal dashed lines in each figure are at the values of $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ for each stationary phase in air as a reference.

In the polar solvents methanol, acetonitrile, and water, stationary-phase conformational order is highly dependent on surface coverage, consistent with the observations made for each phase in air.⁵ For all stationary phases except that with the lowest alkylsilane surface coverage (MFC18, 3.09 $\mu\text{mol}/\text{m}^2$), conformational order decreases slightly in polar solvents with increasing π^* . In addition to these solvent trends, it is also important to make note of changes in conformational order in solvents relative to air. For the phases prepared by surface polymerization, TFC18SF (6.45 $\mu\text{mol}/\text{m}^2$) and DFC18SF (5.00 $\mu\text{mol}/\text{m}^2$), the conformational order increases in polar solvents relative to that in air. In contrast, the phases prepared by solution polymerization, TFC18SL (5.26 $\mu\text{mol}/\text{m}^2$) and DFC18SL (4.17 $\mu\text{mol}/\text{m}^2$), are more disordered in polar solvents than in air. The lowest surface coverage material, MFC18, is also more disordered in polar solvents than in air.

These observations are consistent with interaction of the polar solvents with the surface-polymerized materials (TFC18SF and DFC18SF) primarily according to an adsorptive model, as a result of high surface coverage, solvent self-association ability, and more importantly, surface homogeneity (as determined by NMR experiments performed on these materials).^{7,8} In other words, values of this order indicator comparable to those observed in air for polar solvents with surface-polymerized stationary phases suggest that these solvents do not intercalate into these stationary phases to any significant extent. The stationary phase only presents a sorption site for solvent interaction at the distal methyl end of alkyl chains extended away from the surface. This picture of solvation for polar solvents indicates that solvent-alkyl chain interaction is weaker than alkyl chain-alkyl chain interaction in these systems.

Polar solvent interaction with the solution-polymerized materials (TFC18SL and DFC18SL) also appears to be primarily adsorptive; however, conformational order differences relative to the surface-polymerized phases are a consequence of stationary-phase properties. These solution-polymerized materials are lower in surface coverage (comparing the surface-polymerized and solution-polymerized trifunctional systems and the surface-polymerized and solution-polymerized difunctional systems, respectively) but, more importantly, have been proposed to be two-dimensionally heterogeneous with isolated patches of densely populated alkyl chains and regions with reduced alkyl surface coverage.⁷ As a result of this heterogeneity in surface coverage, regions exist in which the average chain spacing is greater and solvent molecules can interact not only with the distal methyl groups but with the underlying terminal methylene groups as well, inducing slightly greater conformational disorder (and hence lower values of $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$).

For MFC18 in polar solvents, although possessing homogeneous alkylsilane coverage, the relatively low surface coverage and steric hindrance between silane-bound methyl groups give rise to large interchain spacings. Small angle neutron scattering experiments on monofunctional stationary phases of comparable surface coverage suggest that the alkyl chains in such systems are bent and disordered on the silica surface, thereby maximizing hydrophobic interactions.^{16,54} In this case, solvent interaction with the stationary phase is primarily partitioning, where the more hydrophobic solvent, methanol, solvates the stationary phase more effectively (i.e., induces more disorder) than the less hydrophobic solvent (water). As a result, the conformational order for MFC18 increases with π^* .

The conformational order of these materials in nonpolar solvents (Figure 3) is also dependent on surface coverage but is generally more disordered than in polar solvents. The trend in conformational order with π^* observed for the polar solvents is absent for these materials in nonpolar solvents. When the conformational order of these materials in nonpolar solvents is compared to those in air, the results are quite different from those in polar solvents. An increase in conformational order relative to air is only observed for the highest surface coverage material, TFC18SF, in hexane, benzene, THF, and acetone. In this case, the high surface coverage dictates that solvent interaction can only occur via adsorptive sites at distal methyl groups of the alkyl

(53) Taft, R. W.; Abboud, J. M.; Kamlet, M. J.; Abraham, M. H. *J. Solution Chem.* **1985**, *14*, 153–175.

