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Raman spectroscopy of octadecylsilane stationary phase conformational order
Effect of solvent

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Abstract

The effect of solvent on the conformation of alkyl chains of two octadecysilane-based stationary phases is probed using Raman spectroscopy. Spectral data indicate that the alkyl chains of commercially available polymeric and monomeric solid-phase extraction stationary phases are disordered to a varying extent by solvents of different polarity. For the polymeric octadecylsilane stationary phase, the polar solvents water, acetonitrile, methanol, acetone and isopropanol have little impact on the conformational order of the octadecylsilane bonded phase relative to air. However, the alkyl portion of this stationary phase is substantially disordered in the low-polarity solvents tetrahydrofuran, chloroform, benzene, toluene and hexane. The monomeric octadecylsilane stationary phase is less susceptible to disordering by solvents, although more disorder in the less polar solvents is also observed for this system. These results are interpreted in terms of the local surface bonding density and interchain spacing of these two stationary phases, and the ability of the solvent to penetrate the chains as a function of polarity. The results clearly demonstrate the ability of Raman spectroscopy to precisely indicate subtle changes in conformational order of alkylsilane stationary phases.

Keywords: Raman spectrometry; Stationary phases, LC; Solvent effects

1. Introduction

Chemically-modified silicas are popular stationary phases for reversed-phase liquid chromatography (RPLC) and solid-phase extraction [1–3]. These stationary phases are typically formed by covalent attachment of alkylchlorosilanes to a silica gel support using mono-, di- or trichlorosilanes [3]. The properties of these stationary phases play an important role in governing the selectivity and efficiency of chromatographic separations [2–5]. In order to elucidate the retention mechanisms for such separations, an understanding of the stationary phase behavior under various separations conditions is essential. A variety of experimental techniques including chromatographic methods [6–14], fluorescence spectroscopy [15–22], nuclear magnetic resonance (NMR) [23–28], IR spectroscopy [29–32], Raman spectroscopy [33–36], and differential scanning calorimetry [37–41] have been used to study these stationary phases. Despite the valuable knowledge and insight provided by these studies, additional information would further the development of a complete molecular understanding of chromato-

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graphic retention. An enhanced understanding of the conformational order and intermolecular interactions of the alkyl moieties of the stationary phase, and the interactions of the solute and the mobile phase constituents with the alkylsilanes in the separation process would be particularly useful towards this end. This information can best be provided by investigating the stationary phase using techniques that are sensitive to alkyl chain conformation.

Raman spectroscopy is a powerful tool for characterization of conformational changes in alkyl chains [34,35,42,43]. In contrast to most previous methods used to study these alkylsilane stationary phases (in which conformational state of the alkane is indirectly inferred from the data), Raman spectroscopy provides a *direct measure of conformational order* in the alkane. Furthermore, these measurements are relatively free from spectral interference from the silica or any adsorbed water which plague Fourier transform (FT)-IR studies of these systems [29].

In previous reports [34,35], we demonstrated the feasibility of using Raman spectroscopy for the elucidation of conformational information about alkysilane modified silica-based chromatographic stationary phases. As part of an ongoing project to elucidate retention mechanisms in liquid chromatography, we present here a Raman spectroscopic investigation of the effect of solvent and temperature on the conformational state of commercially available octadecylsilane stationary phase systems. A monomeric stationary phase formed from dimethyloctadecylchlorosilane, and a polymeric stationary phase formed from octadecyltrichlorosilane have been studied. In the monomeric stationary phase, the dimethyloctadecylsilane can only form one bond with the surface. In contrast, in the trifunctional polymeric system, octadecylsilane can form multiple bonds with the surface or with other octadecylsilane molecules leading to surfaces which are potentially more heterogeneous than the monofunctional systems. In the work reported here, both polymeric and monomeric systems were studied in an attempt to elucidate any disparities in the response of conformational order to solvent and temperature that might be attributable to differences in surface distribution of the alkylsilanes in these systems.

2. Experimental

Raman spectra were collected using 50–100 mW of 514.5 nm or 532.0 nm radiation from either a Coherent Innova 90-5 Ar^+ laser or a Coherent Verdi Nd–vanadate laser on a Spex 1877 Triplemate. Slit settings of the Triplemate were somewhat variable between experimenters and between studies, but typical values included 0.5/2.0/0.2 mm, 0.5/2.0/0.05 mm, and 0.5/7.0/0.05 mm. Laser polarization was parallel to the plane of incidence. The detector in these experiments was a Princeton Instruments charge-coupled device (CCD) system based on a thinned, back-illuminated, anti-reflection coated RTE-1100-PB CCD of pixel format 1100×330 which was cooled with liquid N_2 to −90°C. Samples were sealed in NMR tubes held in a copper sample mount through which a temperature control medium [water between 5 and 95°C and ethylene glycol–water (50:50, v/v) between −15 and 5°C] was circulated using a Neslab NTE-110 temperature controller.

