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Positional effect of solute functional group among positional isomers in hydroxyl group–solvent and carbonyl group–solvent specific interactions in methanol–water mixed solvents monitored by high-performance liquid chromatography

Won Jo Cheong*, Young Ik Keum

Department of Chemistry and Center of Advanced Bioseparation Technology, Inha University, 253 Yonghyun-Dong, Nam-ku, Incheon 402-751, South Korea

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Abstract

We have evaluated the hydroxyl group–solvent and carbonyl group–solvent specific interactions by using mostly an Alltima C_{18} stationary phase and subsidiarily squalane-adsorbed C_{18} phase, and by measuring the retention data of carefully selected solutes in 60:40, 70:30, 80:20 and 90:10 (%, v/v) methanol–water eluents at 25, 30, 35, 40, 45 and 50°C. The selected solutes are four positional isomers of phenylbutanol, 5-phenyl-1-pentanol, three positional isomers of alkylarylketone derived from butylbenzene, and 1-phenyl-2-hexanone. The magnitudes of carbonyl group–solvent specific interaction enthalpies are larger than those of hydroxyl group–solvent specific interaction enthalpies in general. We observed clear discrepancies in functional group–solvent specific interactions among positional isomers. The spatial accessibility of the functional group by the solvent molecules seems to govern the strength of interaction. The relationships between molecular structures and functional group accessibilities have been discussed. The specific functional group–mobile phase interactions obtained by the Alltima C_{18} stationary phase were systematically different from those obtained by the squalane-impregnated C_{18} stationary phase, which may be due to structural differences between the two phases.

Keywords: Functional group; Positional effect; Hydroxyl group; Carbonyl group; Spatial accessibility; Solute–solvent interactions

1. Introduction

Chromatography is useful to obtain information on solute–solvent thermodynamic interactions. Such information can be obtained by measuring retention data over a wide range of temperature [1–13]. In some of our previous reports [14,15], we showed that the carbonyl group–solvent specific interaction of acetophenone in aqueous–methanol mixtures is much stronger than the hydroxyl group–solvent specific interaction of phenol by measuring solute retention on a squalane-impregnated C_{18} phase. We proposed accessibility of solvent molecules to the solute functional group as the criterion for determin-

*Corresponding author. Tel.: +82-32-8607-114; fax: +82-32-8675-604.

E-mail address: wjcheong@inha.ac.kr (W.J. Cheong).

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ing the magnitude of specific solute–solvent interaction. In later reports [16,17], we confirmed that spatial accessibility is a very crucial factor to the specific functional group–solvent interaction by comparing such interactions in acetonitrile–water mixed solvents among solutes of different functional group accessibilities, for example phenol vs. benzylalcohol and acetophenone vs. benzylacetone.

We had used a squalane-impregnated C_{18} phase to secure a partition mechanism in the previous studies. In this study, we employed mostly a regular C_{18} stationary phase and methanol–water mobile phases and examined differences in functional group–solvent interactions among positional isomers.

The enthalpy and entropy of solute transfer from the mobile to the stationary phase are easily obtained from the slope and intercept in the van 't Hoff plot ($\ln k'$ vs. $1/T$). If we consider a pair of polar and nonpolar solutes which are of the same size and shape except for a polar functional group, the enthalpy of specific functional group–mobile phase interaction can be obtained only by subtracting the solute transfer enthalpy of the nonpolar solute from that of the polar solute [14].

2. Experimental

Methanol and water were of HPLC grade and purchased from Fisher (Pittsburg, PA, USA) and used without further purification. The selected solutes (butylbenzene, pentylbenzene, hexylbenzene, 1-phenyl-1-butanol, 1-phenyl-2-butanol, 4-phenyl-2-butanol, 4-phenyl-1-butanol, 5-phenyl-1-pentanol, butyrophenone, 1-phenyl-2-butanone, benzylacetone and 1-phenyl-2-hexanone) were purchased from Aldrich (Milwaukee, WI, USA) and used without purification.

The experimental details were basically the same as those in the previous reports [14–17]. We used mostly a laboratory-made Alltima (Alltech, Deerfield, IL, USA) C_{18} column (250×4.6 mm) in this study. It was packed under pressure (8000 p.s.i.; 1 p.s.i.=6894.76 Pa) by the Alltech slurry packer. 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. The stationary phase volume was determined from the weight of the stationary phase in the column and the carbon load (16%) provided by the maker under assumption that the density of effective stationary phase is approximated by the density of hexadecane. The mobile phase volume was determined by averaging the retention volume of KNO_3 over the temperature range and mobile phase composition used. Thus we obtained the phase ratio of 0.28. The variation of KNO_3 retention volume was less than 2%. The method for determining the phase ratio is certainly not the best way possible. 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 with respect to mobile phase composition or among solutes.

The mobile phases used were methanol–water mixtures (60:40, 70:30, 80:20, 90:10, v/v) and the flow-rate was fixed at 1 ml/min. The solute retention data were collected at 25, 30, 35, 40, 45 and 50°C. KNO_3 was used as the void volume marker.

The thermodynamic solute retention data for a few selected solutes (4-phenyl-1-butanol, 5-phenyl-1-pentanol, benzylacetone and 1-phenyl-2-hexanone) on the squalane-impregnated C_{18} stationary phase were also measured in order to compare the results with those of the Alltima C_{18} phase. Preparation of the squalane-impregnated C_{18} column using the Spherisorb ODS-2 stationary phase can be found elsewhere [15].

