

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

### Hydrogen-Bonding Interactions of 1-Naphthol in Polar Mobile Phases and on a Silica Column VIA an Ultraviolet Spectroscopic Comparison Method

L. D. Olsen<sup>a</sup>; R. J. Hurtubise<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Wyoming, Laramie, Wyoming

**To cite this Article** Olsen, L. D. and Hurtubise, R. J.(1991) 'Hydrogen-Bonding Interactions of 1-Naphthol in Polar Mobile Phases and on a Silica Column VIA an Ultraviolet Spectroscopic Comparison Method', *Journal of Liquid Chromatography & Related Technologies*, 14: 10, 1837 – 1859

**To link to this Article:** DOI: 10.1080/01483919108049658

**URL:** <http://dx.doi.org/10.1080/01483919108049658>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# HYDROGEN-BONDING INTERACTIONS OF 1-NAPHTHOL IN POLAR MOBILE PHASES AND ON A SILICA COLUMN VIA AN ULTRAVIOLET SPECTROSCOPIC COMPARISON METHOD

L. D. OLSEN AND R. J. HURTUBISE\*

*Department of Chemistry  
University of Wyoming  
Laramie, Wyoming 82071*

## ABSTRACT

Two solutes of widely different hydrogen-bonding donation ability were investigated by ultraviolet spectroscopy in several n-heptane:2-propanol and n-heptane:ethyl acetate solvents. The ultraviolet spectral data were correlated with chromatographic data obtained from a silica column and the displacement model for normal-phase HPLC. The general approach developed was useful in studying mono-hydroxyl aromatics that donate a proton in hydrogen-bonding interactions in polar mobile phases. Two major hydrogen-bonding regions were revealed from the solvent data. One in which monomeric species were formed and another region in which dimeric or polymeric species were formed. By using the spectral data and the chromatographic data, it was possible to construct four diagrams that permitted a general description of the distributions and interactions of the solute and strong solvents in the mobile phase and stationary phase.

## INTRODUCTION

While normal-phase high-performance liquid chromatography (HPLC) is an extremely useful technique for separating complex mixtures, more

information is needed about several aspects of the basic retention mechanism. The displacement model developed by Snyder is one of the more widely accepted models used to explain retention in normal-phase HPLC (1-4). The assumptions made in using the displacement model have been summarized by Snyder and Schunk (5). The displacement model assumes that a solute molecule migrates in the column by displacing solvent molecules from specific adsorbent sites (1-5). A lot of the research with the displacement model has been done using relatively nonpolar solutes and weak mobile phases and taking into account mainly the solute-stationary phase interactions (1). However, if polar solutes and strong mobile phases are to be studied, secondary solvent effects such as hydrogen-bonding interactions between the solute and mobile phase, and stationary phase surface inhomogeneities must be considered (3,4).

Work by Kamlet and others (6-10) using solvatochromic properties of solutes and solvents has resulted in much fundamental information on solute-solvent and solvent-solvent interactions. Also, Reichardt (11) has given an extensive review about numerous solute-solvent interactions. While most of the information from Kamlet and co-workers applies to unitary solvents, two papers they published have dealt with binary solvent systems (7,9). Recently a number of authors (12-21) have attempted to find relationships between different chromatographic terms and solvatochromic properties. Most of these papers have related solvatochromic properties to reversed-phase HPLC (12-19). Rutan et al. (20) compared the Snyder solvent triangle to solvatochromic based scales of solvent strength and selectivity. Park et al. (21) found linear relationships between normal-phase solvent strengths and various solvatochromic properties.

In this study, the hydrogen-bonding donation characteristics of 1-naphthol (1-N) with various n-heptane:2-propanol and n-heptane:ethyl acetate solvent compositions were determined by ultraviolet spectroscopy using an approach somewhat similar to the one developed by Kamlet and others (7,9). The chromatographic data were obtained from a silica column and were previously reported (22). The ultraviolet spectral data were related to a number of different chromatographic parameters obtained from the displacement model for normal-phase HPLC. The main reasons for the comparison of the ultraviolet spectral data with the chromatographic data were to ascertain the general

hydrogen-bonding effects on the displacement model and to develop an approach that would be useful for the investigation of hydrogen-bonding effects in the mobile phase.

## EXPERIMENTAL

### Chromatography

The chromatographic equipment, experimental conditions, and procedures have been previously reported (22).

### Spectroscopy

*Reagents:* 1-N and 1,2,3,4-tetrahydro-1-naphthol (T-1-N) were obtained from Aldrich and were used as received. J.T. Baker HPLC-grade n-heptane, 2-propanol, ethyl acetate, cyclohexane, methylene chloride, carbon tetrachloride, and EM Science OmniSolv-grade 1,2-dichloroethane were obtained from VWR Scientific. The various n-heptane:2-propanol and n-heptane:ethyl acetate compositions were the same as those used in previous chromatography experiments (22).

*Instrumentation:* The ultraviolet-visible spectrophotometer used was a CARY 2390. The sample compartment was kept at a constant 25°C with a Haake Model FE water circulator.

*Wavelength Standard:* A holmium oxide solution wavelength standard was obtained from the National Institute of Standards and Technology, Washington, D.C. (Standard Reference Material 2034).

*Solutions:* Solutions of 200 µg/mL of 1-N and T-1-N were prepared in an appropriate solvent, and then a small amount of the 200 µg/mL 1-N solution was diluted to 40 µg/mL. Solutions were prepared in each of the solvents mentioned under Reagents and for several different compositions of n-heptane:2-propanol and n-heptane:ethyl acetate. All solutions were protected from light by storage in a dark cabinet.

*Procedures:* All standards and samples were allowed to remain in the sample compartment for at least 2 minutes to allow the samples to come to thermal equilibrium before any spectral data were collected. During this time the light path was blocked in order to protect the sample from the source.