(54) Sander, L. C.; Glinka, C. J.; Wise, S. A. *Anal. Chem.* **1990**, *62*, 1099–1101.

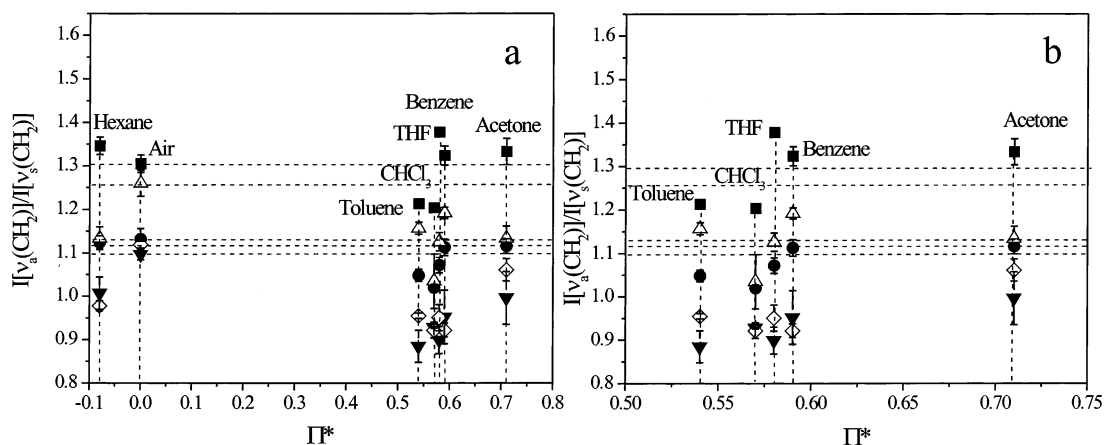


Figure 3. $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ as a function of solvent solvatochromic parameter, π^* , for TFC18SF (■), TFC18SL (△), DFC18SF (●), DFC18SL (◇), and MFC18 (▼) in the nonpolar solvents hexane, toluene, CHCl_3 , THF, benzene, and acetone at 293 K. (a) All solvents and (b) expanded view of region containing data for toluene, CHCl_3 , THF, benzene, and acetone. The error bars represent one standard deviation.