More than two independent measurements on different days were made to calculate the thermodynamic properties. When the difference between the two measurements was larger than 5%, additional measurements were made. 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 on condition that 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. It has been well known that $\ln k'$ of a homologous series of alkylbenzenes in reversed-phase liquid chromatography (RPLC) is a linear function of carbon number (intrinsic molar volume, too). We also personally

checked that our ln k' of alkylbenzenes showed a good linearity with intrinsic molar volume. We ignored the dipole-induced dipole interaction since estimating its magnitude is beyond the scope of this study, thus some error was incorporated in the thermodynamic properties obtained. The specific interaction (hydrogen bonding) is, however, much stronger. Furthermore, the solute functional group–mobile phase interaction was obtained by getting the difference in the thermodynamic properties of solute transfer between the polar solute with a small polar functional group and its hypothetical alkylbenzene counterpart, by which the dipole–induced dipole interactions are cancelled out.

3. Results and discussion

The measured solute transfer enthalpies and entropies from the mobile to the Alltima C_{18} stationary phase and their standard deviations for all the solutes are summarized in Table 1, and the measured thermodynamic solute transfer properties from the mobile to the squalane-adsorbed C_{18} stationary phase, in Table 2. The variation trends of solute transfer enthalpies and entropies obtained by the Alltima C_{18} phase for the alcohols and ketones with respect to mobile phase composition are compared in Figs. 1 and 2.

3.1. The solute transfer enthalpies from the mobile phase to the Alltima C_{18} phase

From the results, we can easily note that the solute transfer from the mobile to the stationary phase is enthalpically favorable (− sign) and entropically unfavorable (− sign) and that the enthalpic contribution (ΔH^0) is predominate compared to the entropic contribution ($-T\Delta S^0$) for the Alltima C_{18} stationary phase (Table 1). On the other hand, the entropic contribution is rather comparable to the enthalpic contribution for the squalane-adsorbed C_{18} phase (Table 2).

We can see that the solute transfer enthalpies of alcohols are considerably more negative than those of ketones, which means that the carbonyl group/methanol–water interaction is stronger than the hydroxyl group/methanol–water interaction (Fig. 1).

The really interesting observation is that there exist clear discrepancies in ΔH^0 among positional isomers. The effect of variation among positional isomers is greater for ketones (butyrophenone, 1-phenyl-2-butanone and benzylacetone) than for alcohols (1-phenyl-1-butanol, 1-phenyl-2-butanol, 4-phenyl-2-butanol and 4-phenyl-1-butanol). We guess that such effects are related to the structural differences of the compounds, and consequently to the different functional group–solvent interactions. We will discuss about it in detail later.

3.2. The solute transfer entropies from the mobile to the Alltima C_{18} phase

The entropy decrease accompanied by the solute transfer from the mobile to the stationary phase is much greater for alcohols than for ketones (Fig. 2). It is difficult to explain. ΔS^0 is the sum of the solute entropy change and the solvent entropy change in the mobile and stationary phases upon solute transfer, and maybe a delicate function of some entangled factors such as the solute size relative to the solvent, the solute shape, the type and position of the functional group, the type and strength of the specific solute–solvent interaction, and the type of solvent and its own intermolecular interactions. We had better just confirm that the type and position of the functional group greatly influence ΔS^0 as shown in Fig. 2.

3.3. The solute transfer free energies

The solute transfer free energies from the mobile to the stationary phase were calculated as $\Delta G^0 = \Delta H^0 - T\Delta S^0$, and shown in Table 1 (for the Alltima C_{18} stationary phase) and Table 2 (for the squalane-impregnated C_{18} stationary phase). ΔG^0 values are denoted by an asterisk.

ΔG^0 values of Table 1 are all negative, which means that all the solutes are favored to stay in the Alltima C_{18} phase rather than stay in the mobile phase. Considering four isomeric alcohols, we can note that the differences in ΔG^0 among positional isomers are smaller than those in ΔH^0 owing to a canceling effect of $-T\Delta S^0$ against ΔH^0. Such a trend is more obvious as the methanol content in the mobile phase increases. As for the three ketone

Table 1
The solute transfer enthalpies (ΔH^0) with their standard deviations in comparison with the solute transfer entropies (ΔS^0) times temperature (308.15 K) given in parentheses and the solute transfer free energy (based on the relationship $\Delta G^0 = \Delta H^0 - T\Delta S^0$, denoted by an asterisk) from the mobile phase to the stationary phase obtained by the Alltima C_{18} stationary phase (unit: J/mol)

