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Solvatochromic studies of solvation effects in reversed-phase liquid chromatography with addition of 1-propanol

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Abstract

The work presented here illustrates solvation effects in reversed-phase liquid chromatography in the presence of 1-propanol. A small amount of 1-propanol changes the solvatochromic parameters of the stationary phase significantly, but does not affect those of the mobile phase. Based on solvatochromic experimental results in methanol- and acetonitrile-aqueous systems, it is concluded that 1-propanol has a significant wetting effect on C₁₈ bonded silica stationary phases with mobile phase compositions in the medium to high water content range. Such a wetting effect is believed to affect the stationary phase composition, the organization of the C₁₈ chains on the surface of silica support, as well as the retention mechanism for solutes. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In reversed-phase liquid chromatography (RPLC), the environment of a solute in both the stationary and mobile phases can greatly affect the retention process. In order to obtain a direct picture of the properties of liquid chromatographic (LC) phases, several spectroscopic methods for characterization of the stationary and mobile phases in RPLC systems have been reported in the literature. Infrared [1] and Raman [2] spectroscopies have revealed information about the conformations of the bonded chains at the surface of the stationary phase. NMR spectroscopy can deter-

mine the phase structures, anisotropies, and motions of both the chain and mobile phase components [3–5]. ESR spectroscopy can probe molecular rotational motion and the polarity of the environment surrounding a solute [6–11]. Fluorescence techniques can also be used to sense the polarity of stationary phases [11–20]. However, most of these probes are sensitive to the overall solvent polarity. By using linear solvation energy relationships (LSERs), the retention of different solutes in RPLC have been correlated with their individual properties [21–30], such as molecular size, dipolarity, and hydrogen-bonding abilities. These results showed that the retention of solutes has different sensitivities to the above parameters as the system conditions, such as stationary or mobile phases, change.

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There are two main retention mechanisms that are thought to play a role in RPLC: adsorption and partitioning. In an adsorption mechanism, the solute molecules stay on the surface of the stationary phase, i.e., outside the “bulk” stationary phase. With a partitioning mechanism, the solute molecules penetrate to the inside of the “bulk” stationary phase. In liquid chromatography with bonded chain stationary phases, both mechanisms may be involved, and this strongly depends on the condition of the stationary phase. It is generally agreed that a bonded phase has two basic organizations [13–16,20,31–34]. One is termed the extended chain arrangement, where the bonded chains on the silica surface are extended away from the surface. Another is called the collapsed chain arrangement, in which the bonded chains on the surface are aggregated together and folded over onto the surface of the silica support. Under reversed-phase conditions, organic aqueous mixtures are most commonly used as mobile phases. In phases with a low water composition, the bonded chains generally have an extended arrangement. The major retention mechanism is through partitioning. But with mobile phases of high water ratios, the bonded chains collapse. In such cases, adsorption may become the major mechanism for retention.

At very low organic modifier compositions, consistent wetting, i.e., solvation of the bonded C_{18} chains, is an important issue. Mobile phases with high water contents do not wet alkyl bonded stationary phases very well [35].

It has been reported in the literature that short chain alcohols, such as 1-propanol or 1-butanol, have good wetting ability at low concentrations. Dorsey et al. [36] compared chromatograms obtained with 0–10% methanol mobile phases and concluded that addition of 3% 1-propanol to the mobile phase provides an excellent improvement in column efficiency and peak asymmetry for separation of phenol, acetophenone, nitrobenzene, benzene and toluene. Scott and Simpson [37] demonstrated that, in RPLC, more than 95% of the surface is covered with alcohol when ~7% (w/v) 1-propanol or 1-butanol is present in the water mobile phase, but only 86% and 67% of the surface is covered at same concentration of ethanol and methanol, respectively. With 3% alcohol in water, more than 90% of the surface is covered by 1-propanol, but only ~50% of the surface is covered by methanol. The

distribution coefficient, K , is increased from methanol to 1-butanol as the carbon chain length increases. Cole and Dorsey [38] found that addition of 3% 1-propanol in methanol- and acetonitrile-aqueous mixture mobile phases can significantly reduce the re-equilibration time following gradient elution from 0% to 100% organic modifier.

