

The Hydroxyl Group-Solvent and Carbonyl Group-Solvent Specific Interactions for Some Selected Solutes Including Positional Isomers in Acetonitrile/Water Mixed Solvents Monitored by HPLC

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We have evaluated the specific hydroxyl group-solvent and carbonyl group-solvent interactions by using an Alltima C₁₈ stationary phase and by measuring the retention data of carefully selected solutes in 60/40, 70/30, and 80/20(v/v%) acetonitrile/water eluents at 25, 30, 35, 40, 45, and 50 °C. The selected solutes are phenol, acetophenone, alkylbenzenes (benzene to hexylbenzene), 4 positional isomers of phenylbutanol, 5-phenyl-1-pentanol, 3 positional isomers of alkylarylketone derived from butylbenzene, and 1-phenyl-2-hexanone. The magnitudes of hydroxyl group-acetonitrile/water specific interaction enthalpies are larger than those of carbonyl group-acetonitrile/water specific interaction enthalpies in general while the magnitudes of carbonyl group-methanol/water specific interaction enthalpies are larger than those of hydroxyl group-methanol/water specific interactions. We observed clear discrepancies in functional group-solvent specific interaction among positional isomers. The variation trends of solute transfer enthalpies and entropies with mobile phase composition in the acetonitrile/water system are much different from those in the methanol/water system. The well-known pocket formation of acetonitrile in aqueous acetonitrile mixtures has proven to be useful to explain such phenomena.

Keywords : Carbonyl group, Hydroxyl group, Specific interaction, Aqueous acetonitrile, Positional isomers.

Introduction

The chromatographic enthalpies and entropies for the solute transfer from the mobile to the stationary phase can be obtained by measuring retention data over a wide range of temperature¹⁻¹² and the specific solute functional group-mobile phase interaction can be derived from such thermodynamic data.¹³⁻¹⁷ In our previous studies, we measured the specific hydroxyl group-solvent and carbonyl group-solvent interaction enthalpies and entropies of phenol and acetophenone in aqueous methanol mixtures using the squalane-impregnated C₁₈ stationary phase,¹³ the specific functional group-solvent interaction enthalpies and entropies of phenol, benzylalcohol, phenethylalcohol, acetophenone, and benzylacetone in aqueous acetonitrile mixtures using the squalane-impregnated C₁₈ stationary phase,¹⁶ and the specific functional group-solvent interaction enthalpies and entropies of 4 positional isomers of phenylbutanol, 5-phenyl-1-pentanol, 3 positional isomers of alkylarylketone derived from butylbenzene, and 1-phenyl-2-hexanone in aqueous methanol mixtures using the Alltima C₁₈ stationary phase.¹⁷ We observed that accessibility of solvent molecules to the solute functional group was a crucial factor for determining the magnitude of specific solute-solvent interaction.^{13,16} In the later study,¹⁷ where a Alltima C₁₈ stationary phase was used, we observed that the carbonyl group-methanol/water interaction is stronger than the hydroxyl group-methanol/water interaction and that there exist clear discrepancies in functional group-solvent interaction among positional isomers.

In this study, we have measured the hydroxyl group-solvent and carbonyl group-solvent specific interactions in acetonitrile/water mixtures using the Alltima C₁₈ stationary phase and analyzed the data and compared the results with those in methanol/water mixtures.

Experimental Section

Acetonitrile and water were of HPLC grade and purchased from Fisher (Pittsburgh, USA) and used without further purification. The selected solutes (benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene, phenol, 1-phenyl-1-butanol, 1-phenyl-2-butanol, 4-phenyl-2-butanol, 4-phenyl-1-butanol, 5-phenyl-1-pentanol, acetophenone, butyrophenone, 1-phenyl-2-butanone, benzylacetone, and 1-phenyl-2-hexanone) were purchased from Aldrich (Milwaukee, IL, USA) and used without purification.