Solute	Mobile phase (MeOH, %)			
	60	70	80	90
1-Phenyl-1-butanol	−11 700±110 (−4600±120) −7100*	−8600±280 (−3700±260) −4900*	−5900±90 (−2900±90) −3000*	−4000±190 (−2800±200) −1200*
1-Phenyl-2-butanol	−11 100±100 (−4400±110) −6700*	−8200±290 (−3500±270) −4700*	−5600±100 (−2700±100) −2900*	−3700±220 (−2500±240) −1200*
4-Phenyl-2-butanol	−11 600±200 (−5100±210) −6500*	−8700±270 (−4100±250) −4600*	−6000±110 (−3200±100) −2800*	−4100±270 (−3100±280) −1200*
4-Phenyl-1-butanol	–	−9200±200 (−4500±190) −4700*	−6700±70 (−3800±60) −2900*	−3700±340 (−2600±340) −1100*
5-Phenyl-1-pentanol	–	−10 800±200 (−5000±200) −4700*	−8000±70 (−4200±60) −3800*	−4800±190 (−3000±200) −1800*
Butyrophenone	−10 300±70 (−2600±80) −7700*	−8000±170 (−2400±160) −5600*	−5700±80 (−1900±70) −3800*	−3200±250 (−1100±260) −2100*
1-Phenyl-2-butanone	−7500±70 (−1500±70) −6000*	−5500±160 (−1300±140) −4200*	−3500±100 (−900±90) −2600*	−1100±390 (−70±400) −1000*
Benzylacetone	−9000±70 (−3000±70) −6000*	−6700±200 (−2500±180) −4200*	−4500±80 (−1900±70) −2600*	−1900±360 (−800±360) −1100*
1-Phenyl-2-hexanone	–	−8400±210 (−1900±200) −6500*	−5700±60 (−1300±60) −4400*	−2800±200 (−400±200) −2400*
Butylbenzene	−16 800±100 (−3700±110) −13 100*	−13 600±250 (−3400±230) −10 200*	−10 100±70 (−2500±60) −7600*	−6300±60 (−1200±60) −5100*
Pentylbenzene	–	−15 700±280 (−4200±260) −11 500*	−11 800±70 (−3200±60) −8600*	−7500±20 (−1700±30) −5800*
Hexylbenzene	–	−17 900±300 (−5000±280) −12 900*	−13 500±70 (−3900±70) −9600*	−8800±10 (−2300±10) −6500*

Table 2
The solute transfer enthalpies (ΔH^0) with their standard deviations in comparison with the solute transfer entropies (ΔS^0) times temperature (308.15 K) given in parentheses and the solute transfer free energies (based on the relationship $\Delta G^0 = \Delta H^0 - T\Delta S^0$, denoted by an asterisk) from the mobile phase to the stationary phase obtained by the squalane-impregnated C_{18} stationary phase (unit: J/mol)

Solute	Mobile phase composition (MeOH, %)			
	60	70	80	90
Benzylacetone	−10 100±230	−7700±450	−5100±290	−3300± 210
	(−8900±220)	(−8400±430)	(−7400±280)	(−7200±220)
	−1200*	700*	2300*	3900*
4-Phenyl-1-butanol	−11 700±220	−9300±450	−6500±340	−4600±280
	(−10 100±210)	(−9700±440)	(−8700±320)	(−8600±290)
	−1600*	400*	2200*	4000*
5-Phenyl-1-pentanol	−13 700±220	−11 000±480	−7700±280	−5500±260
	(−10 700±210)	(−10 300±470)	(−9100±270)	(−8800±270)
	−3000*	700*	1400*	3300*
1-Phenyl-2-hexanone	−11 900±240	−9200±520	−5900±230	−3500±180
	(−8000±230)	(−7700±500)	(−6500±220)	(−6200±190)
	−3900*	−1500*	600*	2700*
Butylbenzene	−16 100±100	−12 800±390	−8700±240	−5500±40
	(−8100±110)	(−7500±390)	(−6100±230)	(−5400±50)
	−8000*	−5300*	−2600*	−100*
Pentylbenzene	−18 600±140	−15 000±400	−10 400±260	−6800±30
	(−9000±140)	(−8500±390)	(−6700±250)	(−5900±40)
	−9600*	−6500*	−3700*	−900*
Hexylbenzene	−20 900±150	−17 100±460	−12 000±300	−8000±80
	(−9800±160)	(−9400±460)	(−7400±290)	(−6400±90)
	−11 100*	−7700*	−4600*	−1600*

isomers (butyrophenone, 1-phenyl-2-butanone and benzylacetone), ΔG^0 values of 1-phenyl-2-butanone are almost identical to those of benzylacetone while ΔG^0 values of butyrophenone are quite different from those of the two solutes. The unique structure of butyrophenone and its consequences in solute functional group–mobile phase interaction will be discussed later.

ΔG^0 values of Table 2 are positively shifted compared to those of Table 1, and the sign of ΔG^0 of some solutes is even positive especially for mobile phases of high methanol content. This implies that the solute tend to retain longer in the Alltima C_{18} phase than they do in the squalane-adsorbed C_{18} phase, which was actually observed in our experiments. It is mostly due to entropic effect. The enthalpic and entropic effects between the squalane-adsorbed C_{18} phase and the Alltima C_{18} phase are compared in Tables 3 and 4, respectively, and their comparison will be discussed later.