Two commercial solid-phase extraction stationary phases, Isolute C18MF and Isolute C18TF, were a gift from International Sorbent Technologies. C18MF is a monomeric stationary phase and C18TF is a polymeric stationary phase. These materials were used as received. Perdeuterated solvents were obtained from Cambridge Isotope Labs., and used as received.

3. Results and discussion

3.1. Characteristics of Isolute stationary phases

The two stationary phases that are the subject of this investigation are from the Isolute series of solid-phase extraction materials from International Sorbent Technologies. These materials consist of tri- and monofunctional alkylsilanes covalently bonded to a rather unique silica substrate of relatively large particle size (~50–60 μm), relatively high surface area [~300–500 $m^2\ g^{-1}$ as measured by Brunauer–Emmett–Teller (BET) analysis] and small average pore diameter (~60 Å) compared to the silica substrates typically used for the fabrication of alkylsilane stationary phases for reversed-phase liquid chromatography (RPLC) [44]. The polymeric stationary phase studied, C18TF, was formed by the reaction of octadecyltrichlorosilane with silica of particle diameter 62 μm, surface area 561 m^2 g^{-1}, and an average pore diameter of 54 Å. The bonded material has a surface carbon loading of 19.3% and a surface coverage based on the total surface area of 1.6 μmol m^{-2}. The monomeric stationary phase, C18MF, was formed by the reaction of dimethyloctadecylchlorosilane with silica of particle diameter 63 μm, surface area 300 m^2 g^{-1}, and an average pore diameter of 60 Å. The resulting bonded material has a surface carbon loading of 13.9% and a surface coverage of 1.9 μmol m^{-2} based on the total surface area.

Despite the high absolute surface area of these silica substrates as measured by BET analysis, these systems have been previously characterized as having fractal-like porosity with a large fraction of the surface area in very small pores that are inaccessible to alkylsilane surface modifiers [45]. Thus, even though the absolute surface coverage of alkylsilane is relatively low, the *effective surface coverage*, that takes into account the inaccessibility of a significant fraction of the absolute surface area, is expected to be much higher. Although it is obviously difficult to quantify this effective surface coverage in an absolute sense, evidence for chain–chain interactions in both systems comes from the observation of surface phase changes in air in their temperature-dependent Raman spectral responses. This behavior has been described previously for C18TF [35] and is discussed below for C18MF. Thus, the effective surface coverage must be ≥2.5–3 μmol m^{-2} based on statistical arguments to account for such chain–chain interactions [3]. Given the heterogeneity of the silica substrates used for these stationary phase materials, the resulting bonded-phase materials are expected to be equally heterogeneous, probably with patches of alkylsilanes on particularly accessible regions of the surface.

3.2. Raman spectroscopy of alkylsilane stationary phases

Raman spectroscopy is a powerful tool for investigation of alkylsilane stationary phase structure and conformational order due to (i) limited spectral interference from the silica substrate and any silica surface-bound water, (ii) accessibility to the entire frequency region between ~150 and 4000 cm^{-1}, and (iii) the plethora of spectral indicators of alkyl structure and conformational order that can be observed within this frequency region. Spectra for C18TF and C18MF in air at room temperature in the frequency regions between 800 and 1400 cm^{-1} and 2700 and 3100 cm^{-1} are shown in Fig. 1 along with spectra of the liquid and crystalline reactant alkylsilanes, octadecyltrichlorosilane (OTS) and dimethyloctadecylchlorosilane (DOS), prior to silica bonding. Peak frequencies and vibrational mode assignments are given in Table 1.

In the lower frequency region, the major vibrational modes observed for both systems are the stretches of the C–C bonds, designated as ν(C–C) modes, which occur as separate peaks for *trans* and *gauche* C–C bonds, the backbone twisting vibrations involving the C–C and C–H bonds of the methylene groups, designated as $\tau(CH_2)$ modes, and bending and scissoring of the methyl and methylene C–H bonds, designated as $\delta(CH_3)$ and $\delta(CH_2)$ modes, respectively. In addition to these vibrations of the alkyl chain, the dimethyloctadecylsilane and C18MF systems exhibit additional weak modes at 1263 and 1403 cm^{-1} due to bending vibrations of the two methyl groups bonded to the Si atom. These modes are designated as $\delta(CH_3)_{Si}$ modes.