The first sample run was the wavelength standard solution. Using the derivative feature of the spectrophotometer, first derivative data were collected in triplicate at each of the following wavelength ranges: 334.50-332.00 nm, 288.50-285.50 nm, 279.50-276.50 nm, and 251.50-248.50 nm. The data were collected using air as the reference. The next step was to run a baseline using the reference and sample cells containing the solvent of interest. This baseline was then stored so that all other spectra could be corrected for a given solvent. Then the normal spectrum for the 1-N solution was collected. The results from the normal spectrum were used to decide approximately where the peak maxima were occurring. Using the approximate peak maxima data, first derivative data were collected in at least triplicate scans over a 3 nm range around each peak maxima. The sample solution was changed between each wavelength range measurement and between collecting the normal spectrum and the first set of first derivative data. These steps were repeated for the T-1-N solutions. The data for each of the pure solvents were collected in triplicate, and the data for most of the binary solvent systems were collected in duplicate.

*Wavelength Determination:* The first derivative data for the holmium oxide solution wavelength standard were plotted as wavelength versus  $dA/d\lambda$  for 5 points on each side of a peak maximum. Plots of wavelength versus  $dA/d\lambda$  were made for each peak maxima of 1-N and T-1-N in each solvent studied. Least squares analysis was then performed for each first derivative scan collected based on the linear ranges as determined by the wavelength versus  $dA/d\lambda$  plots. The linear ranges used consisted of 7 to 10 data points with 10 being the most common. Using the least squares information, the wavelength of the peak maximum could be determined, since this was the point where the derivative was equal to zero. Then, using the wavelengths published for the wavelength standard solution, at the spectral bandpass used, plots of the published wavelengths versus observed wavelengths of the standard were made. Data from the least squares analysis of these plots were used to correct the observed wavelengths of the 1-N and T-1-N solutions. After the corrected wavelengths for each of the peak maxima for 1-N and T-1-N were determined, the results were converted to the corresponding wavenumber ( $\text{cm}^{-1}$ ). It was

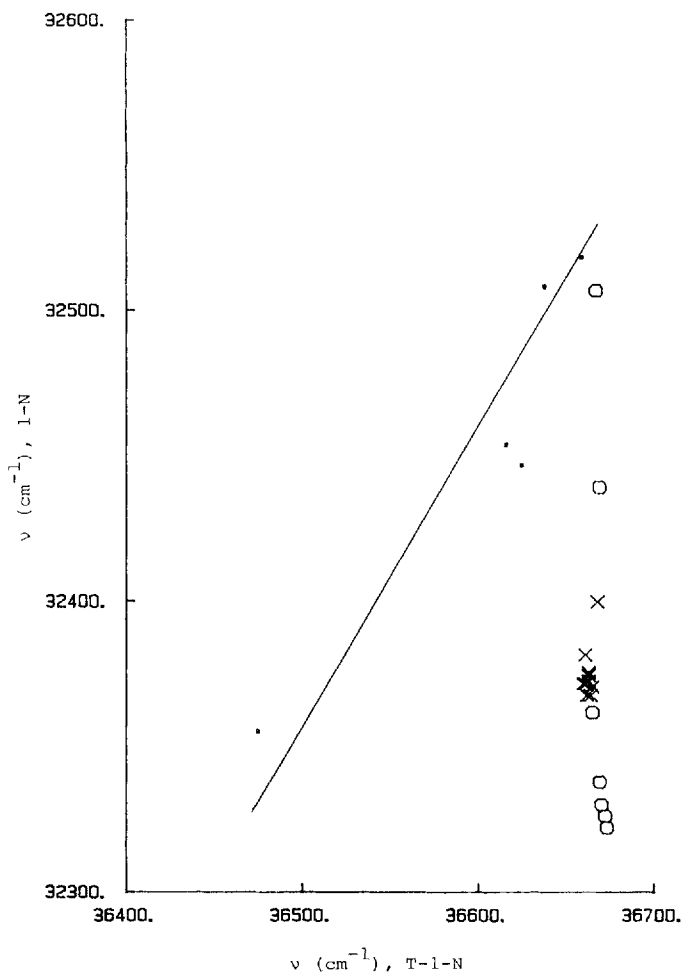
determined that the reproducibility of the overall approach was  $\pm 0.02$  nm, or  $\pm 2$   $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

### Solvatochromic Comparison Method

The solvatochromic comparison method (SCM) has been used to correlate spectral shifts of various solutes in different solvents to a number of physical and chemical properties. Frequently the spectral characteristics of a hydrogen bonding solute are compared to the spectral characteristics of a solute with a weaker hydrogen bonding ability. Under these conditions, the SCM requires that three conditions be satisfied: first, a plot of observed  $\nu$  ( $\text{cm}^{-1}$ ) values for two substrates of different hydrogen bonding abilities in a series of solvents, which do not hydrogen bond, give a linear relationship with a statistically acceptable correlation coefficient; second, the observed  $\nu$  values obtained in solvents, which do hydrogen bond, be offset from the regression line, obtained in the first condition, in the same direction by statistically significant amounts; third, the direction of displacement should be indicative of the chemistry involved (8). In this work, 1-N was chosen as a solute which is a relatively strong hydrogen bond donor and T-1-N was chosen as a very weak hydrogen bond donor. Laha et al. (23) have shown that no ultraviolet shifts were observed for T-1-N in the presence of the proton acceptor, dioxane. As discussed later, this was generally true for T-1-N in 2-propanol and ethyl acetate in that very minor spectral shifts were observed. The results of Laha et al. (23) and our results show that ultraviolet spectroscopy is "blind" to any proton donation properties of T-1-N, and it can be used as a reference compound for determining the proton donation properties of 1-N.

For the first condition described in the preceding paragraph, the two solutes used with different hydrogen bonding abilities were the 1-N and T-1-N, and the solvents employed with no hydrogen bonding ability were n-heptane, cyclohexane, carbon tetrachloride, 1,2-dichloroethane, and methylene chloride. The normal spectrum of 1-N showed three bands of possible interest, while the spectrum of T-1-N showed two bands. Plots of the various observed  $\nu$  values



1. Observed  $\nu$  (cm<sup>-1</sup>) values of 1-N versus observed  $\nu$  (cm<sup>-1</sup>) values for the 272 nm band of T-1-N for the nonhydrogen bonding solvents (•), the n-heptane:2-propanol binary solvents (o), and the n-heptane:ethyl acetate binary solvents (x).