3.4. The solute functional group–mobile phase specific interaction enthalpies

Now let us examine the differential solute transfer enthalpies and entropies between a pair of solutes (a polar solute with a functional group and a hypothetical alkylbenzene whose intrinsic volume is exactly the same as the polar solute). Such results are shown in Figs. 3 and 4. The differential solute transfer enthalpy is equal to the specific functional group–mobile phase interaction enthalpy if the solute retention follows a perfect partition mechanism [13]. We again see that the carbonyl group/methanol–

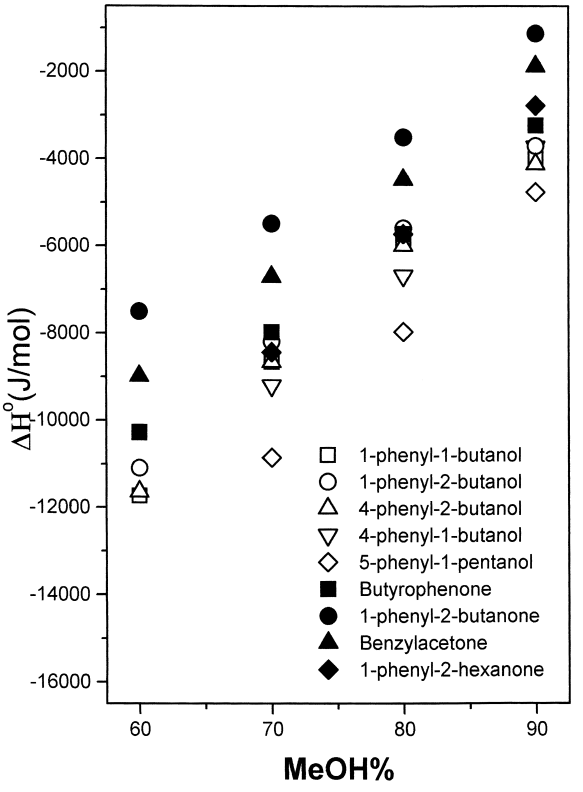

Fig. 1. The solute transfer enthalpies from the aqueous methanol solvents to the Alltima C_{18} stationary phase.

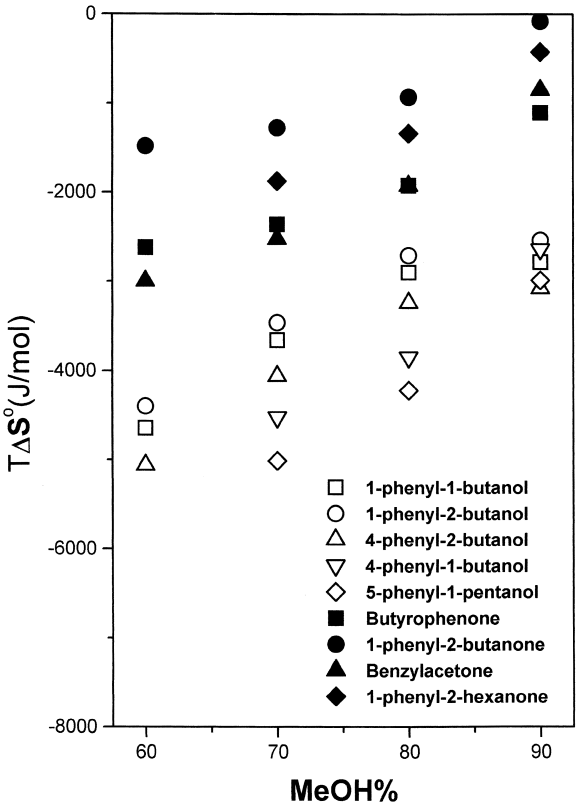

Fig. 2. The solute transfer entropies times temperature (308.15 K) from the aqueous methanol solvents to the Alltima C_{18} stationary phase.

water interaction enthalpies are more negative than the hydroxyl group/methanol–water interaction enthalpies and that the interactions are greatly influenced by the position of the functional group (Fig. 3). The positional effect of functional group is greater for the carbonyl group than for the hydroxyl group. It seems that the structural differences induced by the functional groups or among the positional isomers play an important role in the functional group–solvent interactions. We have drawn the molecular structures of the isomeric alcohols (1-phenyl-1-butanol, 1-phenyl-2-butanol, 4-phenyl-2-butanol and 4-phenyl-1-butanol) and ketones (butyrophenone, 1-phenyl-2-butanone and benzylacetone) using the Cambridgesoft ChemOffice software (the MM2 method) in order to figure out how the position of functional group induces structural change and consequently influences the strength of interaction with solvent molecules. Such drawings are shown in Fig. 5 (alcohol isomers) and Fig. 6 (ketones). The structure of the reference molecule, butylbenzene is also shown in Fig. 6. The oxygen atoms in Fig. 5 are drawn with their lone pair electrons. The molecular structures are based on lowest energy conformations [18].

Hydrogen bond formation of solute carbonyl group with hydrogen bond donating solvents such as methanol–water mixtures seems to be stronger than that of solute hydroxyl group because the carbonyl group O atom is free of any substituted atom while the hydroxyl group O atom has a hydrogen atom that may serve as a steric barrier to approaching solvent molecules. In addition, the carbon to which the hydroxyl group is bound has an extra hydrogen which causes more steric barrier compared to the carbonyl carbon. We should consider that the solute hydroxyl group is able to make hydrogen bond by donating hydrogen bond toward solvent molecules

Table 3
The solute transfer enthalpies from the mobile phase to the stationary phase obtained by the squalane-impregnated C_{18} stationary phase in comparison with those (given in parentheses) obtained in the Alltima C_{18} phase (unit: J/mol)