The solvatochromic method, which was developed by Kamlet and Taft originally for testing homogeneous solvent systems [49,40–42], is used in this study. A UV–Vis spectrum of a solvatochromic dye can be used to determine solvent polarity. By using different dyes and various mathematical treatments, this method can divide the total polarity of the solvent into contributions from dipolarity, hydrogen-bond donating ability, and hydrogen-bond accepting ability. Three parameters are used in this method: the π^* -scale measuring the dipolarity/polarizability [39,40], the α -scale to measure the hydrogen-bond donating ability [41], and the β -scale for measuring the hydrogen-bond accepting ability [42] of the environment surrounding a solute. This method has been used frequently to characterize mobile phases used in RPLC by using different π^* [43] and α dyes [43–45], and to characterize the stationary phases, for both normal phase [46,47] and reversed-phase [48–51]. The results revealed some important information about chromatographic retention mechanisms.

In a previous paper [51], solvatochromic studies on the RPLC phases with Spherisorb ODS2 and some of the most commonly used mobile phases, such as methanol-, acetonitrile- and tetrahydrofuran-aqueous mixtures, were reported for a broad range of compositions. It was found that the solvation of the stationary phase is strongly affected by the properties of the mobile phase, as has been suggested by other reports in the literature [52]. In order to explore this solvation effect further, in the work discussed here, a small amount of wetting reagent, i.e. 1-propanol, is added to RPLC systems. Three solvatochromic probes, a π^* dye – *N*-methyl-2-nitroaniline (NM2NA), an α dye – 4,6-dichloro-2-[2-(1-methyl-4-pyridinio)vinyl] phenolate (DCMPVP) [53], and a β dye – 2-nitroaniline (2NA) are used in this work with the same stationary phase material as was used previously [52]. Values of solvatochromic parameters obtained in this work will be compared with those from previous work [52]. Important information about the bonded octadecyl silica

stationary phase under reversed-phase conditions in the presence of a 1-propanol modifier has been obtained as a result of this study.

2. Experimental

2.1. Materials

The dyes 2NA and NM2NA were supplied by Lancaster. DCMPVP was synthesized as described in an earlier paper [53]. HPLC grade solvents including methanol, acetonitrile, and 1-propanol were obtained from EM and Fisher Scientific, and were used directly without further purification. Spherisorb ODS2 stationary phase material was obtained from Alltech. This octadecyl bonded silica material is endcapped with methyl groups and has 12% final carbon content and a surface coverage of $2.72 \mu\text{mol}/\text{m}^2$ [54]. A quartz cell with a 1.00 mm path length was used and was manufactured by Starna Cells.

2.2. Sample preparation

A series of 3% 1-propanol samples were prepared by the following procedure. The calculated volume of 1-propanol, methanol or acetonitrile, and water, each with the same concentration of dye, were mixed to form the needed solutions. The dye concentrations were 2×10^{-4} M for all NM2NA and 2NA solutions, and for the DCMPVP in acetonitrile-aqueous solutions and 1×10^{-4} M for the DCMPVP methanol-aqueous solutions. ODS2 slurries were made by mixing 150 mg of stationary phase material with the appropriate volume of 1-propanol, and then adding the required amount of organic solvent (methanol or acetonitrile) and water, respectively, with the same concentration of dye in all solvents, such that the total volume of liquid added was 6.00 ml. The concentrations of NM2NA and 2NA were same as for the solution samples. Concentrations for DCMPVP were 1×10^{-4} M. The 1% and 6% 1-propanol samples were prepared using a different procedure. First, the calculated volume of 1-propanol was mixed with the organic solvent (methanol or acetonitrile) and water. The dye concentration in each of these solutions was 2×10^{-4} M. Then the solution phase mixtures were made by mixing the appropriate volumes of these two

solutions. The ODS2 slurries were made by mixing the stationary phase material first with the organic solvent containing 1-propanol, then adding the required ratio of water, also containing 1-propanol. The slurry samples were allowed to equilibrate for a couple of hours after gently stirring, then the settled particles of the stationary phase were collected and transferred to a 1 mm quartz cell for UV–Vis spectral data collection.

2.3. Procedure

A Shimadzu UV-265 spectrophotometer with an integrating sphere attachment was used for obtaining absorption spectra. The reflectance mode with a 5 nm slit width was used. A BaSO_4 sample was used as a reflectance standard. Data were transferred to an IBM compatible computer via an IEEE-488 interface. All spectra from this study were analyzed using the background subtraction, curve smoothing and peak finding routines, as described in the previous work [52], using programs written with Turbo Pascal software (Borland) on a PC 486 or Pentium computer. The peak position was determined at the zero crossing point of the linear regression line, based on the first derivative of the smoothed curve in the region of the peak. The precision of data is the same as in the previous work (± 0.02 for π^* , ± 0.05 for α , and ± 0.1 for β). Retention data were obtained with a Hewlett-Packard model 1050 HPLC instrument with an autosampler and a vacuum degassing device. A 75 mm \times 4.6 mm column packed with Spherisorb ODS2 was purchased from Metachem. Each series of retention data collection always started at 100% and progressed to lower organic solvent compositions. Void volumes were determined by measuring the retention of uracil.