TABLE 1.

Wavenumbers for the 307 nm Band of 1-N and the 272 nm Band (a) and the 265 nm Band (b) for T-1-N in the Nonhydrogen Bonding Solvents.

Solvent	$\nu$ (cm <sup>-1</sup> ) 1-N	$\nu$ (cm <sup>-1</sup> ) T-1-N	
		a	b
n-Heptane	32520	36654	37681
Cyclohexane	32510	36633	37666
Methylene Chloride	32455	36611	37628
CCl <sub>4</sub>	32357	36470	37483
1,2-Dichloroethane	32448	36620	37637

of 1-N versus the observed  $\nu$  values of T-1-N from the nonhydrogen bonding solvents showed that only certain combinations of the spectral bands gave linear relationships. The three spectral bands of interest for 1-N were at about 322 nm, 307 nm, and 289 nm, and the two bands in T-1-N were at about 272 nm and 265 nm. The observed  $\nu$  plots showed that if the 1-N spectral band at 307 nm was plotted against either of the spectral bands from T-1-N a linear relationship was obtained. The correlation coefficient was 0.947, if the 272 nm spectral band of T-1-N was used, and the correlation coefficient was 0.966 if the 265 nm spectral band was used (see Figure 1). The observed  $\nu$  values for 1-N and T-1-N obtained with the nonhydrogen bonding solvents are given in Table 1.

For the second condition discussed above, binary solvents of n-heptane:2-propanol and n-heptane:ethyl acetate were used. The observed  $\nu$  values (column three) are given in Tables 2 and 3, respectively, for the binary mixtures. It is clear that these results are offset from the line in statistically significant amounts and in the same direction (see Figure 1).

For the third condition, namely, that the direction of displacement should be indicative of the chemistry involved, Figure 1 can be considered. The results



Table 2. Wavenumbers for the Observed and Calculated  $\nu$  Values for the 307 nm Band of 1-N and the 272 nm Band (a) and the 265 nm Band (b) of T-1-N in the n-Heptane:2-Propanol (v/v) Binary Solvents.

Solvent	$\nu$ ( $\text{cm}^{-1}$ ) 1-N		$\nu$ ( $\text{cm}^{-1}$ ) T-1-N	$\Delta\Delta\nu$
	Calculated	Observed	Observed	
a				
99.8:0.2	32514	32507	36665	7
99.5:0.5	32516	32439	36667	77
99:1	32513	32362	36663	151
98:2	32516	32338	36667	178
97:3	32517	32330	36668	187
96:4	32518	32326	36669	192
95:5	32520	32322	36671	198
b				
99.8:0.2	32519	32507	37696	12
99.5:0.5	32520	32439	37698	81
99:1	32518	32362	37695	156
98:2	32522	32338	37701	184
97:3	32523	32330	37701	193
96:4	32525	32326	37704	199
95:5	32528	32322	37707	206

Table 3. Wavenumbers for the Observed and Calculated  $\nu$  Values for the 307 nm Band of 1-N and the 272 nm Band (a) and the 265 nm Band (b) of T-1-N in the n-Heptane:Ethyl Acetate (v/v) Binary Solvents.

Solvent	$\nu$ ( $\text{cm}^{-1}$ ) 1-N		$\nu$ ( $\text{cm}^{-1}$ ) T-1-N	$\Delta\Delta\nu$
	Calculated	Observed	Observed	
			a	
98:2	32516	32400	36666	116
96:4	32509	32382	36659	127
94:6	32511	32376	36661	135
92:8	32508	32372	36658	136
90:10	32509	32372	36659	137
88:12	32510	32368	36660	142
86:14	32511	32373	36661	138
84:16	32511	32375	36661	136
82:18	32512	32368	36662	144
80:20	32513	32371	36663	142
			b	
98:2	32509	32400	37697	109
96:4	32513	32382	37689	131
94:6	32518	32376	37695	142
92:8	32512	32372	37688	140
90:10	32515	32372	37692	143
88:12	32516	32368	37693	148
86:14	32515	32373	37692	142
84:16	32516	32375	37692	141
82:18	32517	32368	37694	149
80:20	32517	32371	37694	147

in Figure 1 indicate that the type of hydrogen-bonding interactions between 1-N and 2-propanol, or ethyl acetate, are similar since the data for 2-propanol and ethyl acetate are on the same side of the line for the nonhydrogen bonding solvents. Because ethyl acetate can only accept a proton from 1-N and because the results for 2-propanol in Figure 1 lie on the same side of the line as ethyl acetate, then both 2-propanol and ethyl acetate must be accepting a proton from 1-N in hydrogen bond formation. Also, it is known that 1-N is a stronger acid than 2-propanol, hence 1-N is more likely to donate a proton to 2-propanol in forming a hydrogen bond.

The results for the first two conditions discussed earlier were used to calculate enhanced solvatochromic displacement values ( $\Delta\Delta\nu$ ) in a manner somewhat similar to Kamlet and Taft (8). The  $\Delta\Delta\nu$  results in Tables 2 and 3 approximate the hydrogen bonding interactions of the solute in a binary solvent after the nonhydrogen bonding interactions are subtracted out. The  $\Delta\Delta\nu$  results depended on a couple of assumptions for 1-N and T-1-N in the binary solvents. First, it was assumed that the observed  $\nu$  values for T-1-N would not be significantly influenced by hydrogen bonding in the binary solvents. This was proven by the results in Figure 1. Second, it was assumed that the observed  $\nu$  values for 1-N would be influenced by hydrogen bonding in the binary solvents. This is strongly supported by the results in Figure 1. In addition, the  $pK_a$  values for 1-N and T-1-N are 9.3 (24) and 15.7 (25), respectively. Thus, the  $pK_a$  values clearly indicate that 1-N is a much stronger acid than T-1-N. The results in Figure 1 and in column four of Tables 2 and 3 show that T-1-N was not greatly influenced by a change in the composition of the binary solvents because the ranges of the observed  $\nu$  values were narrow for the different binary solvents and spectral bands studied. In contrast, the results in Figure 1 and in column three of Tables 2 and 3 indicate that 1-N was influenced by hydrogen bond donation because of the wide range of the observed  $\nu$  values.