Solute	Mobile phase composition (MeOH, %)			
	60	70	80	90
Benzylacetone	−10 100 (−9000)	−7700 (−6700)	−5100 (−4500)	−3300 (−1900)
4-Phenyl-1-butanol	−11 700 (–)	−9300 (−9200)	−6500 (−6700)	−4600 (−3700)
5-Phenyl-1-pentanol	−13 700 (–)	−11 000 (−10 800)	−7700 (−8000)	−5500 (−4800)
1-Phenyl-2-hexanone	−11 900 (–)	−9200 (−8400)	−5900 (−5700)	−3500 (−2800)
Butylbenzene	−16 100 (−16 800)	−12 800 (−13 600)	−8700 (−10 100)	−5500 (−6300)
Pentylbenzene	−18 600 (–)	−15 000 (−15 700)	−10 400 (−11 800)	−6800 (−7500)
Hexylbenzene	−20 900 (–)	−17 100 (−17 900)	−12 000 (−13 500)	−8000 (−8800)

Table 4
The solute transfer entropies times temperature (308.15 K) obtained by the squalane-impregnated C_{18} stationary phase in comparison with those (given in parentheses) obtained by the Alltima C_{18} stationary phase (unit: J/mol)

Solute	Mobile phase composition (MeOH, %)			
	60	70	80	90
Benzylacetone	−8900 (−3000)	−8400 (−2500)	−7400 (−1900)	−7200 (−800)
4-Phenyl-1-butanol	−10 100 (–)	−9700 (−4500)	−8700 (−3800)	−8600 (−2600)
5-Phenyl-1-pentanol	−10 700 (–)	−10 300 (−5000)	−9100 (−4200)	−8800 (−3000)
1-Phenyl-2-hexanone	−8000 (–)	−7700 (−1900)	−6500 (−1300)	−6200 (−400)
Butylbenzene	−8100 (−3700)	−7500 (−3400)	−6100 (−2500)	−5400 (−1200)
Pentylbenzene	−9000 (–)	−8500 (−4200)	−6700 (−3200)	−5900 (−1700)
Hexylbenzene	−9800 (–)	−9400 (−5000)	−7400 (−3900)	−6400 (−2300)

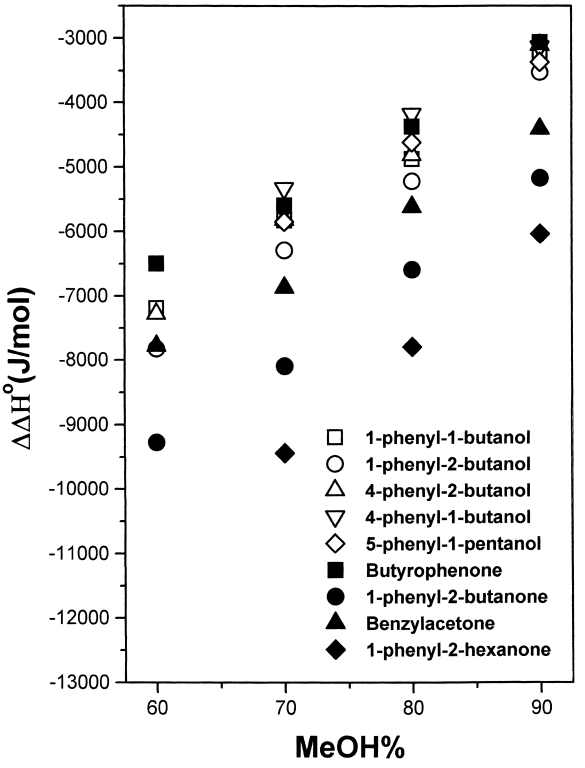

Fig. 3. The differential solute transfer enthalpies which are equivalent to the specific functional group/methanol–water interaction enthalpies obtained by the Alltima C_{18} stationary phase.

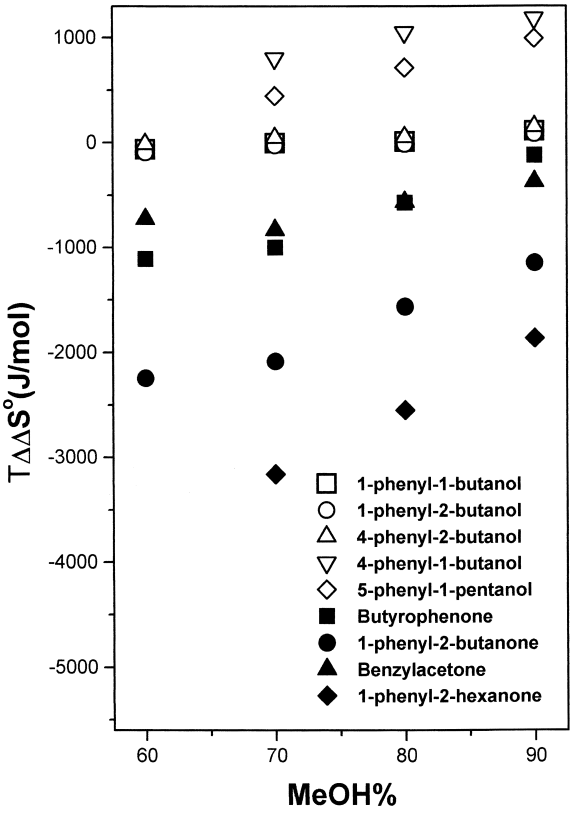

Fig. 4. The differential solute transfer entropies times temperature (308.15 K) obtained by the Alltima C_{18} stationary phase.