3. Results and discussion

The UV–Vis absorption spectra of three probe dyes, NM2NA, DCMPVP and 2NA, are employed to monitor the phase environments of solutes in RPLC systems. As mentioned in the previous paper [52], the spectra of the ODS2 slurries consist of contributions from the dye in or on the stationary phase particles and from the dye in the mobile phase remaining in the slurry. An attempt to eliminate the solvent spectral contribution to the slurry spectrum by using an

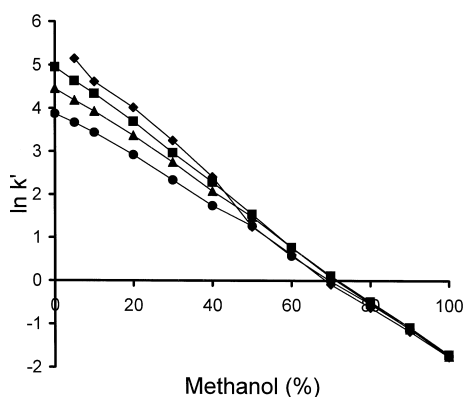


Fig. 1. Plot of $\ln k'$ for NM2NA vs. % water in the mobile phase, with varying amounts of 1-propanol added to the mobile phase: (◆) no propanol; (■) 1% propanol; (▲) 3% 1-propanol; (●) 6% 1-propanol.

adaptive Kalman filter failed [51,55]. However, based on retention measurements (for example, see Fig. 1), we estimate that the contribution from the mobile phase-resident dye is less than 10% for organic phase compositions of less than 40%. Therefore, we will focus our discussion on this range of mobile phase compositions.

A second issue that must be addressed before proceeding with the interpretation of the results given here is that of whether or not there is a significant depletion of one or more of the mobile phase components (methanol, water or 1-propanol). If this were to occur, the stationary phase conditions in our spectroscopic experiments would not be the same as those in the analogous chromatography experiments, since the relative amounts of these components in the mobile phase would be altered. Based on the literature reports described in Section 1 that report preferential adsorption of 1-propanol as compared with methanol, we estimate that the solution composition should change by less than 0.1% under our experimental conditions.

A third topic that must be addressed is the effect of pressure. Our spectroscopic experiments are done under atmospheric pressure conditions, while stationary phases in chromatographic systems experience pressures ranging up to as much as 200 bar [56]. While normally solid and liquid phases are assumed to be incompressible over this range, it is reasonable to expect that wetting effects (including penetration of the mobile phase into the porous particles) might be

much more sensitive to these pressure differences, especially for organic phase compositions below 40%. Bliesner and Sentell [57] have attempted to address this factor by dry-packing the stationary phase in a column, exposing the column to the appropriate mobile phase and pressure, and then extruding the wetted phase as a paste from the end of the column. The phases prepared in this manner were stable enough for subsequent NMR measurements, but as in our experiments, did not allow the effect of the pressure to be directly assessed. We are in the process of designing experiments that will allow us to directly monitor the effects of pressure, but feel that our approach of pre-wetting the phase with the organic component, and only measuring those particles that appear “wetted” should give satisfactory results until we develop a measurement approach that allows us to control the pressure.

3.1. Dipolarity/polarizability

The π^* parameter measures the environmental dipolarity experienced by the solute molecules. Here, NM2NA was used as a probe for this parameter, by measuring the peak shift of the longest wavelength band in the visible absorption spectra [52]. In the work shown here, π^* values were measured for systems that had different amounts of 1-propanol, with the methanol or acetonitrile compositions ranging from 0% to 40%. Fig. 2 shows the data for additions of 0%, 1%, 3%, and 6% 1-propanol for both the solutions and the ODS2 slurries. There are two groups of curves in Fig. 2(A) and (B). One set represents the data for the solutions, with or without the addition of 1-propanol (represented by the (×) symbols). The other set represents the π^* values for the ODS2 stationary phase slurries at different mobile phase compositions, with or without 1-propanol addition. All solution curves are essentially identical; the π^* values increase as organic content in the solvent decreases (water increases). This means that the dipolarity of the solutions is not affected by the presence of up to 6% by volume of 1-propanol. On the contrary, different amounts of 1-propanol added do show significant effects on the curves for the ODS2 slurries. The most pronounced effect is for solutions with the highest amount of water (lowest % organic). In this region, stationary phases exposed to the mobile phases with the largest amount

