Revisionist look at solvophobic driving forces in reversed-phase liquid chromatography
IV. Partitioning vs. adsorption mechanism on various types of polymeric bonded phases

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Abstract

The partition and adsorption mechanisms of retention in reversed-phase liquid chromatography have been examined based on a comparison of the free energy of transfer of methylene groups from aqueous–organic mixtures to bulk hexadecane with those to a variety of polymeric bonded phases. The stationary phases studied include: conventional silica-based polymeric phases of various alkyl chain lengths, a so-called "horizontally polymerized" octadecyl phase on silica and a series of polybutadiene-coated zirconia phases. The data indicate that for methylene groups a partition-like mechanism is dominant on all phases. On the polybutadiene-coated zirconia and "horizontally polymerized" octadecyl phases the partition mechanism holds at all mobile phase compositions. In contrast on conventional polymeric silica phases the retention mechanism seems to become more adsorption-like at methanol compositions greater than about 70% (v/v).

Keywords: Free energy of transfer; Retention mechanisms; Thermodynamic parameters; Solvophobic driving forces; Stationary phases, LC

1. Introduction

Despite the great popularity of reversed-phase liquid chromatography (RPLC), our understanding of the retention mechanism in this type of chromatography is still incomplete. One of the major and long standing issues in the theory of bonded phase RPLC is whether solute molecules are retained by a partition-like or by an adsorption-like process. Indeed

many different models of both partition and adsorption type mechanisms have been proposed [1–9].

Recently, we [10] showed for a methylene group that most of the free energy of retention in RPLC arises from the net attractive (exoergic) processes (interaction and cavity formation) of the methylene group in the stationary phase, and not from the net repulsive (endoergic) processes (interaction and cavity formation) of the methylene group in the mobile phase. This conclusion is based on using gas as a reference phase in which intermolecular interactions are taken to zero. However, we have also shown that

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variations in retention and selectivity of nonpolar moieties upon changing the eluent are dominated by alterations in the net mobile phase processes [10]. Most significantly we have shown that the free energy of transfer of a methylene group from the mobile phase to a bonded reversed-phase, over a rather wide range in the mobile phase composition, is almost equal to the free energy of transfer of a methylene group from the mobile phase to bulk hexadecane [10]. This observation strongly supports partition type models of the mechanism of RPLC. That is, it suggests that the methylene group is fully embedded in the layer of bonded phase and is not merely positioned on top of the bonded phase. A subsequent study [11] has shown for monomeric alkyl bonded phases that as the stationary phase chain length is decreased to less than about eight carbon units the transfer free energy of a methylene group into a bonded phase becomes increasingly different from that in a pure bulk partition process. However, even when a very short silane (trimethyl-silyl chloride) is used to make the bonded phase where the partition mechanism can not be at all accurate, the free energies of transfer per methylene group in bonded phase RPLC and in a true bulk phase system differ by only a factor of two [11].

The present work extends the previous study of monomeric phases [11] to various types of very different polymeric-type phases including a series of polymeric alkyl silica-based phases with different chain lengths, a so-called "horizontally polymerized" (self-assembled) octadecyl silica phase [12] and a polybutadiene-coated zirconia material [13]. Polymeric type phases possess quite different chromatographic and physicochemical properties from monomeric type phases. It is known that discrimination of planar from non-planar polyaromatic hydrocarbons is better obtained on polymeric alkyl bonded silica phases than on monomeric phases [14,15]. This is attributed to the idea that the alkyl groups on polymeric phases provide some locales having alkyl chains so close to each other that they become locally more ordered than are monomeric type phases. In essence the polymer phases are said to provide "slots" for selective retention of planar molecules [14–17]. An NMR study reported a reduced mobility of alkyl chains in such sites of a polymeric alkyl bonded phase [18]. Better hydrolytic stability of polymeric phases indicates that a smaller number of siloxane bonds between silica surface and alkyl silyl groups and residual surface silanol groups are exposed to the mobile phase for polymeric phases compared to monomeric phases. Horizontally polymerized C_{18} phases have much higher densities of alkyl chains on the silica surface boundary than do the conventional "vertically polymerized" phases and shows better hydrolytic stability than do monomeric phases. However, the polycyclic aromatic hydrocarbon selectivity of a horizontally polymerized phase more closely resembles that of a monomeric phase than that of a vertically polymerized material [19]. Polybutadiene (PBD)-coated zirconia is a true polymer like phase [13]. These polymeric phases may show different retention behavior for a methylene group from that shown by monomeric phases.