while the solute carbonyl group is not. However, the solute molecules are much larger than solvent molecules (water and methanol) thus the solute hydroxyl group will have a higher electron density (induction effect) than the solvent hydroxyl group. In such a situation, the solute hydroxyl group will prefer accepting hydrogen bond to donating hydrogen bond, and the contribution of hydrogen bond formation where the solute hydroxyl group donates hydrogen bond to solvent molecules, will be much less important. Of course, hydrogen bond donating ability of water is greater than that of methanol for the same reason, and $\Delta\Delta H^0$ gets more negative as the water content in the mobile phase increases (Fig. 3).

3.5. The positional effect in functional group–mobile phase interaction among isomers

Now let us examine the positional effect of functional group. As we can see in Figs. 3 and 4, the positional effect is much more dramatic for the ketone isomers than for the alcohol isomers. The absolute magnitude of $\Delta\Delta H^0$ of butyrophenone is smaller than those of benzylacetone and 1-phenyl-2-butanone. It can be explained by the following arguments. All the carbon atoms, the oxygen, and the phenyl hydrogens of butyrophenone are in the same plane and consequently one of the hydrogens of the phenyl ring is forced to be placed in the position in closer proximity to the oxygen atom (Fig. 6), therefore the oxygen atom of butyrophenone will experience more steric barrier when it meets solvent molecules. The reason why the absolute magnitude of $\Delta\Delta H^0$ of 1-phenyl-2-butanone is larger than that of benzylacetone should also be related to the steric factor. As we can see in Fig. 6, the oxygen atom of benzylacetone is close to benzyl CH_2 hydrogens and

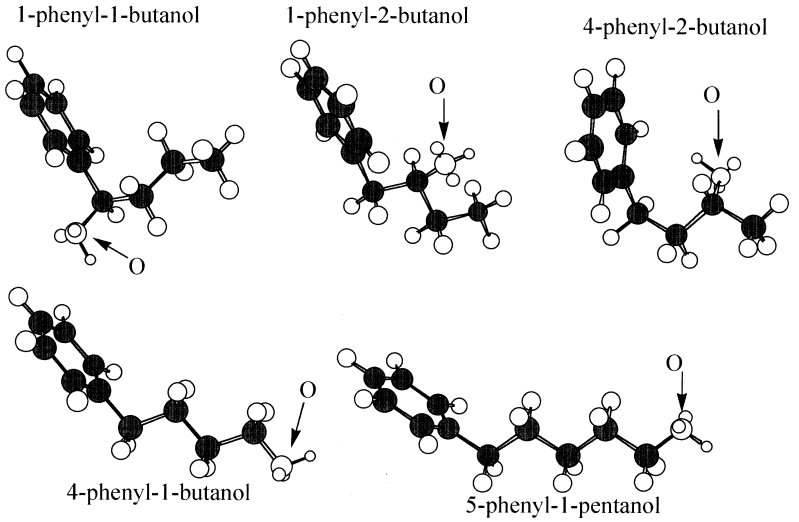

Fig. 5. The molecular structures of 1-phenyl-1-butanol, 1-phenyl-2-butanol, 4-phenyl-2-butanol, 4-phenyl-1-butanol and 5-phenyl-1-pentanol.

CH_3 hydrogens whose carbon is directly attached to the oxygen while the oxygen atom of 1-phenyl-2-butanone is close enough to only the terminal CH_3 hydrogens whose carbon is next to the carbon in bondage with the oxygen. Thus we may acknowledge that the oxygen of 1-phenyl-2-butanone feels less steric barrier. An interesting thing we should note is that the absolute magnitude of $\Delta\Delta H^0$ of 1-phenyl-2-hexanone is still considerably larger than that of 1-phenyl-2-butanone (Fig. 3). The steric difference between the two solutes is terminal CH_3 (1-phenyl-2-butanone) vs. CH_2 (1-phenyl-2-hexanone) as shown in Fig. 6, which seems to be insufficient to explain such a large discrepancy. We

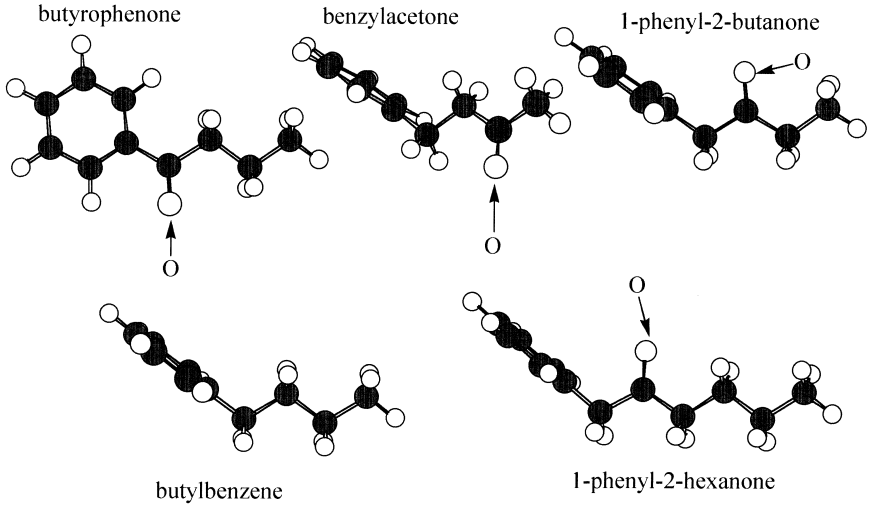

Fig. 6. The molecular structures of butyropheneone, benzylacetone, 1-phenyl-2-butanone, butylbenzene and 1-phenyl-2-hexanone.