The experimental details were basically the same as those in the previous reports.¹⁴ We used a home-made Alltima (Alltech, Deerfield, IL, USA) C₁₈ column (4.6 × 250 mm). The amount of stationary phase was carefully determined by measuring the weight of stationary phase used for the slurry and the weight of residual stationary phase left in the slurry reservoir and the transfer tubing after packing.¹⁷ The effective stationary phase volume and the phase ratio were determined from the weight of the stationary phase in the column and the carbon load (16%).¹⁷ The determined phase ratio could include some error, but such error will cause a

consistent systematic deviation and will not affect trends of variation of thermodynamic properties. The mobile phase used were acetonitrile/water mixtures (60/40, 70/30, 80/20 v/v %) and the flow rate was fixed at 1 mL/min. The long retention of large alkylbenzenes forced us to examine in such a narrow range of mobile phase composition. The solute retention data were collected at 25, 30, 35, 40, 45, and 50°C. KNO₃ was used as the void volume marker. Three independent measurements on different days were made to calculate the thermodynamic properties.

In order to estimate retention data of a hypothetical nonpolar solute whose intrinsic volume is the same as that of its polar counterpart, we measured retention data of two alkylbenzenes under condition where the intrinsic volume of the polar solute lies between those of the alkylbenzenes. The capacity factor of the hypothetical nonpolar solute was calculated based on the retention data of the two alkylbenzenes under assumption that $\ln k'$ is linear with intrinsic molar volume.

The thermodynamic relationship between the capacity factor (k') and temperature (T) was used to obtain solute transfer enthalpies and entropies and is as follows¹⁻¹⁰:

$$\ln k' = -\Delta H^{\circ}/(RT) + \Delta S^{\circ}/R + \ln \Phi$$

where ΔH° and ΔS° are the standard enthalpy and entropy for the solute transfer from the mobile phase to the stationary phase, respectively, Φ , the phase ratio, and R , the gas constant. We can compute ΔH° from the slope, and ΔS° from the intercept.

When we consider a pair of nonpolar (A) and polar (B) solutes which are of the same size and shape except for a

polar functional group, the functional group-mobile phase specific interaction enthalpy and entropy equal to the differential solute transfer enthalpy ($\Delta\Delta H^{\circ}$) and entropy ($\Delta\Delta S^{\circ}$) between the two solutes¹³ if the stationary phase is a real bulk nonpolar phase.

$$\begin{aligned}\Delta\Delta H^{\circ} &= \Delta H^{\circ}_{\text{A}} - \Delta H^{\circ}_{\text{B}} \\ \Delta\Delta S^{\circ} &= \Delta S^{\circ}_{\text{A}} - \Delta S^{\circ}_{\text{B}}\end{aligned}$$

Results and Discussion

The measured solute transfer enthalpies and entropies times mean temperature (308.15° K) together with the Gibbs free energies of solute transfer from the mobile to the stationary phase for all the solutes are summarized in Table 1. Standard deviations for three replicate measurements of thermodynamic properties (ΔH° , $-T\Delta S^{\circ}$) are less than 300 J/mol for the worst case. The variation trends of solute transfer enthalpies and entropies times temperature (308.15° K) obtained in the MeCN (acetonitrile)/water mixed solvents for alcohols and ketones are shown in Figures 1, 2 (enthalpies) and 3, 4 (entropies), respectively, in comparison with those obtained in the MeOH (methanol)/water mixed solvents.

We note that the solute transfer from the mobile to the stationary phase is enthalpically favorable (-sign) and entropically unfavorable (-sign) in general and that the enthalpic contribution (ΔH°) is predominate compared to the entropic contribution ($-T\Delta S^{\circ}$) as we had also observed in the previous studies.^{14,15,17}

Comparison of magnitudes of ΔH° between alcohols and ketones. The absolute magnitude of solute transfer

Table 1. Comparison of ΔG° , the solute transfer free energies from the MeCN/H₂O mobile phase to the Alltima C₁₈ stationary phase, with ΔH° and $-T\Delta S^{\circ}$ (Unit: J/mol)^{a,b}