A simple calculation shows that on a typical silica gel based RPLC medium (300 m^2/g, 50% internal porosity) something on the order of 20% of all mobile phase eluent molecules that are inside the pores are in direct contact (monolayer) with the surface. If we assume that the surface layer extends for two or three monolayers then one must conclude that retention in bonded phase, narrow pore RPLC is a surface process and by implication an adsorption process. However, this still begs the more fundamental question which we feel is posed by Dill and Dorsey's definitions of partition and adsorption processes for bonded phases by Dill's mean-field lattice model of RPLC [1,20]. According to this concept, "partitioning" of a solute takes place when the solute is fully embedded within the stationary phase, i.e., when almost all of the solute's surface is in contact with the bonded alkyl chains that constitute the interphase. On the other hand, a pure "adsorption" model requires the solute to adsorb onto the nonpolar film established by the nonpolar alkyl chains, i.e., it only makes surface contact with the interphase and is not fully embedded within it.

According to Dill's simplified model [20] when a solute adsorbs not all of its contacts with mobile phase are disrupted in the adsorbed state. Unfortunately due to the fact that the mobile phase composition in the interphase region is different from the bulk mobile phase, as based on many measurements of the surface excess [21–23], it is impossible

to make any predictions about the free energy of adsorption in terms of lattice coordination numbers as Dill does in his approach [20].

It is important to point out that the retention mechanism does not have to be either completely "partition" or "adsorption"; it can be both. To further complicate the issue some types of solutes, particularly those with a very polar functional group, especially ones able to accept or donate a hydrogen bond with a mobile phase component, could well show adsorption-like behavior under the same conditions that a less polar solute shows partition-like behavior [24].

In this work, the free energy of transfer of a methylene group from the eluent into the bonded phase, will be compared to that in a bulk partitioning system, i.e., from the same eluent into bulk hexadecane. Here, bulk hexadecane is used to model the alkyl bonded phase in RPLC. Previous studies have shown that hexadecane is a good model of the bonded phase for nonpolar solutes [10,11]. The approach and results presented here are restricted to nonpolar solutes, and specifically to methylene groups. All comparisons will be based on measurable quantities for each type of system, that is, the capacity factors in RPLC and partition coefficients in bulk phase partitioning system.

The chromatographic capacity factor, k', is the ratio of the number of moles of solute associated with the stationary phase to that associated with the mobile phase. The capacity factor can also be expressed as the product of $K_{\text{stat/mob}}$, the corresponding ratio of solute concentrations in the stationary and mobile phase and Φ, the column "phase ratio". Provided that a single retention process is extant it is easy to show that

$$-RT \ln k' = n_c \cdot \Delta G°(-CH_2)_{\text{stat/mob}}$$
$$+ \Delta G°(\text{functional} + \text{methyl})_{\text{stat/mob}}$$
$$- RT \ln \Phi \qquad (1)$$

where n_c is the number of methylene groups, R is the gas constant and T is the absolute temperature. Thus, the slope obtained from a plot of $-RT \ln k'$ vs. n_c for a homologous series denotes the standard Gibbs free energy of transfer for a methylene group, $\Delta G°(-CH_2)_{\text{stat/mob}}$, from the mobile phase to the stationary phase. The phase ratio term, Φ, that is so

difficult to determine experimentally is not needed to evaluate $\Delta G°(-CH_2)_{\text{stat/mob}}$. Similarly, the partition coefficient between hexadecane and the mobile phase, $K_{C16/\text{mob}}$, can be related to the free energies of transfer:

$$-RT \ln K_{C16/\text{mob}} = \Delta G°_{C16/\text{mob}}$$
$$= n_c \cdot \Delta G°(-CH_2)_{C16/\text{mob}}$$
$$+ \Delta G°(\text{functional}$$
$$+ \text{methyl})_{C16/\text{mob}} \qquad (2)$$

where $\Delta G°_{C16/\text{mob}}$, $\Delta G°(-CH_2)_{C16/\text{mob}}$ and $\Delta G°(\text{functional} + \text{methyl})_{C16/\text{mob}}$ denote the standard free energy of transfer from the mobile phase to bulk hexadecane for a solute, for a methylene group and for the functional and terminal methyl groups, respectively.