In the frequency region between 2800 and 3100 cm^{-1}, bands due to symmetric and antisymmetric stretching vibrations of the C–H bonds are observed. This region is very complex in the Raman spectra of alkanes [46–52], and can contain 11–14 bands depending on the alkane. The vibrations of the 17 methylene groups dominate this region for both C18TF and C18MF, although weaker bands due to the terminal methyl groups of the alkyl chains are observed for both systems. Additional modes are observed for the two methyl groups bonded to the Si atom in C18MF. The most prominent bands in these spectra have been assigned to the $\nu_s(CH_2)$ at 2852 cm^{-1}, the $\nu_a(CH_2)$ at 2888 cm^{-1}, the $\nu_s(CH_2)_{FR}$ at 2924 cm^{-1}, the $\nu_s(CH_3)_{FR}$ at 2935 cm^{-1}, and the $\nu_a(CH_3)$ at 2962 cm^{-1}. For C18MF, the $\nu_s(CH_3)_{Si}$

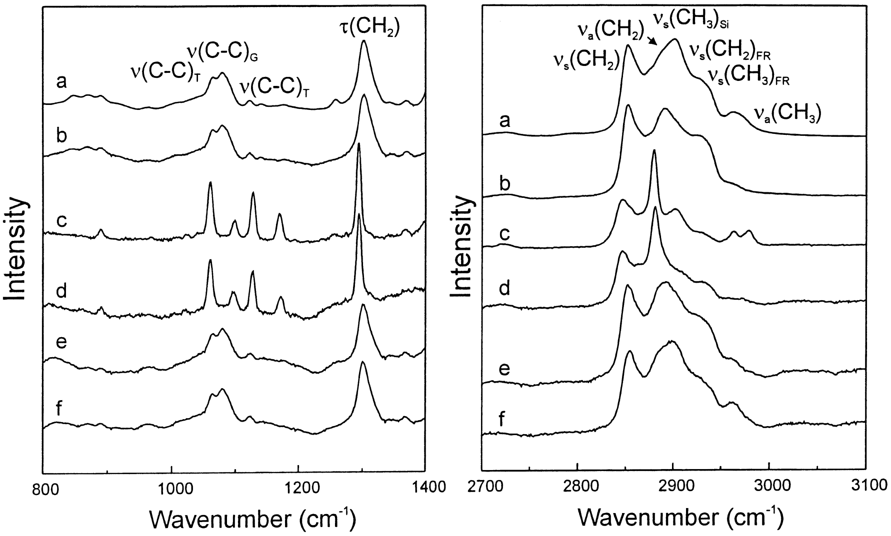

Fig. 1. Raman spectra in the ν(C–C) (left panel) and ν(C–H) (right panel) regions for (a) liquid dimethylocatdecylchlorosilane, (b) liquid octadecyltrichlorosilane, (c) crystalline dimethylocatdecylchlorosilane, (d) crystalline octadecyltrichlorosilane, (e) C18MF at room temperature, (f) C18TF at room temperature.

for the two methyl groups attached to the Si atom is superimposed on the $\nu_s(CH_2)_{FR}$ and exhibits a peak frequency of 2905 cm^{-1}.

Useful spectral indicators of alkyl chain conformational order can be ascertained by comparison of the spectra in Fig. 1 for liquid OTS and DOS with those of the corresponding crystalline solids obtained by freezing these liquids in liquid nitrogen. In the low frequency region, the $\nu(C–C)_G$ is totally absent in the spectra of crystalline OTS and DOS, leaving only