Solute	Mobile phase (MeCN%)								
	60			70			80		
	ΔG°	ΔH°	$-T\Delta S^{\circ}$	ΔG°	ΔH°	$-T\Delta S^{\circ}$	ΔG°	ΔH°	$-T\Delta S^{\circ}$
Phenol	-2800	-8200	5400	-1900	-7900	6000	-700	-5700	5000
1-phenyl-1-butanol	-5200	-5900	700	-3900	-6200	2300	-2800	-5500	2700
1-phenyl-2-butanol	-4900	-5200	300	-3700	-5600	1900	-2600	-4900	2300
4-phenyl-2-butanol	-4400	-5000	600	-3400	-5600	2200	-2200	-4800	2600
4-phenyl-1-butanol	-4400	-5700	1300	-3400	-6300	2900	-2300	-5500	3200
5-phenyl-1-pentanol	-5300	-6200	900	-4100	-6800	2700	-2900	-6300	3400
Acetophenone	-4300	-7100	2800	-3300	-7000	3700	-2200	-5600	3400
Butyrophenone	-6600	-8100	1500	-5200	-8000	2800	-3800	-7100	3300
1-phenyl-2-butanone	-5500	-7400	1900	-4200	-7200	3000	-2900	-6000	3100
Benzylacetone	-5200	-7300	2100	-4000	-7300	3300	-2700	-6100	3400
1-phenyl-2-hexanone	-7600	-8300	700	-5900	-8300	2400	-4300	-7500	3200
Benzene	-6000	-7400	1400	-4800	-7100	2300	-3500	-5700	2200
Toluene	-7000	-7900	900	-5700	-7600	1900	-4300	-6600	2300
Ethylbenzene	-8000	-8300	300	-6500	-8100	1600	-5000	-7300	2300
Butylbenzene	-10200	-9900	-300	-8400	-10000	1600	-6700	-9600	2900
Pentylbenzene	-11400	-10900	-500	-9500	-11200	1700	-7600	-11000	3400
Hexylbenzene	-12500	-11900	-600	-10500	-12400	1900	-8400	-12400	4000

^aStandard deviations for three replicate measurements of thermodynamic properties (ΔH° , $-T\Delta S^{\circ}$) are better than 300 J/mol for the worst case. ^bThe Gibbs free energy of solute transfer was computed as follows: $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

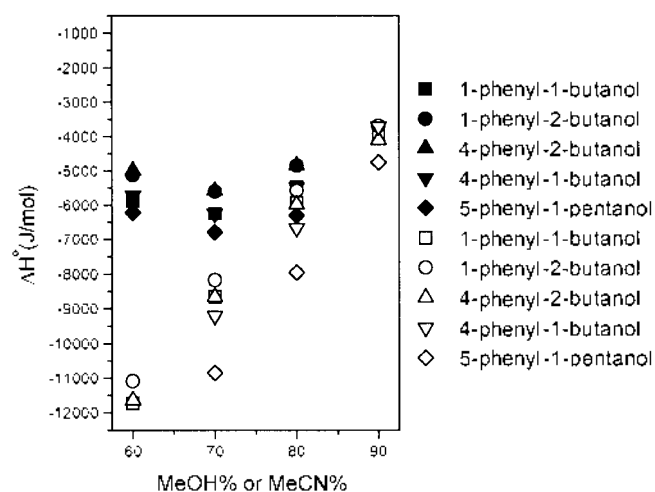


Figure 1. The solute transfer enthalpies of alcohols from the MeCN/H₂O (solid symbols) or MeOH/H₂O (open symbols) mobile phase to the Alltima C₁₈ stationary phase.