In the light of the lattice model proposed by Dorsey and Dill [1,20], we use the ratio of $\Delta G°(-CH_2)_{C16/\text{mob}}$ to $\Delta G°(-CH_2)_{\text{stat/mob}}$, defined here as F, to indicate how similar retention in RPLC is to bulk partitioning:

$$F \equiv \Delta G°(-CH_2)_{C16/\text{mob}} / \Delta G°(-CH_2)_{\text{stat/mob}} \qquad (3)$$

To understand what follows we must point out that in previous studies we experimentally showed that in all mobile phase compositions the free energy of transfer of a methylene group from gas phase to mobile phase was a considerably smaller contributor to the mobile to stationary phase transfer free energy than was the gas to stationary phase transfer free energy [10]. This is an important consideration for if the mobile phase were to totally dominate the overall process then F would have to be very close to unity regardless of which type of process (adsorption or partition) were taking place in the stationary phase.

2. Experimental

The standard Gibbs free energies of transfer for a methylene group in RPLC, $\Delta G°(-CH_2)_{\text{stat/mob}}$, were calculated from the capacity factors of a homolog series of alkylbenzenes on a variety of monomeric and polymeric phases all based on the same silica support particle. These data were taken from the work of Czok, Jungheim and Engelhardt [25–27].

The Gibbs standard free energies of transfer of a methylene group in a hexadecane-organic–aqueous partitioning system, $\Delta G^{\circ}(-CH_2)_{C16/mob}$, were from the work of Li [28]. These free energy values were also based on the use of alkylbenzene homologs. At the lower methanol concentrations, the mutual solubility between the organic aqueous phase and hexadecane are insignificant [29]. Thus, $K_{C16/mob}$ values for 0–50% methanol aqueous mixtures were acquired through the direct measurement of the solute concentrations in bulk hexadecane and organic–aqueous phases by headspace gas chromatographic (HSGC) measurements [28]. On the other hand, the $K_{C16/mob}$ values for the 60–100% methanol aqueous mixtures are calculated values (see Eq. (4)) based on the measurement of K_{mob} (the partition coefficient between an aqueous–organic mixture and the gas phase), and K_{C16} (the partition coefficient between hexadecane and the gas phase).

$$K_{C16/mob} = K_{mob}/K_{C16} \qquad (4)$$

Both the RPLC and bulk phase partitioning measurements were made at 25°C.

A horizontally polymerized C_{18} silica phase was prepared by the method of Wirth and Fatumbi [12]. This material has a very high total density of bonded chains (nearly 8 μmol/m^2), however, two thirds of the bonded phase groups are short propyl chains and the remainder are octadecyl chains. A PBD-coated zirconia was prepared by the method described in the literature [13]. Liquid chromatographic measurements of the retention volumes of a series of *n*-alkylbenzenes were done on these two columns at 25.00±0.05°C in methanol–water and acetonitrile–water mobile phases of various compositions. At least triplicate measurements of the capacity factors were made. The void volumes of the systems were determined as the peak produced by ^2H_2O. All measurements were made with a Hewlett-Packard 1090 liquid chromatograph. A UV detector set at a wavelength of 254 nm was used. Retention times were taken at the peak maximum reported by a Hewlett-Packard 9153 data system. Samples were prepared in the mobile phase under study. Typically the column was flushed with 50 column volumes of mobile phase per each percentage change in composition from pure modifier to the analytical com-

position. HPLC-grade water, methanol and acetonitrile (Fisher Scientific) were used throughout this work. All solutes used were obtained commercially and were analytical grade in the highest purity available.

3. Results and discussion

3.1. Effect of mobile phase on polymeric alkyl bonded silica phases

Fig. 1 shows plots of **F** vs. mobile phase methanol concentration for five conventional polymeric bonded phases of different bonded phase chain lengths. For ease of discussion, each figure is divided into two regions: (I) 0–70% (v/v) and (II) 70–100% (v/v) methanol.