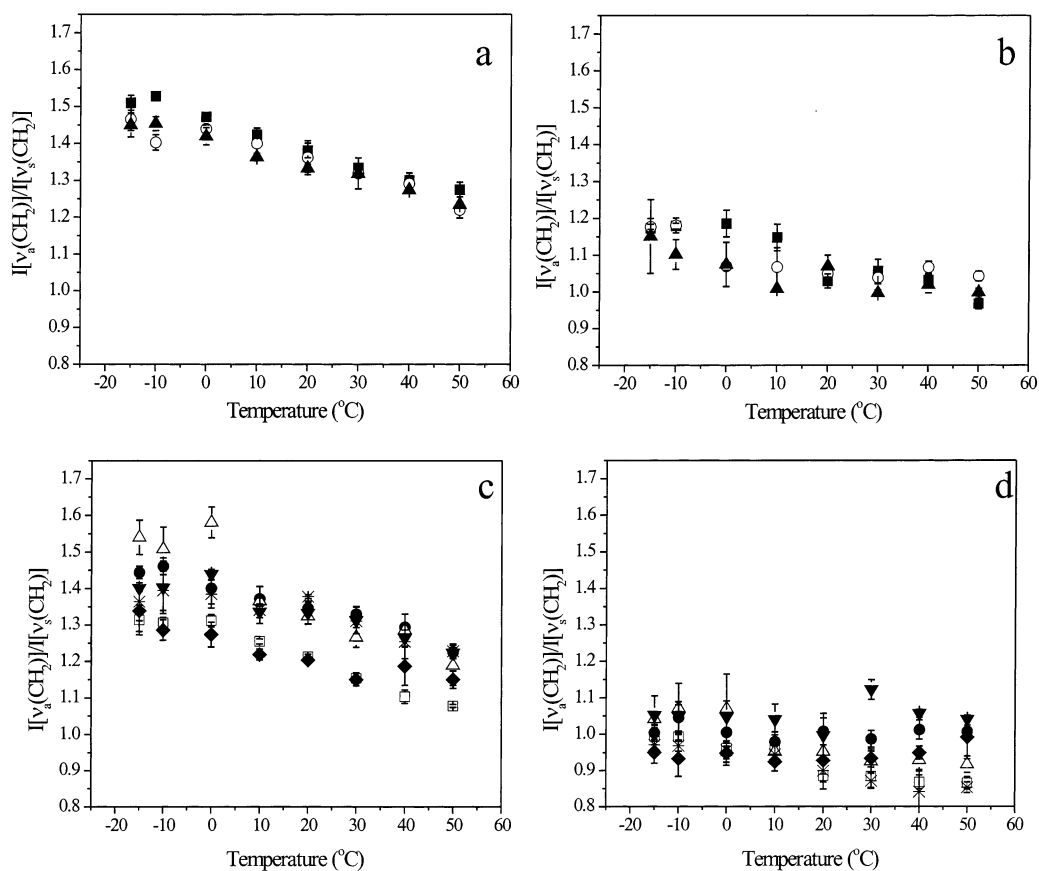


Figure 4. $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ as a function of temperature for TFC18SF [(a) and (c)] and MFC18 [(b) and (d)] in methanol (■), water (▲), acetonitrile (○), toluene (□), benzene (△), hexane (●), CHCl_3 (◆), acetone (▼), and THF (*). The error bars represent one standard deviation.

chains. The other surface-polymerized material, DFC18SF, is disordered in all nonpolar solvents relative to air. According to the adsorption solvation model for polar solvents described above, solvation, and its concomitant impact on conformational order, is primarily a function of surface homogeneity and less dependent on surface coverage. In nonpolar solvents, solvation occurs according to a partitioning model and is more dependent on surface coverage. Nonpolar solvents intercalate and solvate the alkyl chains to a greater extent even on homogeneously covered surfaces, suggesting that solvent–alkyl chain interactions rival alkyl chain–alkyl chain interactions in strength in these systems.

Similar disordering is observed for the solution-polymerized and monofunctional materials, indicating that nonpolar solvent interaction is partitioning in these systems, causing considerable conformational disorder in the alkyl chains.

The complexity of the solvation mechanisms dictated by the molecular interactions between solvents and the alkyl chains is better examined by considering (1) similar conformational behavior of these materials in dissimilar solvents and (2) distinctly different conformational order of the stationary phases in similar solvents. As shown in Figure 3, the stationary phases TFC18SF, DFC18SF, and MFC18 each have statistically the same confor-