The calculated  $\nu$  values in column two in Tables 2 and 3 for the binary solvents were calculated for 1-N assuming that hydrogen bonding was not occurring. This was done by using the linear regression results from the

nonhydrogen bonding solvents and the observed  $\nu$  values for T-1-N in the binary solvents. The  $\Delta\Delta\nu$  results were then calculated by taking the difference between the observed  $\nu$  values and the calculated  $\nu$  values for 1-N (see Tables 2 and 3). The  $\Delta\Delta\nu$  results for the n-heptane:2-propanol binary solvents indicated that the hydrogen-bonding interactions between 1-N and the solvent got stronger, since the  $\Delta\Delta\nu$  values got larger as the amount of 2-propanol in the binary solvents increased. This trend was observed with 1-N for both spectral bands of T-1-N used in the calculation of the  $\Delta\Delta\nu$  results.

The  $\Delta\Delta\nu$  results for the n-heptane:ethyl acetate binary solvents were somewhat different. At low amounts of ethyl acetate, the  $\Delta\Delta\nu$  results (Table 3) showed that the hydrogen-bonding interactions between 1-N and ethyl acetate became stronger because the  $\Delta\Delta\nu$  values got larger as the amount of ethyl acetate in the binary solvents increased. However, at higher amounts of ethyl acetate the hydrogen-bonding interactions were fairly constant, represented by relatively constant  $\Delta\Delta\nu$  values in Table 3. This indicated that the hydrogen-bonding interactions between the molecules had reached a saturation level. Also, there was more of a random pattern in the data at the higher concentrations of ethyl acetate.

A saturation level for the hydrogen-bonding interactions between the solute and solvent was not reached for the 2-propanol binary solvents. This is most likely related to the fact that 2-propanol is more polar than ethyl acetate. Also, the amount of ethyl acetate required to elute the solutes in the  $k'$  range of 1 to 10 was much larger than the amount of 2-propanol required. Thus, because larger amounts of ethyl acetate than 2-propanol were used in the spectral study, it is more likely that a saturation level for the hydrogen-bonding interactions would be reached for ethyl acetate.

#### Solute-Solvent Mobile Phase Interactions

The  $\Delta\Delta\nu$  values in Table 2 and 3 reflect primarily the hydrogen-bonding interactions of 1-N with the mobile phase, as determined by ultraviolet spectroscopy. The mole fraction of the solute in the mobile phase,  $\theta_M$ , can be related to the solute's interactions with the mobile phase as determined by

chromatography. The  $\theta_M$  values can easily be calculated, since the capacity factor,  $k'$ , is equal to the total moles of the solute in the stationary phase divided by the total moles of the solute in the mobile phase. Using this information, it can be shown that  $\theta_M = 1/(1 + k')$ . The calculated  $\theta_M$  values are given in Table 4.

Figure 2 shows two major regions that are approximately linear. In the first region ( $\theta_M$  from 0.094 to 0.361), with weaker solvents, the hydrogen-bonding interactions rapidly got stronger between the solute and solvents. Then, in the second region ( $\theta_M$  from 0.361 to 0.764), with stronger solvents, the hydrogen-bonding interactions between the solute and solvents got stronger, but not as rapidly as in the first region. In Figure 2, where the  $\Delta\Delta v$  values are changing the most (first region), the  $\theta_M$  values did not change as much relative to the  $\theta_M$  values in the second region. This indicated that the relative hydrogen-bonding interactions of the mobile phase with the solute undergo a greater change for a given mole fraction of solute in the weaker solvents relative to the stronger solvents. This is most likely related to the stronger solvent, 2-propanol, more effectively displacing the solute from the stationary phase at weaker solvent strengths. In addition, the hydrogen-bonding interactions between the solute and strong solvent in the mobile phase will be greater as the solvent becomes more polar and hydrogen bonding occurs more extensively. However, the results in Figure 2 show that the  $\Delta\Delta v$  values do not change as rapidly in the second region compared to the first region. This is most likely related to the self-association of 2-propanol by hydrogen-bonding interactions (26). In general, in the first region of Figure 2, the hydrogen-bonding interactions between 2-propanol and 1-N are as follows, where 2-P represents 2-propanol.



While in the second region of Figure 2, one possible hydrogen-bonding interaction can be represented as follows.

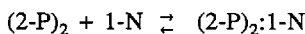
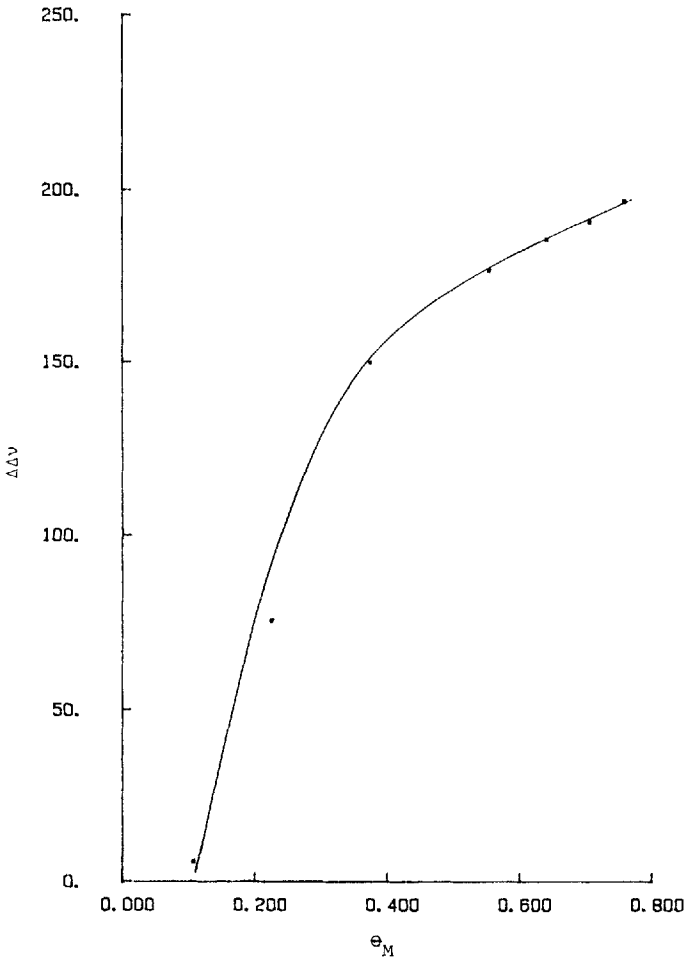