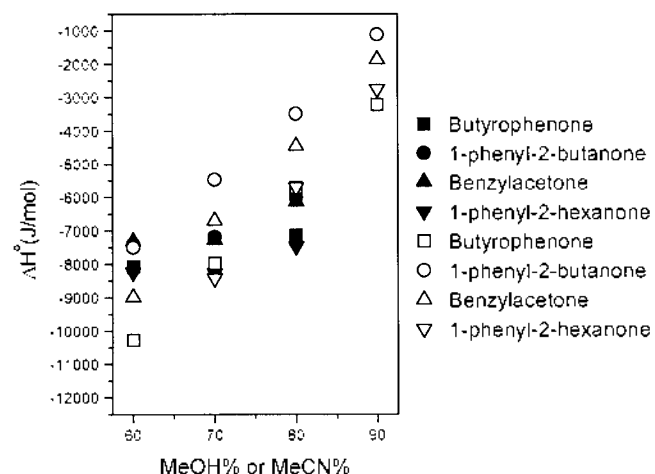


Figure 2. The solute transfer enthalpies of ketones from the MeCN/H₂O (solid symbols) or MeOH/H₂O (open symbols) mobile phase to the Alltima C₁₈ stationary phase.

enthalpy of ketones (butyrophenone and its positional isomers) is greater than that of phenylbutanols in the MeCN/water solvent system (Table 1), which means that the hydroxyl group-solvent interaction is stronger than the carbonyl group-solvent interaction in the MeCN/water mixed solvents. On the other hand, we had observed that the carbonyl group-solvent interaction was greater than the hydroxyl group-solvent interaction in the MeOH/water solvent system.¹⁷ Acetonitrile and ketones are able to accept but unable to donate a hydrogen bond while alcohols are able to accept and donate a hydrogen bond. Therefore, there exists hydrogen bond interaction between an alcohol and acetonitrile while there is no hydrogen bond between a ketone and acetonitrile. For such reasons, the hydroxyl group-MeCN/water specific interaction is stronger than the carbonyl group-MeCN/water specific interaction. We can also note clear discrepancies among positional isomers (Figures 1-4). The orders of strength of solute transfer enthalpies and

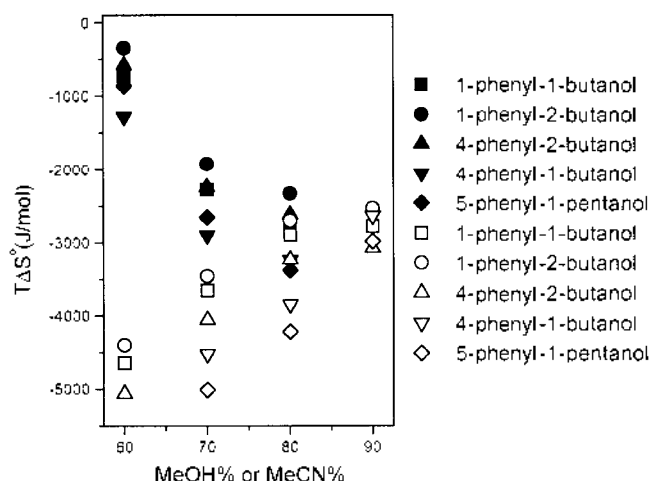


Figure 3. The solute transfer entropies of alcohols from the MeCN/H₂O (solid symbols) or MeOH/H₂O (open symbols) mobile phase to the Alltima C₁₈ stationary phase.

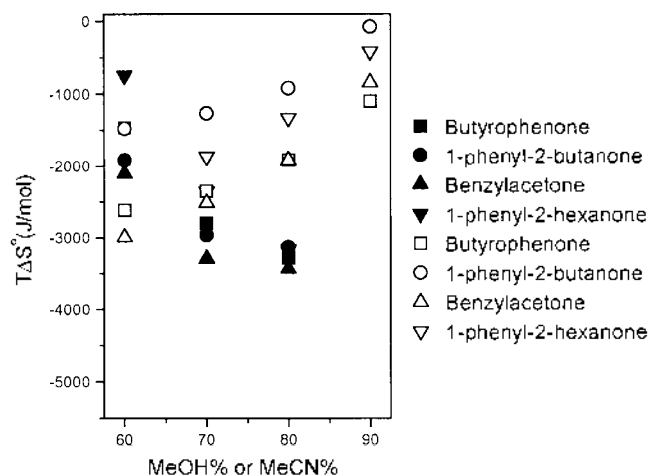


Figure 4. The solute transfer entropies of ketones from the MeCN/H₂O (solid symbols) or MeOH/H₂O (open symbols) mobile phase to the Alltima C₁₈ stationary phase.