In region I, the free energy ratios are close to unity, gradually decreasing from 1.6 to 1.1 as the bonded phase chain length increases from 1 to 16. Clearly, the ratios are nearly independent of mobile phase composition. At most there is a slight upward trend with volume fraction of methanol. According to the Dill lattice model, a free energy ratio close to unity indicates that a partition-like mechanism is dominant. Therefore, in the mobile phase composi-
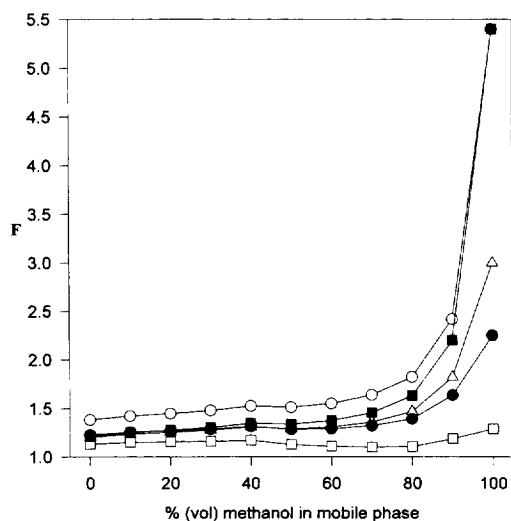

Fig. 1. Plots of **F** vs. composition of methanol–water mobile phase for polymeric alkyl bonded phases: RP-1 (○), RP-3 (■), RP-5 (△), RP-8 (●) and RP-18 (□).
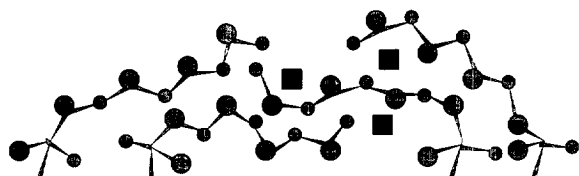
Fig. 2. The bonded chains assume a folded configuration in highly aqueous mobile phase. The solute molecules are shown as small cubes.

tion range from 0 to 70% methanol, a methylene group shows a partition-like retention mechanism on all the bonded phases regardless of chain length. As shown in Fig. 2, in the 0–70% methanol range, the bonded chains are expected to be in a rather more folded configuration due to the favorable dispersive (London) interactions among the chains, and the unfavorable interactions of the chains with the "hostile" mobile phase. Thus "hydrophobic clustering" of the bonded phase chains provides a liquid-like environment in which solute methylene groups are retained via a partition-type mechanism.

We now turn to region II (>70% methanol) in Fig. 1. Here we see a distinct upward trend in the F ratio. Given the absence of such a trend with either the horizontally polymerized or the PBD-coated zirconia phases are examined (see Figs. 3 and 4) we
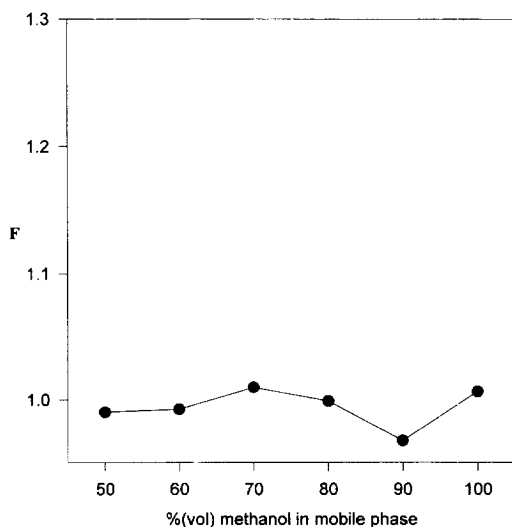

Fig. 3. Plot of F vs. composition of methanol–water mobile phase for the horizontally polymerized C_{18} silica phase. Note the vertical axis is greatly expanded relative to that in Fig. 1.
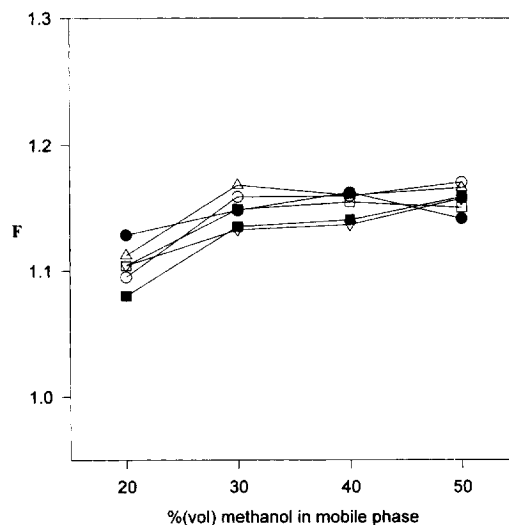

Fig. 4. Plots of F vs. composition of methanol–water mobile phase for polybutadiene-coated zirconia phases with various carbon loading: 0.38% (○), 0.75% (●), 1.53% (△), 2.68% (▽), 3.91% (□), 5.59% (■). Note the vertical axis is greatly expanded relative to that in Fig. 1.

believe that the trend is real and not due to an error in the measurement of dead volume. It is very tempting to attribute this increase in F to a gradual shift from full embedding to partial embedding. However, other factors may be at work.