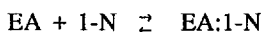
Table 4. Chromatographic Results for 1-N and  $\theta_{AD}$  Values for T-1-N in n-Heptane: 2-Propanol (a), and n-Heptane:Ethyl Acetate (b) Mobile Phases

Solvent	$N_B$	$k'$	$\theta_M$	$\theta_B$	%1c	$\theta_{AD}$ 1-N	$\theta_{AD}$ T-1-N
a							
99.8:0.2	0.004	9.6	0.094	0.791	0.449	0.906	0.932
99.5:0.5	0.010	3.72	0.212	0.816	0.363	0.788	0.847
99:1	0.019	1.77	0.361	0.834	0.297	0.639	0.741
98:2	0.038	0.85	0.541	0.851	0.239	0.459	0.605
97:3	0.056	0.59	0.629	0.865	0.191	0.371	0.500
96:4	0.074	0.44	0.694	0.876	0.157	0.306	0.437
95:5	0.092	0.34	0.746	0.886	0.125	0.254	0.382
b							
98:2	0.030	6.81	0.128	0.761	0.544	0.872	0.959
96:4	0.059	3.13	0.242	0.808	0.389	0.758	0.917
94:6	0.087	1.93	0.341	0.847	0.252	0.659	0.877
92:8	0.115	1.42	0.413	0.867	0.184	0.587	0.840
90:10	0.143	1.04	0.490	0.884	0.132	0.510	0.792
88:12	0.170	0.87	0.535	0.898	0.093	0.465	0.748
86:14	0.196	0.69	0.592	0.908	0.069	0.408	0.712
84:16	0.222	0.58	0.633	0.914	0.058	0.367	0.670
82:18	0.248	0.52	0.654	0.921	0.042	0.346	0.631
80:20	0.273	0.41	0.709	0.927	0.032	0.291	0.606

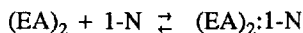


2.  $\Delta\Delta\nu$  versus  $\theta_M$  for 1-N using the 272 nm band of T-1-N and the n-heptane:2-propanol mobile phases.

The remarks in this section apply to the  $\Delta\Delta v$  values determined from both spectral bands of T-1-N and for both the n-heptane:2-propanol and n-heptane:ethyl acetate mobile phases. A major difference between the 2-propanol and ethyl acetate mobile phase data was the somewhat random pattern in the  $\Delta\Delta v$  values with ethyl acetate for  $\theta_M$  values  $> 0.350$ . The random pattern is related to the weaker interactions found with ethyl acetate relative to 2-propanol. Also, the changes in the  $\Delta\Delta v$  values for ethyl acetate ( $\theta_M < 0.350$ ) were not as dramatic as those for 2-propanol. For  $\Delta\Delta v$  versus  $\theta_M$  for ethyl acetate in the first region ( $\theta_M$  values  $< 0.350$ ), the hydrogen-bonding interactions could be as follows, where EA represents ethyl acetate.



The  $\Delta\Delta v$  values became fairly constant in ethyl acetate for  $\theta_M > 0.350$  because of the relatively strong dipole-dipole interactions between the ethyl acetate molecules. For the second region ( $\theta_M$  values  $> 0.350$ ) for ethyl acetate, the hydrogen-bonding interactions could be as follows.



#### Solute and Solvent Interactions on the Stationary Phase

Both the solutes and solvent molecules interact with the stationary phase. An approximate measure of the interactions of the solvent can be viewed as the mole fraction of the strong solvent on the stationary phase,  $\theta_B$ . The  $\theta_B$  values were calculated for the various n-heptane:2-propanol and n-heptane:ethyl acetate mobile phases using equations and other information developed by Snyder (4) and Snyder and Glajch (28,29). Also, an approximate measure of the interactions of the solute with the stationary phase is represented by the mole fraction of the solute on the stationary phase,  $\theta_{AD}$ . The  $\theta_{AD}$  values can be determined from  $k'$  values using the following,  $\theta_{AD} = k'/(1 + k')$ . The  $\theta_B$  and  $\theta_{AD}$  values are given in Table 4. The results for  $\theta_B$  versus  $\theta_{AD}$  for 1-N and T-1-N were similar in a given mobile phase system. However, the results for  $\theta_B$  versus  $\theta_{AD}$  were quite different for the two mobile phase systems investigated. The results for 1-N on a silica column using n-heptane:2-propanol