entropies among positional isomers in the MeCN/water system are in general similar to those in the MeOH/water system studied previously.¹⁷ Discussion on the relationships between molecular structures and strengths of functional group-solvent interactions can be found elsewhere.¹⁷

Comparison of variation trends of ΔH° and ΔS° between the MeCN/water and MeOH/water systems. The variation trends of solute transfer enthalpies and entropies with mobile phase composition in the MeCN/water system are much different from those in the MeOH/water system. Guillaume *et al.*^{12,18-20} also observed remarkable differences in solute retention between the MeCN/water and MeOH/water systems. ΔH° values follow a curved line as the composition of the organic solvent decreases in the MeCN/water system while a monotonous linear change in ΔH° is observed in the MeOH/water system as shown in Figures 1 and 2. ΔS° gets less negative in the MeCN/water system and more negative in the MeOH/water system as the composi-

tion of organic solvent decreases (Figures 3 and 4). Getting less negative in ΔH° and ΔS° with increase of water content (decrease of composition of organic solvent) in the mixed solvent is a peculiar symptom of hydrophobic interaction.¹⁴ However, it is difficult to admit hydrophobic interaction in the MeCN/water system since no symptom of hydrophobic interaction was observed in the MeOH/water system for the same solvent composition range (Figures 1-4). Hydrophobic effect can be identified by observing a sudden shift of ΔH° and ΔS° in the positive direction compared to the predicted value based on the cavity formation effect.¹⁷ If the peculiar phenomenon in the MeCN/water system were owing to the hydrophobic effect, then such phenomenon should have been observed in the MeOH/water system, too. Discussion concerning the peculiar trend (getting less negative in ΔH° and ΔS° with increase of water content in the mixed solvent) will be continued in the next sections.

Comparison of ΔH° and ΔS° in the MeCN/water system between the Alltima C₁₈ phase and the squalane impregnated C₁₈ phase. We had measured ΔH° and ΔS° values of phenol, acetophenone, benzylacetone, and butylbenzene in the MeCN/water system over the composition range of 30-70% MeCN using the squalane-impregnated C₁₈ stationary phase in one of the former studies.¹⁵ The measured thermodynamic data obtained from the Alltima C₁₈ stationary phase in this study included the data for the solutes mentioned above. Thus we plotted the ΔH° and ΔS° values of the two data sets comparatively in Figures 5 and 6. As we can see in Figures 5 and 6, no symptom of hydrophobic interaction was observed for the data set of the squalane-impregnated C₁₈ stationary phase in the composition range of 30-70% MeCN, and the predominant cavity formation effect (getting more negative in ΔH° with increase of water content) was observed instead. The same phenomena should be observed for the thermodynamic data obtained from the Alltima C₁₈ phase since the hydrophobic interaction is related only to the

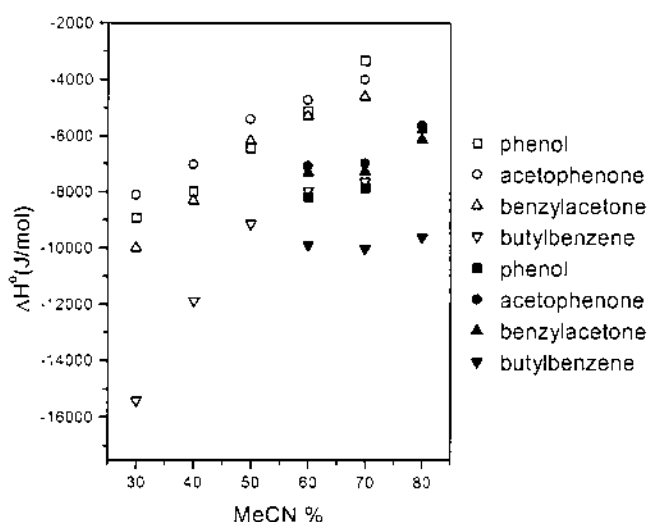


Figure 5. The solute transfer enthalpies from the MeCN/H₂O mobile phase to the Alltima C₁₈ (solid symbols) or squalane-impregnated C₁₈ (open symbols) stationary phase.