To understand the effect of mobile phase composition on the F ratio it is necessary to appreciate the fact that the solubilities of methanol and water in bulk hexadecane are extremely low [29,30]. Previous work in this laboratory has demonstrated that when methanol and water are equilibrated with bulk hexadecane they have very little effect on the gas-to-hexadecane partition coefficients of alkylbenzenes [29,31]. Thus to a good approximation we attribute variations in F with mobile phase composition to the effect of the mobile phase on solute interactions in the bonded phase only.

At low volume fractions of methanol in the mobile phase not much methanol is sorbed into the bonded phase consequently F is close to unity. As the volume fraction of methanol in the mobile phase is increased the amount sorbed into the bonded phase increases [32–34] whereas very little partitions into bulk hexadecane. We believe that this will cause F to increase at least to some extent because sorption of

methanol into the bonded phase should decrease $\Delta G°(-CH_2)_{stat/mob}$. We hypothesize that sorption of a polar species into the bonded phase will decrease $\Delta G°(-CH_2)_{stat/mob}$ because measured gas-to-bulk phase free energies of transfer of methylene groups systematically decrease as the bulk phase is varied from octanol to methanol [35]. Furthermore the gas-to-octanol and gas-to-hexadecane free energies of transfer of a methylene group are nearly equal. In addition sorption of mobile phase components induces the *trans* conformation of the bonded chains and causes them to become more extended [36]. As a result, the bonded chains may no longer provide an environment such that a methylene moiety may be totally surrounded by the bonded chains (see Fig. 5). If such is the case then perhaps only a fraction of the solute surface is in contact with the bonded chains and concomitantly **F** would increase. Thus we believe that methanol sorption into the bonded phase, but not into the bulk phase, contributes to the rise in the **F** ratio in region II (high volume fraction methanol). To sum up the increase in **F** in region II may reflect either a greater contribution to retention by the adsorption mechanism, or be a result of sorption of eluent into the bonded phase or both.

Recent molecular dynamics simulations of the bonded phase RPLC by Klatte and Beck [37] show that at the composition studied [about 50:50 (v/v) methanol–water] the methanol and water sorbed by the bonded phase do not penetrate very far into the interphase region. Rather they are in contact with only the outermost several methylene and terminal methyl segments of the bonded phase chain. Further, their theoretical calculations show that a solute methane molecule finds a condition of minimal local free energy somewhat deeper into the bonded phase
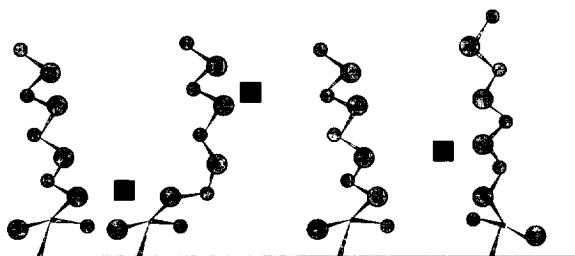
chain than where methanol concentrates. Nonetheless they find that a substantial fraction of methane's nearest neighbor contacts, which approximates 10%, are with sorbed water and methanol even in a slightly water rich eluent. At higher volume fractions of methanol one expects more methanol to be sorbed, as has been shown experimentally [32–34] and that it will therefore be better able to solvate any solute in the bonded chain. We believe that our finding of an increase in **F** at greater than 70% methanol is consistent with these simulations.