Table 1
Raman peak frequencies and assignments for OTS, DOS, C18TF and C18MF

OTS liquid	OTS crystalline	C18TF	DOS liquid	DOS crystalline	C18MF	Assignment[a]
1065[b]	1062	1065	1065	1062	1065	$\nu(C–C)_T$
1080		1081	1080		1078	$\nu(C–C)_G$
	1100			1100		$\tau(CH_2)$
1124	1128	1125	1124	1128	1124	$\nu(C–C)_T$
			1263	1261	1263	$\delta(CH_3)_{Si}$
1303	1293	1303	1303	1293	1301	$\tau(CH_2)$
1370	1371	1369	1362	1369	1369	$\delta(CH_3)$
			1403	1401	1403	$\delta(CH_3)_{Si}$
1440	1441	1441	1441	1441	1440	$\delta(CH_2)$
1450	1463	1454	1448	1462	1454	$\delta(CH_2)/\delta(CH_3)$
2852	2849	2852	2852	2849	2854	$\nu_s(CH_2)$
2890	2881	2888	2886	2881	2887	$\nu_a(CH_2)$
			2905	2905	2903	$\nu(CH_3)_{Si}$
2925	2925	2924	2923	2923	2925	$\nu_s(CH_2)_{FR}$
2935	2935	2933	2935	2935	2935	$\nu_s(CH_3)_{FR}$
2965	2962	2962	2965	2962	2962	$\nu_a(CH_3)$

[a] ν=Stretch; τ=twist; δ=bend and/or scissor.

[b] Peak frequencies in units of cm^{-1}.

the $\nu(C{-}C)_T$ modes. In addition, the $\tau(CH_2)$ narrows considerably, becomes more symmetric, and shifts by ~10 cm^{-1} to lower frequencies for crystalline OTS and DOS compared to the corresponding liquids. In the $\nu(CH)$ region, the intensity ratio of the $\nu_a(CH_2)$ at ~2890 cm^{-1} to the $\nu_s(CH_2)$ at ~2850 cm^{-1} clearly increases in going from the liquid to the crystalline state. Indeed, this intensity ratio has been used extensively in elucidating conformational order in alkyl chain systems in previous work [34,35,42,43,51,53,54]. As was shown previously [33–35], this ratio is an excellent indicator of conformational order in alkylsilane stationary phase materials, particularly polymeric materials. As will be shown below, this ratio can also be used as a conformational state indicator for monomeric stationary phases, but because of the spectral interference from the $\nu(CH_3)_{Si}$ at 2905 cm^{-1}, the absolute values do not vary over the same range as the polymeric systems; therefore, they cannot be directly compared to the corresponding values of normal alkyl systems such as the polymeric stationary phase materials that do not suffer this spectral interference.

One additional indicator of conformational order in the $\nu(CH)$ region is the peak frequency of the $\nu_s(CH_2)$ mode. The frequency of this mode decreases from 2856 cm^{-1} in the pure liquid state of alkanes to 2849 cm^{-1} in the crystalline state.

3.3. Conformational order of stationary phases

As an example of the utility of these spectral indicators for understanding conformational order in stationary phase materials, the temperature dependence of three spectral indicators is shown in Fig. 2 for C18TF and C18MF in air. Fig. 2a shows the peak frequency of the $\nu_s(CH_2)$, Fig. 2b shows the intensity ratio of the $\nu(C{-}C)_T$ to the $\nu(C{-}C)_G$, and Fig. 2c shows the peak frequency of the $\tau(CH_2)$. For both C18TF and C18MF, these parameters vary systematically with temperature in the directions indicated in the discussion above.