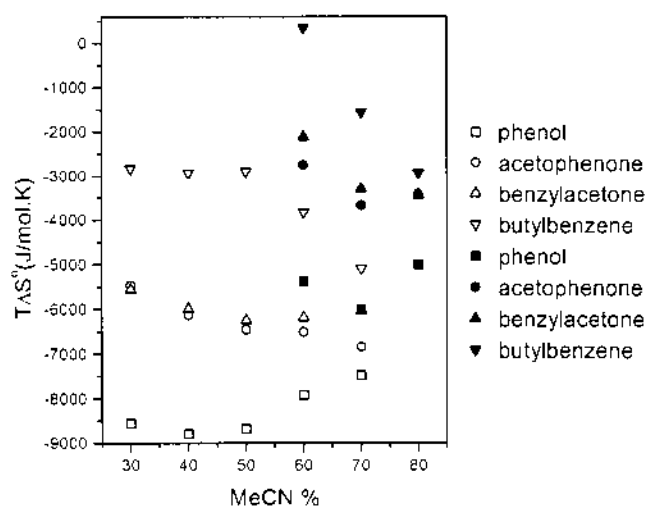


Figure 6. The solute transfer entropies from the MeCN/H₂O mobile phase to the Alltima C₁₈ (solid symbols) or squalane-impregnated C₁₈ (open symbols) stationary phase.

mobile phase.

Adsorption of mobile phase by the Alltima C₁₈ phase. Now that the peculiar trend (getting less negative in ΔH° and ΔS° with increase of water content in the MeCN/water solvent) is not due to hydrophobic interaction, we had better consider that the Alltima C₁₈ phase may be unable to form a perfect bulk phase but should include adsorbed mobile phase and consequently be composed of a ligand-mobile phase mixed phase. Solute will have higher entropy in the mixed phase than in the bulk nonpolar phase. In this mixed stationary phase region, different things will happen in comparison to situations in the real nonpolar bulk stationary phase. First, the effective stationary phase volume will be larger than the volume of collapsed ligands, which causes more retention and more negative ΔH° than is expected based on the volume of collapsed ligands. Second, the solutes in this region will cause higher cavity formation enthalpy than the solutes in the bulk nonpolar phase and this effect will result in less negative ΔH° . Third, the solutes in this region still feel some functional group-solvent specific interactions, which will give more negative ΔH° . The second effect will override the third effect since both effects are caused by the entrapped mobile phase in the stationary phase and the cavity formation effect overrides the solute-solvent interaction effect in the mobile phase. The overall effect can be determined by summing the first effect and the combined effect of the second and the third. The former is greater for all the solutes in the MeCN/water system as shown in Figure 5, while variant trends were observed depending on solute types in the MeOH/water system.¹⁷

Preferential uptake of acetonitrile by the Alltima C₁₈ phase. Getting far less negative in ΔS° for the Alltima C₁₈ phase compared to the squalane-adsorbed C₁₈ phase (Figure 6) seems to be related to the preferential uptake of acetonitrile by the Alltima C₁₈ phase. We can see that the ΔS° value of butylbenzene is even positive at the composition of 60% MeCN. The ΔS° of butylbenzene will be at least close

to zero if we consider an experimental error, which means that the solute maintains its freedom when it transfers from the mobile phase to the stationary phase. The $\Delta\Delta S^\circ$ of pentylbenzene (500 J/mol) or hexylbenzene (600 J/mol) is even more positive than that of butylbenzene (300 J/mol) as shown in Table 1. The solute in the Alltima C_{18} phase will have more freedom than the solute in the squalane-impregnated phase. Nevertheless, it is unlikely that a solute has the same freedom in the stationary phase as that in the mobile phase. The only way to make it rational is assuming preferential uptake of acetonitrile in the effective stationary phase. Butylbenzene (or pentylbenzene or hexylbenzene) is likely to feel similar or more freedom in acetonitrile/ligand mixture (stationary phase) than in acetonitrile/water mixture (mobile phase). Such gain of solute entropy could be cancelled by the loss of solute entropy owing to the confined ligand structures in the stationary phase to give virtually the same solute entropy in both of the mobile and stationary phases. Getting more negative in $\Delta\Delta S^\circ$ with change of MeCN content from 60 to 80% in the mobile phase (Figure 6) will be explained in the next section.