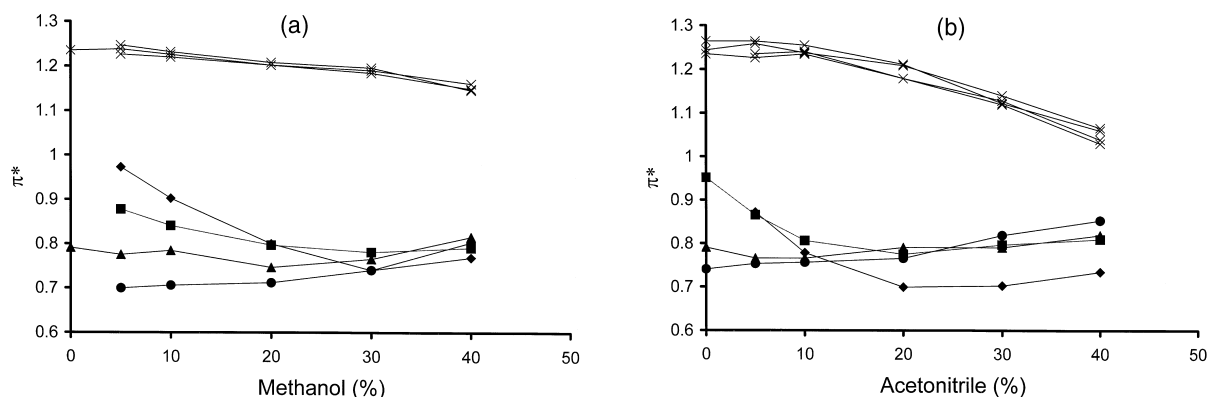


Fig. 2. Dipolarity comparison for ODS2 slurries conditioned with organic–aqueous mixtures and up to 6% of 1-propanol. π^* values were measured with NM2NA and have errors of approximately ± 0.02 : (x) solution phase measurements; (◆) 0% propanol; (■) 1% propanol; (▲) 3% propanol; (●) 6% propanol. (A) Methanol/water mobile phases. (B) Acetonitrile/water mobile phases.

of 1-propanol have the lowest dipolarity. We attribute the decrease in the dipolarity of these phases as being due to the solvating effect that 1-propanol has on the C_{18} chains. In the presence of 3–6% 1-propanol, enough alcohol partitions within the chains to maintain an extended chain arrangement, such that the solutes are completely partitioned within the chains, and not exposed to the bulk mobile phase. For stationary phases exposed to lesser amounts of 1-propanol, we believe that the C_{18} chains are aggregating and are in a collapsed state on a surface. In this case, solutes are absorbed to the surface of the phase and are exposed to the high water content mobile phase, and experience a much more dipolar environment. While the “extended” and “collapsed” chain states have been described in the literature previously, we believe that these data offer some of the strongest support to date for the existence of these different chain arrangements, and the effect of 1-propanol.

If the above suppositions are true, and solutes are retained by a different mechanism in high water content phases (only when 1-propanol is not present), it is possible that this effect would show up as a break in a plot of $\ln k'$ vs. % water. This is indeed the case as observed in Fig. 1. In the presence of 1-propanol, the $\ln k'$ vs. % water plots are linear, with random residuals for the 1%, 3%, and 6% 1-propanol mobile phases, with standard errors of the linear fits of 0.076, 0.062, and 0.062, respectively. The standard error of the linear fit with no propanol present is 0.23, reflecting the break observed in the plot at a composi-

tion of about 40%. This helps to verify the conclusions described above.

In the range of organic composition from 30% to 40%, the presence of 1-propanol has the opposite effect as described above. In this case, the stationary phase appears to be more dipolar. This is more pronounced in the case of the acetonitrile mobile phases (Fig. 2(B)), but also can be observed for the methanol phases. 1-propanol is more dipolar ($\pi^* = 0.52$) than dry C_{18} chains ($\pi^* = 0.0$ for hexadecane) although it is less dipolar than methanol ($\pi^* = 0.60$). The increased amount of 1-propanol partitioned into the stationary phase causes the increase of π^* values in ODS2 slurries.