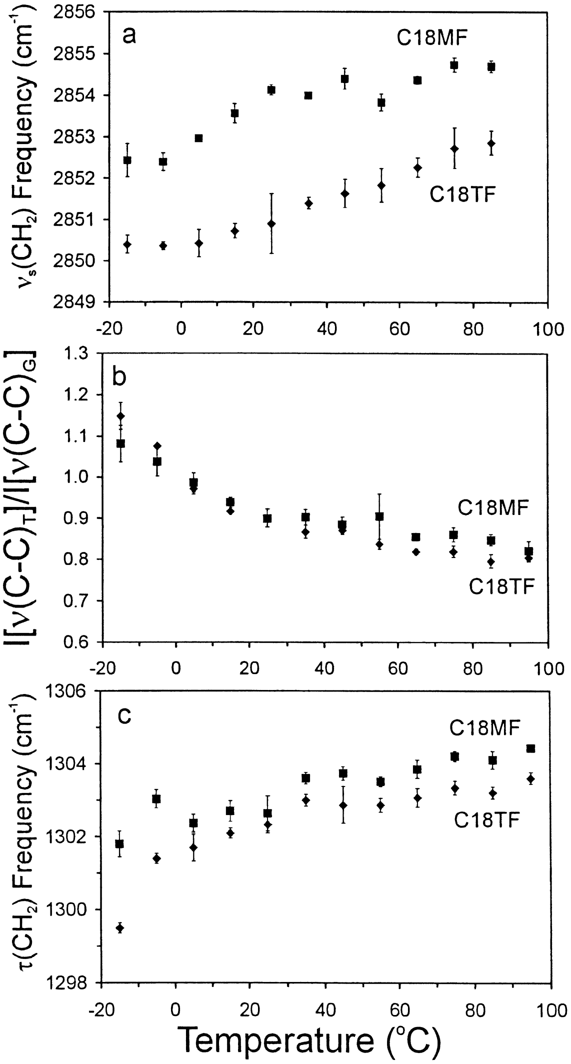

Fig. 2. Plots of (a) peak frequency of the $\nu_s(CH_2)$ mode, (b) intensity ratio of $\nu(C{-}C)_T$ to $\nu(C{-}C)_G$, and (c) peak frequency of $\tau(CH_2)$ as a function of temperature for C18TF and C18MF.

The peak frequency of the $\nu_s(CH_2)$ (Fig. 2a) increases with temperature for both C18TF and C18MF. The absolute values for these stationary phases suggests that the C18TF is slightly more ordered than the C18MF as expected based on the greater chain–chain spacing in C18MF imposed by the presence of the two Si-bound methyl groups. For both systems, the peak frequency appears to level off at the lowest temperatures and then increase in a monotonic fashion at temperatures above 0°C. The peak frequency of the $\tau(CH_2)$ (Fig. 2c) similarly shows two regions of slightly different slope in the temperature dependence of both systems.

The intensity ratio of the $\nu(C{-}C)_T$ to the $\nu(C{-}C)_G$ (Fig. 2b) is a particularly clear and direct indicator of conformational order, since the presence of any *gauche* C–C bonds is manifest in the form of intensity in the ν(C–C)$_G$ band. For C18TF and C18MF, the absolute values of this ratio are similar at all temperatures in air. Of perhaps greater significance is the observation of two distinct regions of different slope in these plots similar to the distinct regions noted in the other two indicators. As has been proposed previously, changes in slope of these parameters suggest phase changes in the alkyl chains of these stationary phase materials [35]. For both C18TF and C18MF, these data indicate a surface phase change in the vicinity of 20°C. Although the presence of this phase change in C18TF was reported earlier [35], it is noted here to re-establish the utility of Raman spectroscopy as a precise indicator of conformational order in these silica-bonded alkylsilane systems.

3.4. Effect of solvent on conformational order in C18TF and C18MF

To assess the effect of stationary phase solvation on conformational order of the alkyl chains in these systems, C18TF and C18MF were exposed to a range of organic solvents. Raman spectra were acquired from the stationary phases after overnight immersion. The presence of intense spectral bands from the solvents presents an additional difficulty in data interpretation relative to studies in air. In order to minimize this spectral interference, the intensity ratio of the ν_a(CH$_2$) at ~2890 cm^{-1} to the ν_s(CH$_2$) at ~2850 cm^{-1} was identified as the conformational order indicator of choice using perdeuterated solvents. Although this indicator for C18MF suffers from the spectral interference from the Si-bound methyl groups as noted above, the ν(CH) spectral window is completely devoid of solvent contributions making it most desirable even in the presence of this other spectral interference. This spectral interference precludes direct comparison of the absolute values of this indicator for C18TF and C18MF. Nonetheless, solvent effects on this ratio can be independently assessed to understand the effects of solvent on conformational order in each system.

The solvents studied include water, methanol, acetonitrile, acetone, isopropanol, tetrahydrofuran, hexane, benzene, toluene and chloroform. These solvents exhibit a wide range of solvent characteristics including polarity, dipole moment, hydrogen bonding, shape and size which have been quantified in terms of their solvatochromic parameters by Kamlet et al. [55]. Fig. 3 shows selected Raman