3.2. Effect of bonded phase chain length on polymeric alkyl bonded silica phases

We now examine the retention of a methylene group as a function of bonded phase chain length. This is most clearly demonstrated in Fig. 6 which is a plot of the **F** ratio at 50% methanol vs. the bonded phase chain length. These data (curve a) were taken from Fig. 1. Essentially the same plot results at all other mobile phase compositions in region I (<70% methanol). We have also plotted our results obtained with monomeric type phases for comparison [11]. At any given mobile phase composition, the free energy ratio decreases towards unity for both monomer and

Fig. 5. The bonded chains assume an extended configuration in highly organic mobile phase.
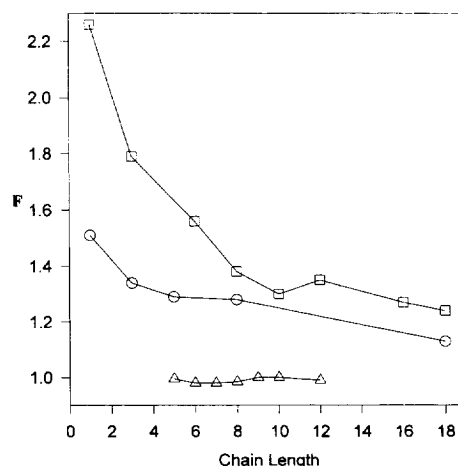

Fig. 6. Plots of **F** vs. bonded and bulk phase chain length: curve a (○), polymeric bonded phases; curve b (□), monomeric bonded phases; curve c (△), bulk alkane phases (in curve c **F** is the ratio for free energy of a transfer of a methylene group from the gas phase to bulk hexadecane relative to the same free energy into an *n*-alkane of the indicated number of carbons).

polymer phases as the bonded phase chain length is increased. Note that the **F** ratio for the polymer phase is closer to unity at any bonded phase chain length than is that of the corresponding monomer phase (see Fig. 6). This means that polymer phases act more like bulk hexadecane than do monomer phases and that longer bonded phases act more like bulk phases than do shorter bonded phases. Also shown in Fig. 6 (curve c) is the free energy of transfer of a methylene group from the gas phase to an n-alkane solvent $(\Delta G°(-CH_2)_{gas/Cn})$ relative to the free energy of transfer into n-hexadecane $[\Delta G°(-CH_2)_{gas/C16}]$. It is evident that there is essentially no variation in the bulk phase data with the solvent chain length. Thus the variations in **F** seen with bonded phases are not due to use of a reference bulk fluid (hexadecane) which has a different carbon number than the bonded phase. We conclude that both the variation in **F** with bonded phase chain length and the fact that **F** is not unity result from methylene-bonded phase interactions and not methylene-bulk phase interactions.

From 0 to 70% methanol, the **F** values for an RP-1 phase vary from 1.4 to 1.7 (see Fig. 1). The **F** values for bonded phases with a chain length of three or longer are virtually the same, that is they vary from 1.1 to 1.4. Based on Dill's model we postulate that the retention mechanism of a methylene group becomes slightly more adsorption-like as the bonded phase chain length decreases. This is in accord with chemical intuition. For an RP-1 bonded phase, there is only a thin layer of alkyl chain on the silica base. A methylene moiety cannot be fully embedded in such a medium (see Fig. 7) especially one constructed from a monomeric silane. The bonded chains are not long enough to contact the entire solute surface, nor can they provide a liquid-like environment for a partition mechanism. As the bonded phase chain length is increased, more solute surface can interact with the bonded phase molecules and the free energy ratio drops. The results agree

with reports that methylene selectivity increases as a function of bonded phase chain length [38–41]. If adsorption were the sole retention governing mechanism, the methylene selectivity for all bonded phases regardless of chain length should not be affected by the bonded phase chain length.

Figs. 8 and 9 compare the **F** curves for the polymeric and monomeric RP-1 and RP-3 phases, respectively. For short chain bonded phases, these figures clearly show that the free energy ratios of the polymeric phase are lower than those of the monomeric phase over the range of 0–70% methanol. This indicates that the retention mechanism of a methylene group is more partition-like on a polymeric phase than on its monomeric counterpart of the same chain length. Although a polymeric phase is generally not more that 50% richer in the amount of bonded carbon [15] than is its monomeric counterpart, the interphase layer is thicker and more disordered and liquid-like due to cross-linking of the bonded chains. As a result, a greater fraction of the solute surface interacts with the bonded chain moieties and retention becomes more "partition-like". Figs. 10 and 11 show models of monomeric and polymeric RP-3 bonded phases, respectively. A solute molecule can only have partial surface contact with the monomeric-bonded propyl chains, however, it can be
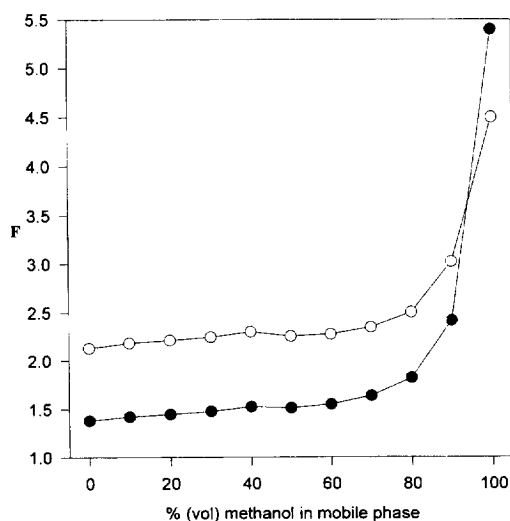
Fig. 7. Bonded phase with short alkyl chains (RP-1).