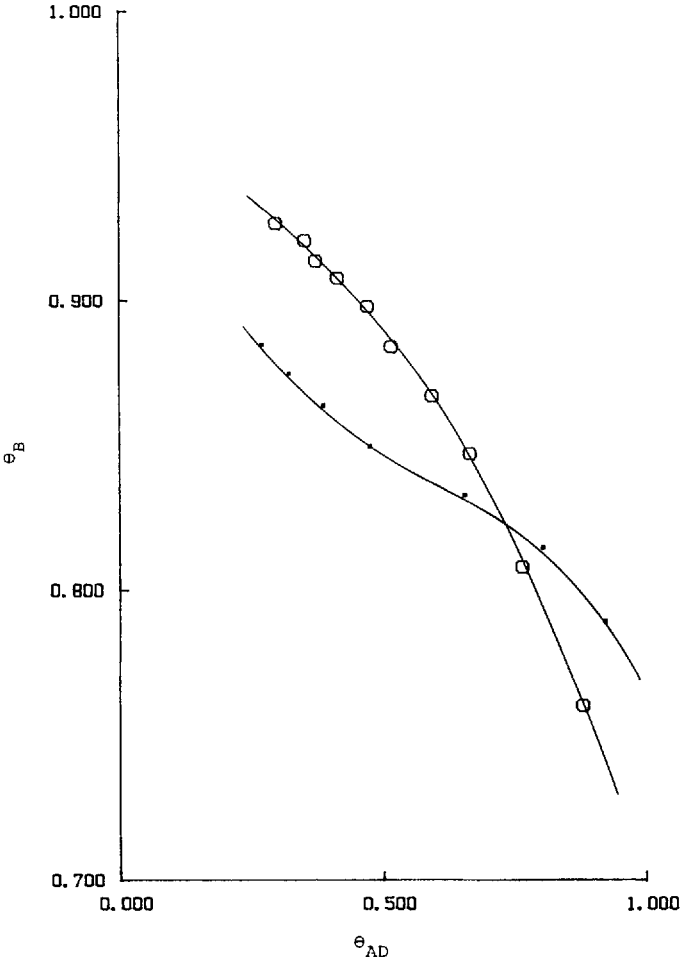


and n-heptane:ethyl acetate mobile phases, graphed as  $\theta_B$  versus  $\theta_{AD}$ , are given in Figure 3.

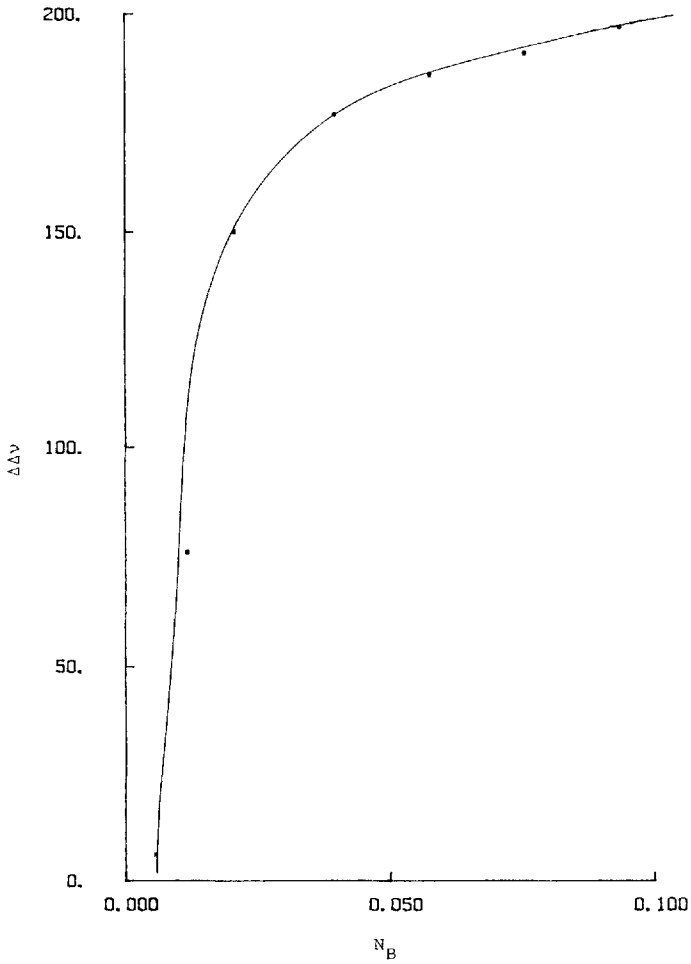
Figure 3 shows that the overall shapes of the graphs of  $\theta_B$  versus  $\theta_{AD}$  were very different for the n-heptane:2-propanol and n-heptane:ethyl acetate mobile phases with 1-N as a solute. The data in Figure 3 give information on the mole fractions of the strong solvent and the solute on the stationary phase over the range of solvent compositions investigated. The curve for ethyl acetate is convex, whereas the curve for 2-propanol has both a convex portion and a concave portion. These differences are most likely due to the stronger localization of 2-propanol relative to ethyl acetate. The graphs in Figure 3 are useful in comparing the mole fractions of the solute on the stationary phase at a given  $\theta_B$  value for the two different polar solvents or in comparing the mole fraction of strong solvent on the stationary phases at a given  $\theta_{AD}$  value. Similar results for  $\theta_B$  versus  $\theta_{AD}$  were obtained for the n-heptane:2-propanol and n-heptane:ethyl acetate mobile phases using T-1-N.

#### Strong Solvent Interactions in the Mobile Phase

As mentioned earlier, the  $\Delta\Delta v$  values can be considered as a measure of the hydrogen-bonding donation properties of the solute with the strong solvent in the mobile phase. In obtaining the  $\Delta\Delta v$  values, only the concentration of the strong solvent was varied, while the concentration of the solute was held constant. Thus, the  $\Delta\Delta v$  values reflect the hydrogen-bonding interactions of the solute with the strong solvent as a function of a concentration of the strong solvent. By graphing  $\Delta\Delta v$  values versus the mole fraction of the strong solvent in the mobile phase ( $N_B$ ), one can obtain information on the effect of the strong solvent in the mobile phase. For example, a graph of  $\Delta\Delta v$  versus  $N_B$  for n-heptane:2-propanol mobile phases indicated that the solute-solvent hydrogen-bonding interactions got stronger as the  $N_B$  values for 2-propanol increased (see Figure 4). Figure 4 shows that at low concentrations of 2-propanol ( $N_B$  values  $< 0.019$ ) the  $\Delta\Delta v$  values change greatly while  $N_B$  values change only slightly. For  $N_B$  values  $> 0.019$ , the  $\Delta\Delta v$  values change moderately while the  $N_B$  values change significantly. The moderate changes in the  $\Delta\Delta v$  values at the higher 2-propanol concentrations are most likely due to self-association of the 2-propanol (see earlier discussion).



3. Results for 1-N graphed as  $\theta_B$  versus  $\theta_{AD}$  using n-heptane:2-propanol (•) and n-heptane:ethyl acetate (o) mobile phases.