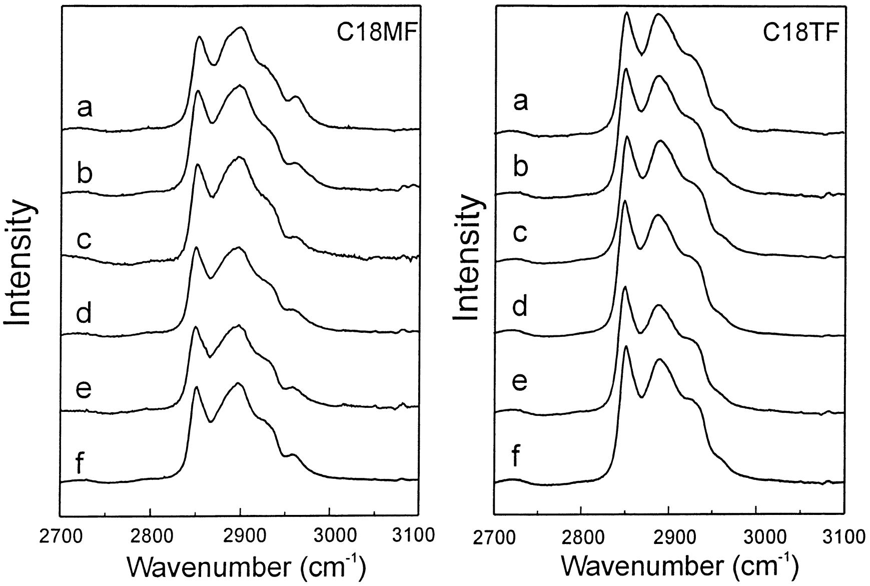

Fig. 3. Selected Raman spectra in ν(C–H) region for C18MF (left panel) and C18TF (right panel) (a) in air and in presence of perdeuterated (b) acetonitrile, (c) methanol, (d) tetrahydrofuran, (e) chloroform, and (f) hexane.

spectra in the ν(C–H) region between 2700 and 3100 cm^{-1} for C18TF and C18MF upon exposure to the deuterated solvents. Clearly the effects of solvent on these spectra are relatively minimal. However, when conformational order indicators are quantified from data such as these, the precision of these measurements allows subtle differences to emerge.

Fig. 4 shows plots of the intensity ratio of the $\nu_a(CH_2)$ at ~2890 cm^{-1} to the $\nu_s(CH_2)$ at ~2850 cm^{-1} as a function of solvent dielectric constant for both systems. Clearly, statistically significant differences in this ratio are observed for both C18TF and C18MF that indicate the effect of solvent on the conformational order in these systems.

In interpreting these differences, the rational starting point for comparison is the conformational order of the stationary phase material in air at room temperature. As indicated by the spectra in Fig. 1, both C18TF and C18MF possess a considerable number of *gauche* C–C conformers as indicated by the relatively intense $\nu(C–C)_G$ at 1080 cm^{-1}. Thus, these systems in air are relatively disordered and liquid-like. For both stationary phases, water very slightly disorders the alkyl chains relative to air. This picture is partly consistent with models previously proposed that polar solvents cause alkyl chain disorder [56–59]. However, in contrast with these previous models which suggest that the stationary phase is completely collapsed from a more ordered state into a liquid-like state in the presence of these solvents, the magnitude of the change in the spectral ratio indicates only a slight perturbation on conformational order relative to air. This discrepancy suggests that the alkyl chains in these Isolutes have insufficient space to completely collapse, a picture which is consistent with the concept noted above that the *effective surface coverage* is considerably greater than the absolute surface coverage of 1.5–2 μmol m^{-2} due to the large fraction of the surface which is inaccessible to alkylsilanes due to the unusual pore structure inherent in these silica substrates [34].

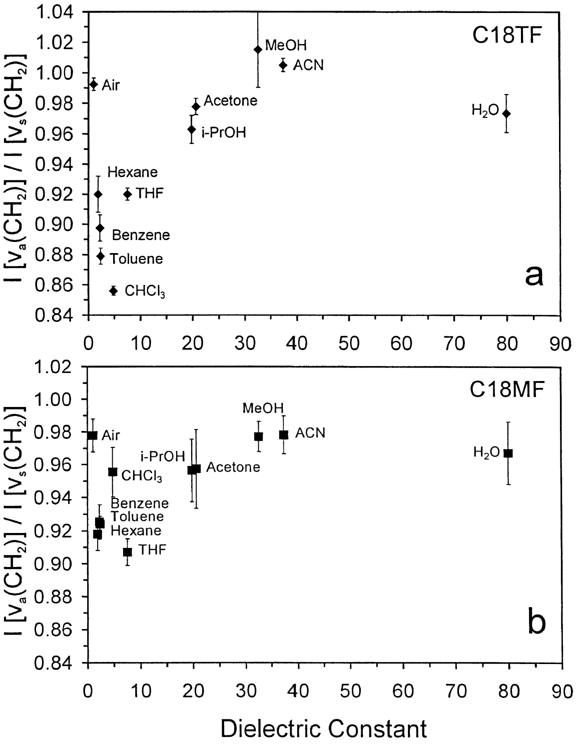

Fig. 4. Plots of intensity ratio of $\nu_s(CH_2)$ to $\nu_a(CH_2)$ as a function of solvent dielectric constant for (a) C18TF and (b) C18MF.