may add the induction effect here. The induction effect of butyl group attached to the oxygen in 1-phenyl-2-hexanone is larger than that of ethyl group in 1-phenyl-2-butanone, thus the electron density of the oxygen atom of 1-phenyl-2-hexanone is higher and the susceptibility to hydrogen bond formation with solvent molecules gets larger than that of 1-phenyl-2-butanone.

On the other hand, it seems that there are not much steric differences for the hydroxyl group among the phenylbutanol isomers since the $\Delta\Delta H^0$ value of 4-phenyl-1-butanol is less negative than any other isomer (Fig. 3) although the hydroxyl group of 4-phenyl-1-butanol looks sterically freer than that of any other isomer (Fig. 5). The steric factor seems to be unimportant for the hydroxyl group–solvent interaction of the phenylbutanol isomers. Instead, the induction effect is the major factor that can explain the trends in strength of interaction. 4-Phenyl-1-butanol has a terminal hydroxyl group and is a primary alcohol while the other isomers are secondary alcohols. Secondary alcohols have a higher electron density in the oxygen atom than primary alcohols. That is why the absolute magnitude of $\Delta\Delta H^0$ of 4-phenyl-1-butanol is the smallest among the positional isomers. 1-Phenyl-2-butanol has the benzyl and ethyl substituents which yield a stronger induction effect than others, and its $\Delta\Delta H^0$ is the most negative among the phenylbutanol isomers. The $\Delta\Delta H^0$ value of 5-phenyl-1-pentanol is also more negative than that of 4-phenyl-1-butanol owing to the larger induction effect (Fig. 3).

3.6. The differential solute transfer entropies

$\Delta\Delta S^0$ is more difficult to analyze. As we mentioned before, it is a delicate function of some entangled factors such as the solute size and shape, the type and position of the functional group, the type and strength of the specific solute–solvent interactions, etc., in the mobile and stationary phases. Furthermore, $T\Delta\Delta S^0$ is much less significant compared to $\Delta\Delta H^0$. The absolute magnitude of $T\Delta\Delta S^0$ is at best less than 30% of that of $\Delta\Delta H^0$. We only emphasize that there is a clear positional effect of functional group on the magnitude of $\Delta\Delta S^0$ and that such effect is greater for the ketone isomers owing to their variant structural differences than for the alcohol isomers as shown in Fig. 4.

3.7. Comparison of thermodynamic properties of solute transfer between the Alltima C_{18} and squalane-adsorbed C_{18} phases

We measured thermodynamic properties for some of the solutes (4-phenyl-1-butanol, 5-phenyl-1-pentanol, benzylacetone and 1-phenyl-2-hexanone) using the squalane-impregnated C_{18} stationary phase in order to compare the results with those of the Alltima C_{18} phase. The results obtained by the squalane-impregnated C_{18} phase are summarized in Table 2. In addition, the solute transfer enthalpies obtained by the squalane-adsorbed C_{18} phase were compared with those obtained by the Alltima C_{18} phase in Table 3, and the solute transfer entropies times temperature (308.15 0K) obtained by the squalane-adsorbed C_{18} phase were compared with those obtained by the Alltima C_{18} phase in Table 4. According to Table 3, the ΔH^0 values of alcohols obtained by the Alltima C_{18} are rather good agreement with those obtained by the squalane-impregnated C_{18} and that the ΔH^0 values of ketones obtained by the Alltima C_{18} are considerably less negative than those obtained by the squalane-impregnated C_{18}. On the other hand, the ΔH^0 values of alkylbenzenes obtained by the Alltima C_{18} are considerably more negative than those obtained by the squalane-impregnated C_{18}. As shown in Table 4, the $T\Delta S^0$ values obtained by the Alltima C_{18} are much less negative than those obtained by squalane-impregnated C_{18} for all the solutes. In general, the difference in $T\Delta S^0$ between the two phases is much more significant than the difference in ΔH^0 (Tables 3 and 4).

Such trends may be due to structural differences between the squalane-impregnated C_{18} phase and the Alltima C_{18} phase. Since all the solutes lose more entropy in the squalane-impregnated C_{18} phase than in the Alltima C_{18} phase for the solute transfer from the mobile to the stationary phase, we can accept that the squalane-impregnated C_{18} phase is more viscous (less freedom in it). Further discussion on the Alltima C_{18} phase is avoided since no supporting data are available at present.

We should mention that there could be residual

silanol group effect, too. Its effect is enhancing solute retention owing to the specific functional group–stationary phase interaction and resulting in more negative ΔH^0. However, the stationary phases used in this study are known to be end-capped, and in addition, the solutes of this study are large enough to avoid contacting with any silanol groups owing to steric hindrance.