4.  $\Delta\Delta v$  versus  $N_B$  for 1-N in n-heptane:2-propanol mobile phases using the 272 nm spectral band of T-1-N for the  $\Delta\Delta v$  values.

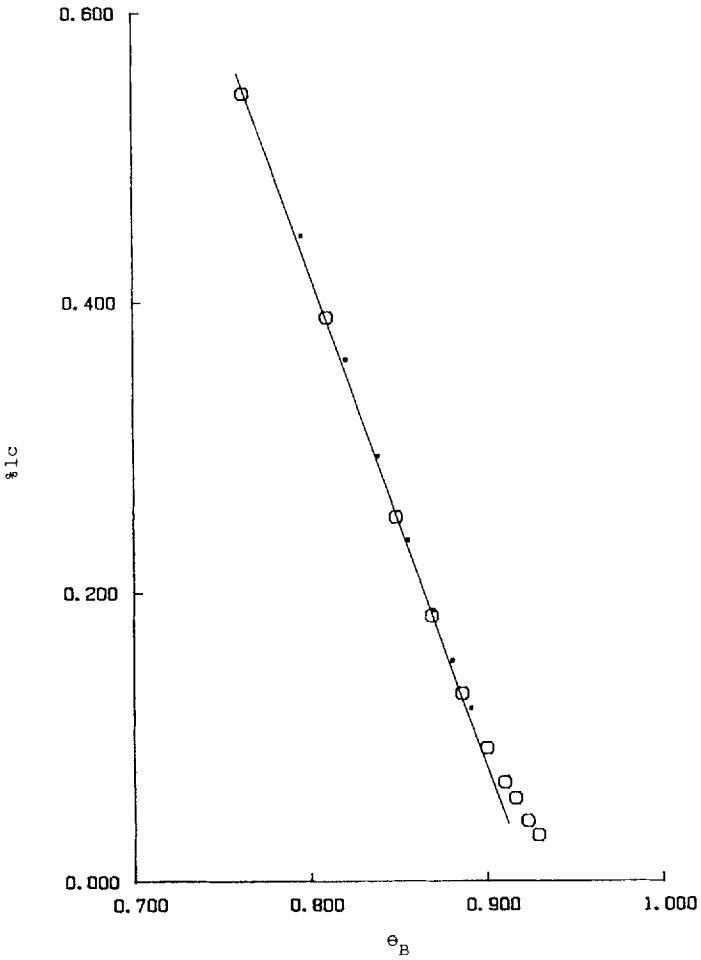
Results for  $\Delta\Delta v$  versus  $N_B$  for n-heptane:ethyl acetate mobile phases were basically the same as those for the n-heptane:2-propanol mobile phase. The greatest changes in the  $\Delta\Delta v$  values occurred with  $N_B$  values  $< 0.010$ , and much more moderate changes occurred in  $\Delta\Delta v$  values at  $N_B$  values  $> 0.010$ . The moderate changes in  $\Delta\Delta v$  values are most likely due to the dipole-dipole interactions between the ethyl acetate molecules (see earlier discussion). However, the major difference between n-heptane:2-propanol and n-heptane:ethyl acetate mobile phases for  $\Delta\Delta v$  versus  $N_B$  was the somewhat random pattern in the  $\Delta\Delta v$  values for the n-heptane:ethyl acetate mobile phases for  $N_B$  values  $> 0.010$  (see earlier discussion). Also, the changes in the  $\Delta\Delta v$  values for ethyl acetate for  $N_B$  values  $< 0.010$  were not as dramatic as with 2-propanol.

#### Strong Solvent Interactions on the Stationary Phase

The interactions of the strong solvent on the stationary phase are represented by the mole fraction of the strong solvent on the stationary phase,  $\theta_B$ , and the fraction of strong solvent that is localized on the stationary phase, %lc. The %lc values were determined using equations and other information developed by Snyder (4) and Snyder and Glajch (27,28). These interactions were graphed as %lc versus  $\theta_B$  (see Figure 5). As Figure 5 shows, the graph for the n-heptane:2-propanol mobile phases was linear (correlation coefficient, -1.00). The data for the n-heptane:ethyl acetate mobile phases were linear over a wide range (see Figure 5). However, slight curvature for the ethyl acetate mobile phases occurred with  $\theta_B$  values  $> 0.900$  (see Figure 5). The results in Figure 5 clearly show that as  $\theta_B$  increases the %lc decreases. This is reasonable since at low  $\theta_B$  values the solvent molecules have a good chance of finding a site on which to localize, but as the  $\theta_B$  values increase, the chances of the solvent molecule finding a site on which to localize are much less. Similar results and conclusions were found by Snyder (4) for graphs of %lc versus  $\theta_B$  for several polar mobile phases.

#### Comparison of $\Delta\Delta v$ Versus $\theta_M$ and $\Delta\Delta v$ Versus $N_B$

The results in Figure 2 correlate with the results in Figure 4 in that at the larger concentrations of 2-propanol the  $\Delta\Delta v$  values do not change as much



5. %1c versus  $\theta_B$  for n-heptane:2-propanol (•) and n-heptane:ethyl acetate (o) mobile phases.

relative to the smaller concentrations of 2-propanol. For example, in the first region of Figure 2 ( $\theta_M$  from 0.094 to 0.361) and the first region of Figure 4 ( $N_B$  values  $< 0.019$ ), the  $\theta_M$  and  $N_B$  values do not change as much relative to the  $\theta_M$  and  $N_B$  values in the second regions of Figures 2 and 4, respectively. As discussed earlier, this means that the hydrogen-bonding interactions are changing more extensively in the first region relative to the second region in terms of both the  $\theta_M$  and  $N_B$  values.