The other polar solvents methanol, acetonitrile, acetone and isopropanol also have a minimal effect on conformational order for both C18TF and C18MF relative to air. In fact, methanol and acetonitrile appear to slightly increase the conformational order of the alkyl chains for C18TF. The marginal impact of these solvents on stationary phase conformational order is significant, because polar mobile phase organic modifiers are known to have a substantial impact on chromatographic behavior for many systems even when present in small amounts. For example, Cole and Dorsey observed a substantial reduction in column reequilibration time following gradient elution RPLC by using a constant volume of 3% 1-propanol in the mobile phase throughout the gradient [60]. This effect was attributed to the role of 1-propanol in providing consistent solvation of the stationary phase alkyl chains. Pronounced effects of small amounts of polar organic modifiers on alkyl chain mobility have also been observed in NMR studies of alkyl stationary phases [25,26,61–71] and fluorescence-based lateral diffusion studies of fluorescent probes partitioned into alkyl stationary phases [72,73]; these effects have usually been attributed to solvation of the alkyl chain by the organic modifier such that the alkyl chains transform from a collapsed state on the silica surface in an aqueous environment to one in which the chains are extended into and mobile within the mobile phase. In contrast to such substantial changes in alkyl chain conformation and order, the Raman spectral results presented here indicate little difference in overall conformational order in water versus these polar organic solvents. This apparent discrepancy can only be explained in a few ways: either the overall conformational order is similar between a collapsed state and a partially solvated extended state of the alkyl chains or the previous results have been misinterpreted in terms of too large an effect or one of the extreme states assumed in previous models (collapsed or extended) is incorrect. The Raman spectral results available to date do not yet allow discrimination between these explanations. Moreover, it must be remembered that the spectral results reported here are for the neat solvents, which may be only partially appropriate as models for polar organic solvent modifiers in binary and ternary aqueous mobile phases. Nonetheless, the lack of significant changes in stationary phase structure indicated in the Raman data may suggest the importance of solute–mobile phase interactions introduced by these polar mobile phase organic modifiers in addition to solute–stationary phase interactions in chromatographic retention. A more complete picture of the effect of polar mobile phase modifiers on stationary phase structure must await further studies in binary and ternary solvent systems. Such studies are currently underway in this laboratory and will be reported at a later date.

The behavior of these stationary phases in the presence of nonpolar solvents is different from that observed in polar solvents. For C18TF, the nonpolar solvents tetrahydrofuran, benzene, toluene, hexane, and chloroform cause a significant decrease in the magnitude of this intensity ratio to values of ~0.9 or lower. These values are essentially identical to those observed for neat liquid octadecyltrichlorosilane at room temperature. Thus, in the presence of these solvents, the stationary phase alkyl chains are provided with considerably enhanced mobility due to solvation. This conclusion supports a picture in which the nonpolar solvents penetrate the octadecyl chains to a greater depth than the more polar solvents, thereby inducing more conformational disorder. These conclusions are similar to those made on the basis of NMR measurements of enhanced alkyl chain mobility [61] in similar nonpolar solvents such as benzene [62,63], chloroform [25,62], carbon tetrachloride, dimethylsulfoxide, tetrachloroethylene [62], dioxane [64], hexane [65], cyclohexane [74,75] and tetrahydrofuran [76].

The picture that emerges from the collective Raman spectral results also implies that, despite the existence of chain–chain interactions in this system as established by the observation of a surface phase change, the alkyl chains exist in an environment in which the additional volume of the nonpolar solvent can be accommodated upon chain solvation. A uniform layer of alkyl chains on the silica surface would not provide the needed chain flexibility or additional volume consistent with this behavior. Therefore, these results imply a considerable degree of surface heterogeneity in the bonding of the alkylsilanes on the silica, perhaps through the formation of islands or patches of bonded alkylsilane.

The results for C18MF are somewhat more difficult to interpret due to spectral interference from the Si-bound methyl groups. Despite this, a similar response of increasing conformational disorder in the alkyl chains in the presence of nonpolar solvents is suggested by the data in Fig. 4 for C18MF as well. The absolute magnitudes of this intensity ratio do not decrease as much as in C18TF, but this is believed to be more a function of the spectral interference than it is a difference in alkyl chain behavior. The absolute magnitudes of this parameter must be interpreted with caution, and the tendency to compare the absolute values with those from C18TF must be avoided. Nonetheless, the decrease in this ratio in the presence of nonpolar solvents supports a similar picture of alkyl chain solvation by chain penetration and corresponding increase in stationary phase volume noted above for C18TF.