3.2. Hydrogen-bond acidity

Another parameter examined here is α , which measures the hydrogen-bond donating ability or hydrogen-bond acidity of the environment. As stated in the previous paper [52], the dye DCMPVP is used as the probe for evaluating the α value. NM2NA is used as the standard to eliminate the dipolarity effect on the absorption spectral shift in order to measure the hydrogen-bond donating ability of the system only. Fig. 3(A) shows the α values in the methanol–water system with solvent compositions ranging from 40% to 0% methanol. The points represented by the diamonds (◆) show the α values without addition of 1-propanol, which have been discussed in a previous paper, and the points represented by triangles (▲)

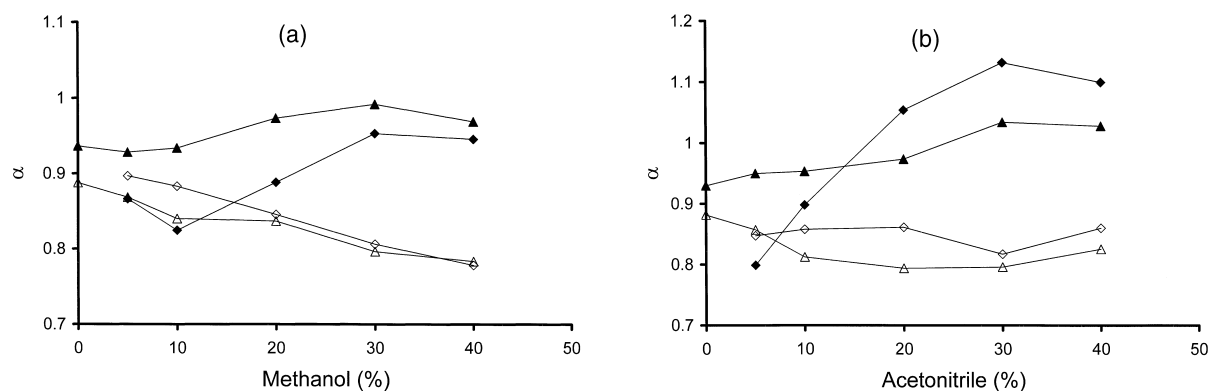


Fig. 3. α values vs. organic content in mobile phases with none (\blacklozenge) and 3% 1-propanol addition (\blacktriangle) for bonded phase slurries (filled symbols) and mobile phases (open symbols). These values were measured with the dye pair of DCMPPV and NM2NA and have errors of approximately ± 0.05 : (\diamond) solution with no propanol; (\triangle) solution with 3% propanol; (\blacklozenge) stationary phase with no propanol; (\blacktriangle) stationary phase with 3% propanol. (A) Methanol/water mobile phases. (B) Acetonitrile/water mobile phases.

show the α values for 3% 1-propanol. In the solution phase, the two curves are essentially completely overlapped. These overlapping curves indicate that addition of 3% 1-propanol does not affect the hydrogen-bond donating ability of the mobile phase. For the ODS2 slurries, 1-propanol shows a significant effect, similar to that observed for the π^* parameter. As the water content increases, the α values when no propanol is present decrease. In contrast, the α values are approximately constant when 3% propanol modifier is used. The drop in the α value is 0.13 from 30% to 10% methanol when no propanol is used (from 0.95 to 0.82), but the α value decreases by only 0.06 with addition of 3% 1-propanol. The consistency of the α values in the presence of 1-propanol supports the supposition that the alkyl chains remain in the extended configuration over a larger composition range.

A similar experiment shows the 1-propanol effect on the α parameter in the acetonitrile–water system. The results for addition of 3% 1-propanol are plotted in Fig. 3(B). Similar to Fig. 3(A) for the methanol–water system, the α values are not affected by addition of 3% 1-propanol in solutions, but this small amount of 1-propanol does affect the α values of the ODS2 phase in the medium to high water content ranges. The most obvious effect is that α values are much smaller than those for the system when no 1-propanol is present. In the range from 20% to 40% acetonitrile, the propanol-solvated phase has smaller α values.

Below 20% acetonitrile, the propanol-solvated phase shows larger α values. From 20% to 0% acetonitrile, the α values are reduced by 0.04, from 0.97 to 0.93 (not significant within our experiment errors), while there is a 0.25 reduction from 1.05 to 0.8 for the case when no 1-propanol is present. As was the case for the methanol–water system, the presence of propanol causes the stationary phase to behave more consistently in terms of its hydrogen-bond acidity.