The overall change in  $\Delta\Delta v$  values in Figures 2 and 4 correlate with the  $k'$  values for 1-N in Table 4. In general, the  $k'$  values of 1-N decrease as the  $\theta_M$  and  $N_B$  values increase. The  $k'$  values change the most when the  $\Delta\Delta v$  values are changing the most. When  $\Delta\Delta v$  values are changing moderately, the  $k'$  values change moderately (see Figures 2 and 4 and Table 4). This means that  $k'$  values changed the greatest when hydrogen-bonding interactions in solution were changing the most. Once the hydrogen-bonding interactions in solution were changing moderately, at the larger values of  $\Delta\Delta v$ , the  $k'$  values were changing moderately. Thus, it is possible to correlate the changes in the  $\Delta\Delta v$  values with changes in the  $k'$  values. Because  $k'$  is a function of several parameters, the correlation of  $k'$  and  $\Delta\Delta v$  is not a simple one. Most likely the correlation is related to both stationary phase and mobile phase interactions, and these factors need to be examined further.

### CONCLUSIONS

The ultraviolet spectroscopic approach used to obtain the  $\Delta\Delta v$  values has been shown to be useful in describing the hydrogen-bonding donation characteristics of a hydrogen bonding solute in n-heptane:2-propanol and n-heptane:ethyl acetate mobile phases. The results showed that in the mobile phases studied there were two major hydrogen-bonding regions. A region in which monomeric hydrogen-bonding solvent molecules were interacting with the solute molecules, and a region in which dimeric or polymeric hydrogen-bonding solvent molecules were interacting with the solute molecules. These two major hydrogen-bonding regions were also correlated to the magnitude of the changes in the capacity factors of the solute with increasing solvent polarity. The

overall approach developed should be applicable to other hydrogen-bonding solutes. However, much more work is needed to elucidate other interactions in these complex systems.

Figures 2-5 permit an accounting of the distributions and interactions of the solute and strong solvent in the mobile phase and stationary phase. For example, one can use the four figures to discern the general interactions by the solute and solvent molecules and to determine their relative amounts at any mobile phase composition. This approach should be very useful in mechanistic studies in normal-phase HPLC.

### ACKNOWLEDGEMENTS

Financial support for this project was provided by the U.S. Department of Energy under contract No. DE-AC22-83PC60015. Partial support was provided to L.D. Olsen by the Patricia Roberts Harris Fellowship program through the University of Wyoming.

### REFERENCES

1. Snyder, L.R. "Principles of Adsorption Chromatography"; Marcel Dekker, Inc.: New York, 1968.
2. Snyder, L.R. Anal. Chem. 1974, 46, 1384.
3. Snyder, L.R.; Poppe, H. J. Chromatogr. 1980, 184, 363.
4. Snyder, L.R. "High-Performance Liquid Chromatography: Advances and Perspectives", Horvath, C.; Ed.; Academic Press: New York, 1983; Vol. 3., pp. 157-223.
5. Snyder, L.R.; Schunk, T.C. Anal. Chem. 1982, 54, 1764.
6. Kamlet, M.J.; Doherty, R.M.; Abboud, J.L.M.; Abraham, M.H.; Taft, R.W. Chemtech 1986, 16, 566.
7. Kamlet, M.J.; Kayser, E.G.; Jones, M.E.; Abboud, J.L.; Eastes, J.W.; Taft, R.W. J. Phys. Chem. 1978, 82, 2477.
8. Kamlet, M.J.; Taft, R.W. J. Am. Chem. Soc. 1976, 98, 377.
9. Minesinger, R.R.; Jones, M.E.; Taft, R.W.; Kamlet, M.J. J. Org. Chem. 1977, 42, 1929.

10. Taft, R.W.; Abboud, J.L.M.; Kamlet, M.J.; Abraham, M.H. J. Sol. Chem. 1985, 14, 153.
11. Reichardt, C. "Solvents and Solvent Effects in Organic Chemistry"; VCH Publishers: New York, 1988.
12. Sadek, P.C.; Carr, P.W.; Doherty, R.M.; Kamlet, M.J.; Taft, R.W.; Abraham, M.H. Anal. Chem. 1985, 57, 2971.
13. Johnson, B.P.; Khaledi, M.G.; Dorsey, J.G. Anal. Chem. 1986, 58, 2354.
14. Carr, P.W.; Doherty, R.M.; Kamlet, M.J.; Taft, R.W.; Melander, W.; Horvath, C. Anal. Chem. 1986, 58, 2674.
15. Leahy, D.E.; Carr, P.W.; Pearlman, R.S.; Taft, R.W.; Kamlet, M.J. Chromatographia 1986, 21, 473.
16. Johnson, B.P.; Khaledi, M.G.; Dorsey, J.G. J. Chromatogr. 1987, 384, 221.
17. Dorsey, J.G.; Johnson, B.P. J. Liq. Chromatogr. 1987, 10, 2695.
18. Park, J.H.; Carr, P.W.; Abraham, M.H.; Taft, R.W.; Doherty, R.M.; Kamlet, M.J. Chromatographia 1988, 25, 373.
19. Kamlet, M.J.; Abraham, M.H.; Carr, P.W.; Doherty, R.M.; Taft, R.W. J. Chem. Soc. Perkins Trans. 2 1988, 2087.
20. Rutan, S.C.; Carr, P.W.; Cheong, W.J.; Park, J.H.; Snyder, L.R. J. Chromatogr. 1989, 463, 21.
21. Park, J.H.; Carr, P.W. J. Chromatogr. 1989, 465, 123.
22. Olsen, L.D.; Hurtubise, R.J. J. Chromatogr. 1989, 474, 347.
23. Laha, S.; Chatterjee, K.; Chakravorti, S.; Ganguly, T.; Banerjee, S.B. Chem. Phys. Lett. 1982, 91 511.
24. Kortum, G.; Vogeland, W.; Andrussow, K. Dissociation Constants of Organic Acids in Aqueous Solutions, Butterworths, London, 1961.
25. Perrin, D.D; Dempsey, B.; Serjeant, E.P. pK<sub>a</sub> Prediction for Organic Acids and Bases, Chapman and Hall, New York, 1981.
26. Vinogradov, S.N.; Linnell, R.H. Hydrogen Bonding, Van Nostrand Reinhold Co., New York, 1971.
27. Snyder, L.R.; Glajch, J.L. J. Chromatogr. 1981, 214, 1.
28. Glajch, J.L.; Snyder, L.R. J. Chromatogr. 1981, 214, 21.