Interpretation of the data based on comparison of solvent structure between the MeCN/water and MeOH/water systems. The different solvent structures between the MeCN/water and MeOH/water systems and the consequences have been well studied by a few research groups.^{4,19,21-26} Their conclusions in such studies seem to be useful to explain our results, too.

Let us rephrase their discussions about the differences in solvent structures between the MeCN/water and MeOH/water mixed solvents. Water is much more similar to methanol than it is to acetonitrile in view of polarity and molecular structure. Water-methanol interaction is known to be more favored than water-water interaction or methanol-methanol interaction.²¹⁻²² There are three species in aqueous methanol solution: methanol/water complex, free water, and free methanol. The major species was found the methanol/water complex when the solution was composed of roughly equal amounts of water and methanol. On the other hand, formation of water-acetonitrile interaction may not be favored compared to maintaining water-water and acetonitrile-acetonitrile interactions.^{4,19,23-26} Therefore water and acetonitrile molecules will tend to form clusters of single components in the mixture although water and acetonitrile are completely mixable at any ratio. Acetonitrile-enriched "microphases" persist in the mobile phase over a wide composition ranges at higher acetonitrile content.⁴ In such a situation, the solute is being solvated primarily in "pockets" of acetonitrile molecules,²³ and the cavity formation effect will be virtually the same for the solvent composition range. The solute-solvent interaction enthalpy will be virtually invariant as well. We can see that variations in $\Delta\Delta H^\circ$ for the MeCN/water system are much less than those of the MeOH/water system in Figures 1 and 2. Getting less negative in $\Delta\Delta S^\circ$ with decreasing acetonitrile content for the MeCN/water system in contrast to getting more negative with decreasing methanol content for the MeOH/water system (as shown in Figure 3

and 4), can also be explained by the peculiar behaviour of the MeCN/water solvent system. Assuming that the solute entropy in the stationary phase is virtually independent of the mobile phase composition, then variation of the solute entropy in the mobile phase governs the variation in $\Delta\Delta S^\circ$. The lower the solute entropy in the mobile phase, the less negative in $\Delta\Delta S^\circ$. Assuming that the solute in the mobile phase is virtually in the acetonitrile "pockets", then the pocket size will be a critical factor. The smaller the pocket size, the lower the entropy of the solute in it. As the acetonitrile content in the mobile phase decreases, the pocket size will be decreased, too, and so is the solute entropy. Such an effect looks like a hydrophobic interaction, but the mechanism of hydrophobic interaction is entirely different from the process taking place here. The effect is vanished if the acetonitrile content decreases below 50% as shown in Figures 6 for the squalane impregnated C_{18} phase.

The real hydrophobic effect caused by water will be found if the acetonitrile content gets even lower (higher water content). Miyabe *et al.*²⁷ observed such effect when the MeCN composition is less than 20% for benzene.

The variation trends of $\Delta\Delta H^\circ$ and $\Delta\Delta S^\circ$ with respect to MeCN composition are not only related to the processes taking place in the mobile phase but also to the processes taking place in the stationary phase since significant differences in the trends between the Alltima C_{18} and the squalane-impregnated C_{18} are observed as shown in Figures 5 and 6.