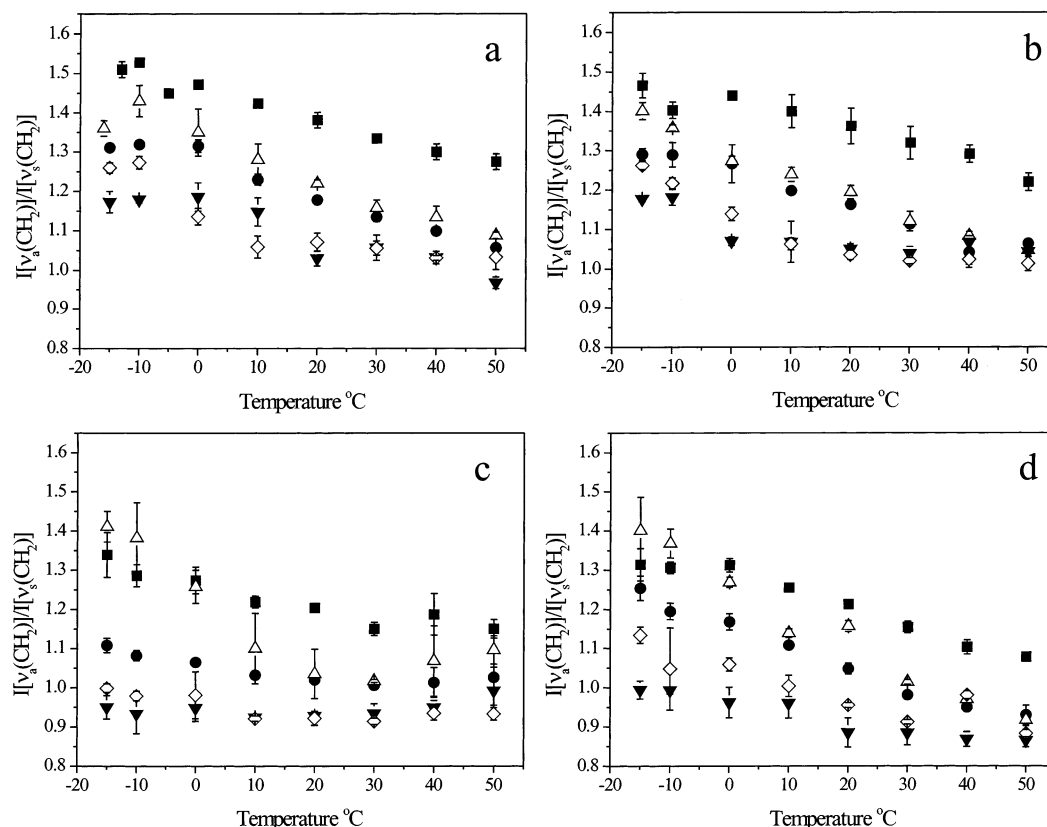


Figure 5. $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ as a function of temperature for TFC18SF (■), TFC18SL (△), DFC18SF (●), DFC18SL (◇), MFC18 (▼) in (a) methanol, (b) acetonitrile, (c) CHCl_3 , and (d) toluene. The error bars represent one standard deviation.

mational order in toluene and CHCl_3 at 293 K despite differences in solvent polarizability, dipole moment, hydrophobicity, dielectric constant, size, and shape. Conversely, the conformational order of the same stationary phases is different in toluene and benzene, two solvents with similar physical properties. The disorder induced by CHCl_3 is the result of its relatively small size and ability to penetrate deep into the alkyl chains, while the planar toluene molecule is envisioned to intercalate between chains and induce disorder primarily due to the steric bulk of the methyl group. The disorder caused by the methyl group of toluene is rationalized to be the difference in conformational order of the stationary phases in toluene and benzene. The subtle differences in molecular interactions between these and other monosubstituted aromatics and these high-density stationary phases will be considered in more detail in forthcoming publications.^{55,56}

Effect of Temperature on Conformation Order in the Presence of Solvent. Examination of the effects of temperature and solvent on the conformational order of these stationary-phase materials extends our understanding of the complex solvation of these systems. Figure 4 shows plots of $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ as a function of temperature for TFC18SF (Figure 4a and c) and MFC18 (Figure 4b and d) in polar (Figure 4a and b) and nonpolar (Figure 4c and d) solvents. For TFC18SF in polar solvents (Figure 4a), temperature-induced disordering of the alkyl chains is observed with a convergence at higher temperatures to a minimum value of conformational order that is independent of solvent. For TFC18SF in nonpolar solvents (Figure 4c) and MFC18

(Figure 4b) in polar solvents, disorder is primarily temperature-induced with the retention of solvated conformational differences over the entire temperature range. The conformational order for MFC18 in nonpolar solvents (Figure 4d) depends more on solvent than temperature. For hexane, acetone, and CHCl_3 , no changes in conformational order with temperature are observed. For benzene, toluene, and THF, only a weak temperature dependence of conformational order is observed, with order decreasing very slightly with increasing temperature. Although difficult to interpret more definitively due to the fact that $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ does not change linearly with order, these results support a subtle interplay between temperature and solvation in disordering of the alkyl chains of these stationary phases. This interplay for different classes of solvents is observed not only for the highest and lowest surface coverage materials examined here but for the stationary phases of intermediate coverage as well. Similar plots of $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ as a function of temperature for DFC18SF, TFC18SL, and DFC18SL are given in the Supporting Information.