3.5. Combined temperature and solvent effects

Initial studies to elucidate the combined effects of solvation and temperature on conformational order of the alkyl chains in these systems were also undertaken. Fig. 5 shows plots of the intensity ratio of the $\nu_a(CH_2)$ to the $\nu_s(CH_2)$ as a function of temperature for C18TF in water, acetonitrile and tetrahydrofuran. For all three solvents, this ratio decreases with increasing temperature indicating an increase in conformational disorder as expected. A difference in the degree of conformational order exhibited at the

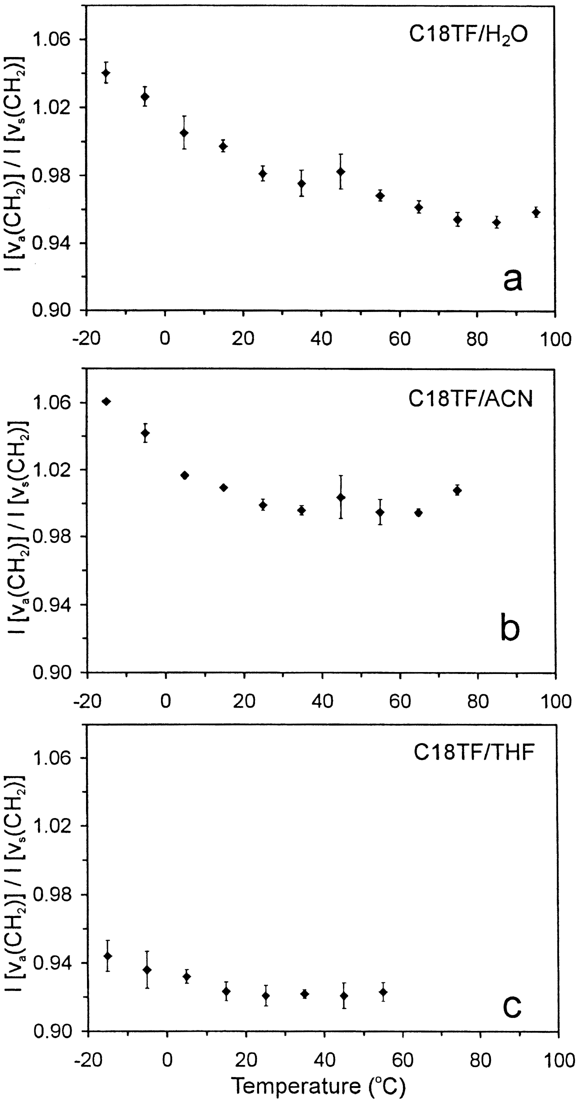

Fig. 5. Plots of intensity ratio of $\nu_s(CH_2)$ to $\nu_a(CH_2)$ as a function of temperature for C18TF in (a) water, (b) acetonitrile, and (c) tetrahydrofuran.

lowest temperatures probed between the polar solvents, water and acetonitrile, and the nonpolar solvent, tetrahydrofuran, is indicated by the absolute magnitude of this ratio. The stationary phase achieves much greater conformational order in the polar solvents than in the nonpolar solvent at lower temperatures. In addition, the *change* in conformational order induced by lowering the temperature in the polar solvents is considerably greater than in the nonpolar solvent as indicated by the difference in magnitudes at high and low temperatures. Both observations are consistent with the picture proposed above that nonpolar solvents penetrate the alkyl chains to a greater depth than the polar solvents.

In summary, the results presented here demonstrate the ability of Raman spectroscopy to precisely elucidate relatively subtle differences in alkyl chain conformational order of alkylsilane stationary phases in response to temperature and solvent perturbations. For polymeric and monomeric octadecylsilane solid-phase extraction stationary phases, evidence for a surface phase change which supports chain–chain interaction is observed in the Raman spectral behavior as a function of temperature. In contrast to the behavior of bulk alkylsilanes, the phase change of the surface-confined alkylsilanes occurs over a much broader temperature range due to the substantially greater heterogeneity of the environments of these molecules on the silica surface.

Evidence for differences in solvation of these stationary phase materials in solvents of varying polarity has also been observed. These stationary phases exhibit greater conformational disorder in more nonpolar solvent environments regardless of temperature. These differences have been interpreted as indicative of greater penetration of the stationary phase chains by nonpolar solvents than by polar solvents. Studies of these effects on stationary phases of varying alkylsilane surface coverage are underway and will be reported at a later date.

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