The differential solute transfer enthalpy for a pair of nonpolar and polar solutes of the same intrinsic volumes obtained in the MeCN/water system. The differential solute transfer enthalpy ($\Delta\Delta H^\circ$) between a polar solute and a hypothetical alkylbenzene whose intrinsic volumes are the same, is not exactly equivalent to the solute functional group-solvent specific interaction enthalpy since acetonitrile is entrapped in the effective stationary phase (Alltima C_{18}). We derived the functional group-MeCN/water specific interaction enthalpies despite the low reliability of their absolute values and plotted them in Figure 7. The results are at least

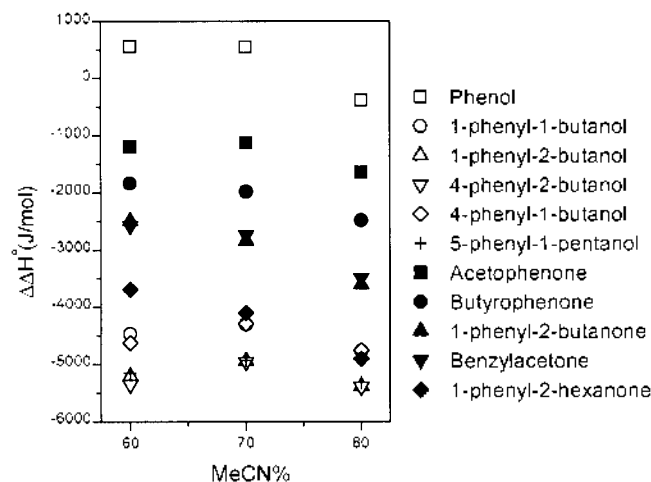


Figure 7. The functional group-MeCN/water specific interaction enthalpies monitored by the Alltima C_{18} stationary phase.

in agreement with chemical senses. The absolute magnitudes of the data are subject to a high error, but the signs and order of magnitudes are consistent to the common sense of chemistry. The hydroxyl group-MeCN/water interactions are in general stronger than the carbonyl group-MeCN/water interactions as we discussed before. There exist clear discrepancies among positional isomers and the variation in the functional group-solvent interaction with respect to mobile phase composition for ketones is much greater than that for alcohols as we observed in the previous study.¹⁷ The general trends of positional effect are also similar to those observed in the previous study¹⁷ although reversion of order is found in one or two cases probably owing to the different solvent behaviors in the MeCN/water system from those in the MeOH/water system.

An interesting thing is the ΔH° values of phenol. They are even positive or at least close to zero if uncertainty is considered. Its meaning is that phenol feels similar or stronger functional group-phase interaction in the stationary phase than in the mobile phase. The unusual aspect of phenol can also be found in the ΔS° data (Table 1). Phenol has abnormally more negative (-19 J/mol.K at 70% MeCN) values than other solutes, for example, benzene (-7 J/mol.K) or toluene (-6 J/mol.K). Residual silanol group effect seems to be related to such a phenomenon. The Alltima C₁₈ stationary phase is known to be end-capped. Nevertheless, there should be still some residual silanol groups which are sterically hindered and are hard for large solutes to approach but are accessible by a small solute such as phenol. Capture of phenol by the silanol group will be accompanied by occurrence of a strong functional group-stationary phase interaction and a large decrease of solute entropy in the stationary phase. This explanation is based on the hypothesis that the residual silanol groups are well hidden to large solutes but are exposed to small molecules such as phenol.

Conclusion

We have measured solute transfer enthalpies and entropies from the acetonitrile/water mobile phase to the Alltima C₁₈ stationary phase and critically analyzed and compared the data with those previously obtained in the methanol/water mobile phase. The hydroxyl group-acetonitrile/water interaction has proven to be stronger than the carbonyl group-acetonitrile/water interaction while the carbonyl group-methanol/water interaction was stronger than the hydroxyl group-methanol/water interaction. There are clear discrepancies in functional group-solvent interaction among positional isomers. Hydrogen bond interaction is the major

factor in specific interactions and dipole-dipole interaction will contribute a little, while steric effect becomes important when positional isomers are comparatively examined. In addition, mobile phase composition is also an important factor in the specific interaction between the solute functional group and the mobile phase. There existed clear differences in trends of variation of ΔH° and ΔS° with respect to mobile phase composition between the methanol/water and acetonitrile/water systems. The formation of acetonitrile pockets described in the literature was useful to explain such results.

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