These results for the effect of temperature on alkylsilane stationary phases are consistent with observations made by McGuffin and Chen in which changes in molar enthalpy and volume were observed for high and low surface coverage stationary phases in solvent as a function of temperature.⁵⁷ For high-density stationary-phase materials, the molar volume and enthalpy increase with temperature and plateau at some maximum value. In contrast, the molar volume and enthalpy remain unchanged by increasing temperature for low-density materials. McGuffin's

(55) Ducey, M. W.; Orendorff, C. J.; Sander, L. C.; Pemberton, J. E. Submitted.
(56) Orendorff, C. J.; Ducey, M. W.; Sander, L. C.; Pemberton, J. E. Submitted.

(57) McGuffin, V. L.; Chen, S. *J. Chromatogr., A* **1997**, 762, 35–46.

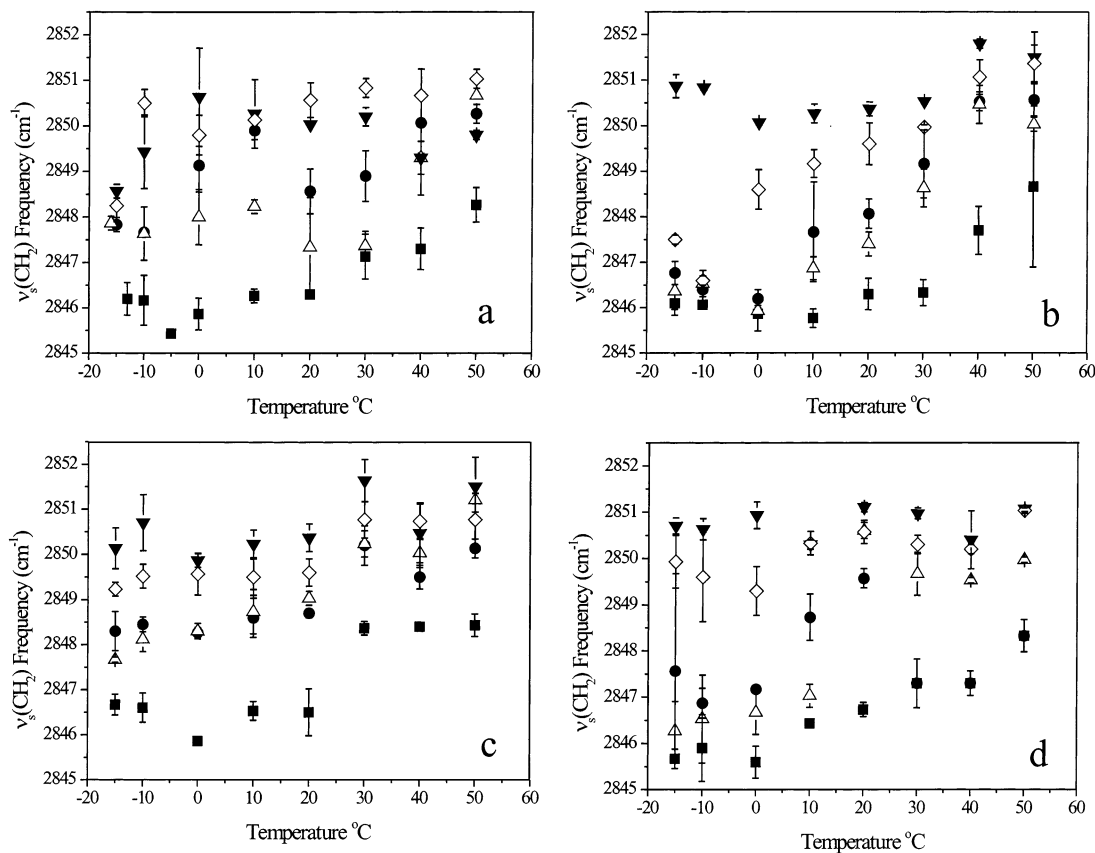


Figure 6. $\nu_s(\text{CH}_2)$ peak frequency as a function of temperature for TFC18SF (■), TFC18SL (△), DFC18SF (●), DFC18SL (◇), and MFC18 (▼) in (a) methanol, (b) acetonitrile, (c) CHCl_3 , and (d) toluene. The error bars represent one standard deviation.

work again illustrates the interplay between temperature- and solvent-induced disorder in chromatographic stationary phases.