We should note that the specific functional group–mobile phase interactions measured by the Alltima C_{18} may be somewhat overestimated although trends of thermodynamic properties such as the positional effects are still valid. The $\Delta\Delta H^0$ measured by the Alltima C_{18} and squalane-impregnated C_{18} are compared in Fig. 7. An interesting idea is to use our method to characterize C_{18} stationary phases. We expect that measured ΔH^0, ΔS^0, $\Delta\Delta H^0$, $\Delta\Delta S^0$ values of some selected solutes such as 4-phenyl-2-butanol and benzylacetone should serve as good indexes to describe properties of stationary phases in comparison with the values obtained by a real nonpolar bulk-like stationary phase. We will carry out such study in the future.

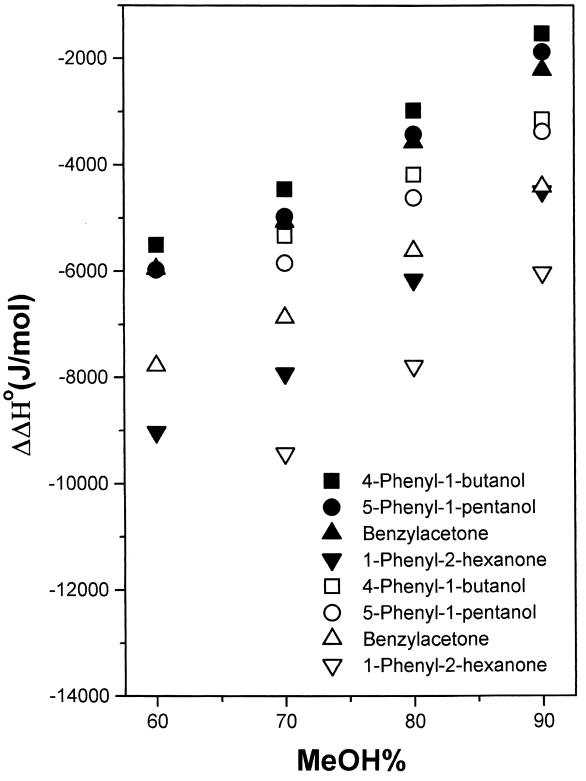

Fig. 7. Comparison of the specific functional group–methanol–water interaction enthalpies obtained by the Alltima C_{18} stationary phase (open symbols) with those obtained by the squalane-impregnated C_{18} stationary phase (solid symbols).

4. Conclusion

The specific solute functional group–mobile phase interaction enthalpies and entropies have been estimated based on retention data obtained by a C_{18} stationary phase. The carbonyl group/methanol–water interactions are stronger than the hydroxyl group/methanol–water interactions. The hydrogen atom of the hydroxyl group seems to serve as a steric barrier to solvent molecules approaching toward the oxygen atom to donate hydrogen bond and consequently yield weaker hydrogen bond than the carbonyl group. There exists a clear positional effect on the magnitude of specific functional group–solvent interaction. The spatial accessibility based on the molecular structure was important to explain the discrepancies in functional group–solvent interaction among the positional isomers. The thermodynamic properties of solute transfer obtained by the Alltima C_{18} phase were systematically different from those obtained by the squalane-adsorbed C_{18} phase probably owing to their structural differences.

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References

[1] E. Grushka, H. Colin, G. Guichon, Anal. Chem. 248 (1982) 325.
[2] H.J. Issaq, M. Jaroniec, J. Liq. Chromatogr. 12 (1989) 2067.
[3] L.A. Cole, J.G. Dorsey, Anal. Chem. 64 (1992) 1317.
[4] L.A. Cole, J.G. Dorsey, K.A. Dill, Anal. Chem. 64 (1992) 1324.
[5] A. Alvarez-Zepeda, B.N. Barman, D.E. Martire, Anal. Chem. 64 (1992) 1978.

[6] A. Tchapla, S. Heron, H. Colin, G. Guichon, Anal. Chem. 60 (1988) 1443.
[7] F.M. Yamamoto, S. Rokushika, H. Hatano, J. Chromatogr. Sci. 27 (1989) 704.
[8] L.C. Sander, L.R. Field, Anal. Chem. 52 (1980) 2009.
[9] C.M. Bell, L.C. Sander, S.A. Wide, J. Chromatogr. A 757 (1997) 29.
[10] V.L. McGuffin, S. Chen, J. Chromatogr. A 762 (1997) 35.
[11] K. Miyabe, M. Suzuki, AIChE J. 41 (1995) 548.
[12] K. Miyabe, S. Takeuchi, Anal. Chem. 69 (1997) 2567.
[13] Y. Guillaume, C. Guinchard, J. Liq. Chromatogr. 17 (1994) 2807.
[14] C.S. Lee, W.J. Cheong, J. Liq. Chromatogr. Rel. Technol. 22 (1999) 253.
[15] C.S. Lee, W.J. Cheong, J. Chromatogr. A 848 (1999) 9.
[16] W.J. Cheong, C.Y. Kim, Y.M. Koo, Bull. Korean Chem. Soc. 21 (2000) 105.
[17] W.J. Cheong, C.Y. Kim, Bull. Korean Chem. Soc. 21 (2000) 351.
[18] CS Chem3D 5.0 User's Guide, CambridgeSoft Corporation, Cambridge, MA, 1998.