3.3. Hydrogen-bond basicity

The third parameter used here is the α -scale that measures the hydrogen-bond accepting ability of a system. The dye 2NA was used as the β probe. The β measurements are less precise due to the lower solvatochromic sensitivity of the β dyes. The results for the β measurements with no 1-propanol and 3% 1-propanol for the methanol– and acetonitrile–water system are shown in Fig. 4. The two plots are very similar. At the high water range, i.e., when the methanol ratio is below 30% and the acetonitrile ratio is below 20%, the effect of the 1-propanol can be observed. In this range, as the ratio of organic solvent decreases, the β values of the ODS2 slurries decrease very quickly without 1-propanol present and the curves have a strong trend toward the solution curve. This trend reflects the fact that the chain collapse forces the dye molecule to stay outside of the collapsed chain layer. So, the dye molecules experience an environment having more

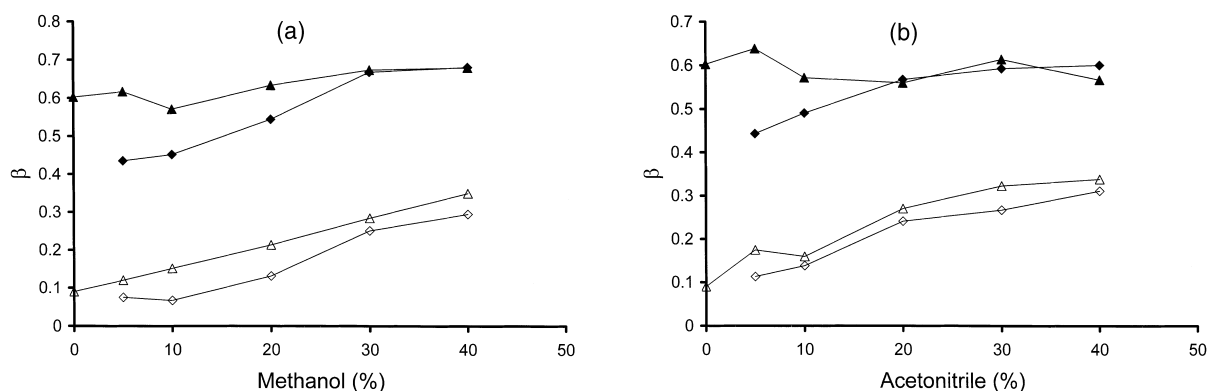


Fig. 4. β values vs. organic content in mobile phases with none (\blacklozenge) and 3% 1-propanol addition (\blacktriangle) for bonded phase slurries (filled symbols) and mobile phases (open symbols). The values were measured with dye pair of 2NA and NM2NA and have errors of approximately ± 0.1 : (\diamond) solution with no propanol; (\triangle) solution with 3% propanol; (\blacklozenge) stationary phase with no propanol; (\blacktriangle) stationary phase with 3% propanol. (A) Methanol/water mobile phases. (B) Acetonitrile/water mobile phases.

characteristics of the mobile phase. But with the addition of 3% 1-propanol, the trend to reduced β values is less significant. The β values are more consistent when 1-propanol is present, supporting the conclusions made on the basis of the π^* and α measurements.

4. Conclusion

From the work shown here, a small amount of 1-propanol has an obvious effect on the condition of the C_{18} chains, but does not affect the properties of mobile phase. It affects the LC phase conditions not only with high water content of mobile phase as pointed out by literature work, but also for compositions ranging up to 40% organic modifier. In mobile phases with high water content, wetting by a small amount of 1-propanol can affect the degree of chain collapse. As 1-propanol is added, the degree of chain collapse decreases. When the amount of 1-propanol added reaches 6%, the collapsed chain state disappears and the chains remain completely extended, as shown by the results for the π^* . This conclusion is supported by the results for the α and β measurements as well. For mobile phases with a moderate water concentration, the 1-propanol also has an effect on the stationary phase. Since 1-propanol has high affinity for the C_{18} chains, the small amount of 1-propanol added in the mobile phase can significantly modify the composi-

tion of the stationary phase, and increase the dipolarity of the C_{18} chain region. The retention behavior of the NM2NA confirms that the stationary phase conditions have a significant effect on retention, showing a break in the $\ln k'$ vs. % composition at around 50%.

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