Subtle Differences in Temperature Effects between Differently Solvated Stationary Phases. The convolution of temperature and solvent in dictating conformational order in these stationary phases and the distinct differences each of these variables has on the order of a specific stationary-phase material are shown more clearly in the plots in Figure 5. In these plots, $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ is shown as a function of temperature for each of the five stationary phases in four solvents, methanol (Figure 5a), acetonitrile (Figure 5b), CHCl_3 (Figure 5c), and toluene (Figure 5d), chosen to represent the broad range of temperature- and solvent-induced effects on order. For these materials in air, changes in slope of $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ with temperature are observed that are sensitive to the nature of the alkylsilane precursor.⁵ These discontinuities have been interpreted to reflect changes in alkyl phase and have been described by the Clapeyron relationship.⁵

In the presence of solvent, the trend of increasing conformational order with increasing surface coverage is generally maintained. However, the phase changes observed in these materials in air are muted by interactions of the alkyl chains with solvent. In some cases, different, more subtle phase changes are observed that depend on the extent of solvation of the stationary phase and alkylsilane surface coverage. In methanol, all of the tri- and difunctional materials (TFC18SF, TFC18SL, DFC18SF, DFC18SL) have plateau regions of relatively temperature-independent order below 273 K. Above 273 K, the order of these phases decreases monotonically with increasing temperature. The monofunctional

stationary phase exhibits a distinct change in order at ~ 283 K in methanol, with relatively constant values below and above this temperature.

In acetonitrile, plateau regions exist for the surface-polymerized materials (TFC18SF and DFC18SF) below 273 K with a monotonic decrease in order above this temperature. TFC18SL exhibits a monotonic change in order with temperature without any indication of a phase change. However, DFC18SL shows a monotonic decrease in order with temperature but with a phase change (i.e., change in slope) at ~ 273 K. Finally, the monofunctional stationary phase, MFC18, shows two regions of approximately constant order with a change at ~ 273 K.

In CHCl_3 and toluene, all stationary phases are more disordered than in methanol or acetonitrile, as discussed for the nonpolar solvents in general above. In CHCl_3 , the conformational order behavior exploits differences in alkylsilane precursor and surface coverage, rather than polymerization method. The two highest surface coverage materials, both of which are trifunctional, exhibit changes in slope at 303 K, with plateau regions of strictly CHCl_3 -induced disorder at high temperatures. The other three materials display a conformational order that is relatively independent of temperature. In toluene, although TFC18SF shows a low temperature plateau region, all stationary phases generally exhibit a monotonic decrease in this order indicator with temperature.

Although one must interpret these changes carefully in light of the nonlinear dependence of $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ on overall

conformational order,⁵⁸ these results further support the subtle interplay between temperature- and solvent-controlled order in these systems. Furthermore, these results show the broad range of solvent interactions with alkylsilane stationary-phase materials that depend not only on solvent characteristics but on stationary-phase properties as well.

Peak Frequencies of $\nu(\text{C-H})$ Modes as Indicators of Solvent Effects on Conformational Order. In addition to $I[\nu_{\text{a}}(\text{CH}_2)]/I[\nu_{\text{s}}(\text{CH}_2)]$ as an indicator of conformational order, the frequency of either the $\nu_{\text{a}}(\text{CH}_2)$ or $\nu_{\text{s}}(\text{CH}_2)$ can be used to ascertain interchain coupling information for the solvated alkyl chains of these stationary phases. The precision of these measurements is generally not as high as that for the $I[\nu_{\text{a}}(\text{CH}_2)]/I[\nu_{\text{s}}(\text{CH}_2)]$ indicator. Nonetheless, these indicators serve as alternate independent checks of the order of these alkylsilane systems, since they respond to chain coupling and not chain rotational disorder or fraction of C–C bonds in gauche conformations as does the $I[\nu_{\text{a}}(\text{CH}_2)]/I[\nu_{\text{s}}(\text{CH}_2)]$ indicator.