Fig. 8. Plots of **F** vs. composition of methanol–water mobile phase for monomeric (○) and polymeric (●) RP-1 bonded phases.
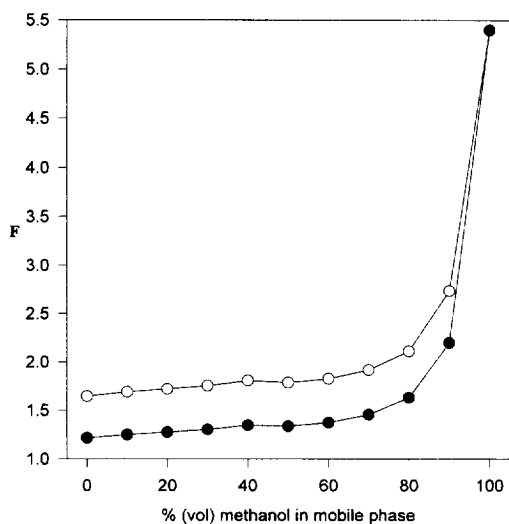
Fig. 9. Plots of **F** vs. composition of methanol–water mobile phase for monomeric (○) and polymeric (●) RP-3 bonded phases.
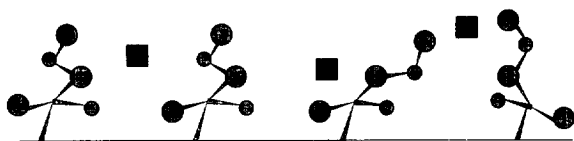

Fig. 10. Monomeric RP-3 bonded phase.

almost totally embedded in a thicker polymeric RP-3 phase.

Nonetheless, as the bonded chain length approaches RP-8, the **F** curves for both monomeric and polymeric phases become virtually the same (see Fig. 6) and closer to unity. The results suggest a partition-like retention mechanism for methylene groups on both types of phases with chain length eight or longer. The bonded octyl chains in a monomeric phase are already long enough to interact with almost all of the solute surface. Thus, any thickening of the
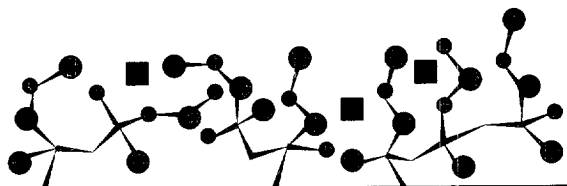
bonded phase as a result of chain cross-linking does not have any additional effect on the degree of solute embedding.

3.3. Polybutadiene-coated zirconia phases

Figs. 4 and 12 show plots of **F** vs. mobile phase composition for six polybutadiene-coated zirconia phases with different carbon loadings. Note how close the **F** ratio is to unity and the use of a greatly expanded scale to present the data. The free energy ratios are very close to unity in both methanol–water (Fig. 4) and acetonitrile–water (Fig. 12) mobile phases. This indicates that the retention mechanism of a methylene group is very partition-like on these true polymer-like phases [13,19]. The crosslinked polybutadiene layer and its interphase layer are thicker and more disordered and liquid-like due to both inherent entanglement of polymer chains and cross-linking than are its monomeric counterparts. As a result, a greater fraction of the solute surface can interact with the polybutadiene chain moieties and retention becomes more "partition-like".