The frequency of the $\nu_{\text{s}}(\text{CH}_2)$ mode is plotted as a function of temperature in Figure 6 for the same four representative solvents, methanol (Figure 6a), acetonitrile (Figure 6b), CHCl_3 (Figure 6c), and toluene (Figure 6d), for all five stationary phases. In all solvents, the $\nu_{\text{s}}(\text{CH}_2)$ frequency is temperature- and surface coverage-dependent, generally increasing (i.e., less chain coupling) with increasing temperature and decreasing coverage, as observed for these materials in air.⁵ However, perhaps not surprisingly, the behavior of this indicator does not exactly track that of the $I[\nu_{\text{a}}(\text{CH}_2)]/I[\nu_{\text{s}}(\text{CH}_2)]$ indicator, since it reflects changes in interchain coupling. Nonetheless, these two indicators of conformational order do change with the same general trends with solvent and temperature. Moreover, the subtle interplay between temperature- and solvent-induced disorder observed in the $I[\nu_{\text{a}}(\text{CH}_2)]/I[\nu_{\text{s}}(\text{CH}_2)]$ indicator behavior is also observed in the $\nu_{\text{s}}(\text{CH}_2)$ peak frequency results. For all stationary phases except the highest surface coverage material, significant chain decoupling occurs for temperatures above 273 K. Indeed, the two lowest surface coverage materials, MFC18 and DFC18SL, are completely decoupled ($\nu_{\text{s}}(\text{CH}_2) \geq 2851 \text{ cm}^{-1}$) or significantly decoupled ($\nu_{\text{s}}(\text{CH}_2) \geq 2850 \text{ cm}^{-1}$), respectively, in all solvents above 273 K. Moreover, the $\nu_{\text{s}}(\text{CH}_2)$ frequency for MFC18 in CHCl_3 and toluene exhibits behavior that is temperature-independent and strictly solvent-dependent. For DFC18SL, the behavior is only slightly temperature-dependent. For TFC18SF, the $\nu_{\text{s}}(\text{CH}_2)$ frequency does exhibit a dependence on temperature, with a similar low-temperature plateau region (i.e., temperature-independent) and a monotonic change at higher temperatures as was observed for the $I[\nu_{\text{a}}(\text{CH}_2)]/I[\nu_{\text{s}}(\text{CH}_2)]$ indicator.

Given that these two indicators reflect different types of alkyl chain disorder, it is interesting to consider how they respond to changes in temperature relative to each other. In general, the temperature dependence of these two indicators for the high-density stationary-phase systems is similar to the behavior observed for the melting of bulk alkanes, where chain coupling (as indicated by the frequency of the $\nu_{\text{s}}(\text{CH}_2)$ mode) requires more thermal energy to change than to induce subtle changes in C–C bond conformation (as indicated by the $I[\nu_{\text{a}}(\text{CH}_2)]/I[\nu_{\text{s}}(\text{CH}_2)]$ indicator).⁵⁸

CONCLUSIONS

A detailed examination of solvent–stationary-phase interactions probed by Raman spectroscopy for a series of high-density octadecylsilane materials is presented. Results indicate that rotational and conformational order information is dependent on solvent parameters, stationary-phase grafting procedure, and surface coverage and can be used to describe specific solvent–stationary-phase interactions. In general, polar solvents increase the rotational order of homogeneously distributed high surface coverage materials, fitting an adsorption model of interaction at the distal methyl group. Nonpolar solvents generally intercalate into the alkyl chains and fit a partitioning model of interaction; heterogeneously distributed and lower coverage materials are more disordered by this partitioning than higher coverage materials. In addition to the solvent–stationary-phase interactions, an interplay between solvent- and temperature-dependent ordering of these materials is observed; more solvent-dependent order is observed for lower coverage materials in nonpolar solvents and more temperature-dependent order is observed for higher coverage materials in polar solvents. The interplay between solvent- and temperature-dependent order for such high-density stationary-phase materials in highly ordering, polar solvents will be addressed in an upcoming report.⁵⁵

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in the text This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(58) Orendorff, C. J.; Ducey, M. W.; Pemberton, J. E. *J. Phys. Chem. A* **2002**, *106*, 6991–6998.