The free energy ratios for the PDB phases are somewhat higher in acetonitrile–water than in methanol–water eluents. Acetonitrile is likely able to
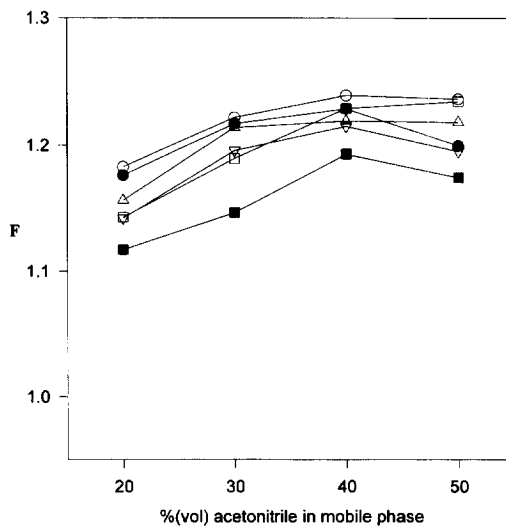

Fig. 11. Polymeric RP-3 bonded phase.

Fig. 12. Plots of **F** vs. composition of acetonitrile–water mobile phase for polybutadiene-coated zirconia with various carbon loading and horizontally polymerized C_{18} silica phases. For symbols for carbon loading, see Fig. 4.

sorb more into the polybutadiene and thus swell it better than does methanol. As discussed above, interaction of the probe solutes with the sorbed acetonitrile acts to decrease the $\Delta G°(-CH_2)_{stat/mob}$ values, which will in turn result in larger F value than that in methanol–water.

3.4. Horizontally polymerized C_{18} silica phase

Horizontally polymerized alkyl bonded silica phases are different from conventional polymeric phases in several respects [12]. Horizontally polymerized phases possess a higher overall density of alkyl chains and better hydrolytic stability due to the paucity of accessible silanol groups than do conventional polymeric phases (see Fig. 13). The chromatographic behavior of the horizontally polymerized phases was found to be similar to the end-capped monomeric phase. Fig. 3 shows a plot of F vs. mobile phase composition for a horizontally polymerized C_{18} silica phase. The free energy ratios are amazingly close to unity even in the 50–100% (v/v) methanol in water mobile phases. This indicates that the retention mechanism of a methylene group is truly partition-like on this type of phase.

With some fear of overinterpreting and overemphasizing the results of our study of the horizontally polymerized material we wish to make two additional comments. First, the fact that F does not increase in the 70–100% methanol range (compare Fig. 3 to Fig. 1) indicates that the upswing seen in Figs. 1,8 and 9 is due to sorption of mobile phase. We say this because identical solutes and mobile phases were used thus it can not be a mobile phase effect. It very

likely rules out an error due to mismeasurement of the dead volume. Second, the F values in Fig. 3 are closer to unity than are the data obtained on other types of conventionally bonded phases. In fact F is statistically indistinguishable from unity for this material. This calls into question the whole issue of how ordered bonded phases are relative to bulk phases [4,20,36,42].

4. Conclusions

The above thermodynamic analysis shows that a methylene group is retained via a partition-like mechanism on conventional polymeric bonded phases regardless of chain length. An adsorption-like mechanism operates appreciably only in mobile phases of very high organic modifier concentrations. For short chain bonded phases, the retention mechanism is relatively more partitioning-like on a polymeric phase than on its monomeric counterpart of the same chain length. A partition-like mechanism is predominant on polybutadiene-coated zirconia phases. The retention mechanism of a methylene group is truly partition-like on the horizontally polymerized C_{18} silica phase.
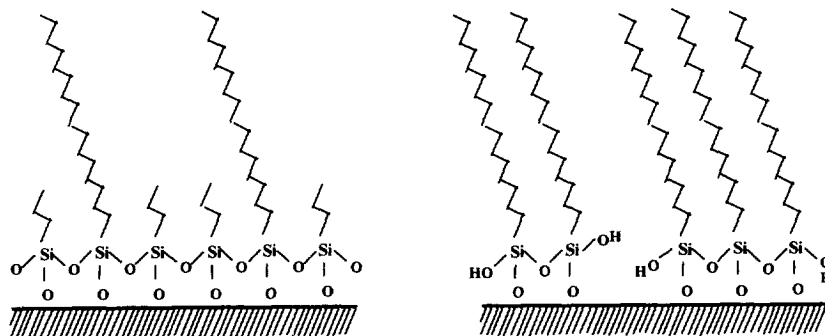
Fig. 13. Horizontally-polymerized (left) and conventional polymeric C_{18} silica phases.

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