

The Positional Effect of Solute Functional Group in Hydroxyl Group-Solvent and Carbonyl Group-Solvent Specific Interactions in Acetonitrile/Water Mixed Solvents Monitored by HPLC

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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.¹⁻⁴ In the previous report,⁵ 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 C₁₈ phase. We proposed accessibility of solvent molecules to the solute functional group as the criterion for determining the magnitude of specific solute-solvent interaction. In this paper, we confirmed that spatial accessibility is a very crucial factor to the specific functional group-solvent interaction by comparing such interactions among solutes of different functional group accessibilities, for example phenol vs. benzylalcohol and acetophenone vs. benzylacetone.

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 polar solute from that of the nonpolar solute.⁵

Experimental Section

Acetonitrile and water were of HPLC grade and purchased from Fisher (Pittsburg, USA) and used without further purification. The selected solutes (benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, phenol, benzylalcohol, phenethylalcohol, acetophenone, and benzylacetone) were purchased from Aldrich (Milwaukee, USA) and used without purification.

The experimental details were basically the same as those in the previous reports.^{5,6} We used the same chromatographic system including the squalane impregnated C₁₈ column. The mobile phase used were acetonitrile/water mixtures (30/70, 40/60, 50/50, 60/40, 70/30 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. 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 non-

polar solute was calculated based on the retention data of the two alkylbenzenes under assumption that $\ln k'$ is linear with intrinsic molar volume.

Results and Discussion

The measured hydroxyl group-acetonitrile/water specific interaction enthalpies for phenol, benzylalcohol, and phenethylalcohol are plotted against solvent composition in Figure 1, and the carbonyl group-acetonitrile/water specific interaction enthalpies for acetophenone and benzylacetone, in Figure 2, respectively. The relative standard deviations for 3-4 independent measurements of thermodynamic properties were generally better than 5% and about 10% for the worst case.

As we observed for the methanol/water mixed solvents in the previous report,⁵ the magnitude of carbonyl group-acetonitrile/water specific interaction enthalpy for acetophenone is also much larger than that of hydroxyl group-acetonitrile/water specific interaction enthalpy for phenol. The hydroxyl group-aqueous acetonitrile interaction would be stronger than the carbonyl group-aqueous acetonitrile interaction in ordinary situations if we consider that a hydroxyl group is able to accept and donate a hydrogen bond while a carbonyl group is only able to accept a hydrogen bond and that a hydroxyl group is generally more polar than a carbonyl group. The spatial accessibility of hydrogen bond seems to be more critical in real situations. The O atom of phenol is directly attached to the phenyl ring while there is a carbon atom

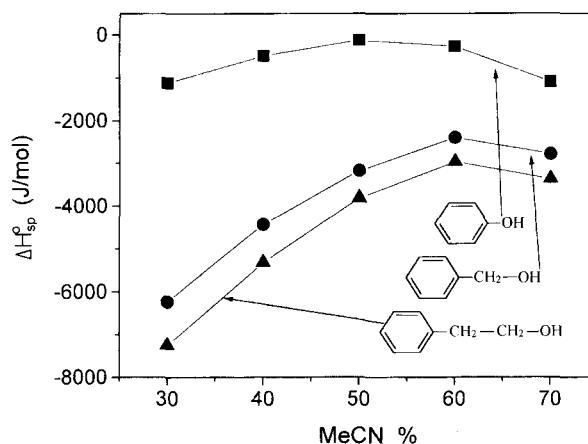


Figure 1. The specific hydroxyl group-aqueous acetonitrile interaction enthalpies as a function of acetonitrile composition for phenol (square), benzylalcohol (circle), and phenethylalcohol (triangle).

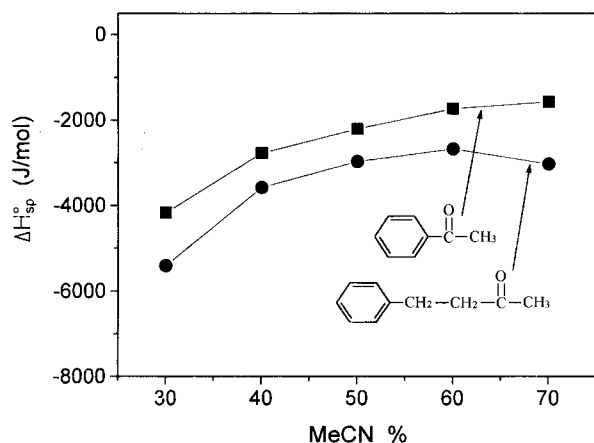


Figure 2. The specific carbonyl group-aqueous acetonitrile interaction enthalpies as a function of acetonitrile composition for acetophenone (square) and benzylacetone (circle).

between the phenyl ring and the O atom in acetophenone. The chance of hydrogen bond formation gets higher as the distance between the phenyl ring and the O atom of the functional group gets wider. The absolute magnitude of specific functional group-solvent interaction enthalpy increases as more spacer units between the phenyl ring and the hydroxyl group are introduced as shown in Figure 1. The increase for the first insert of a CH₂ unit (phenol to benzylalcohol) is dramatic while the increase for the next insert of a CH₂ unit (benzylalcohol to phenethylalcohol) is much smaller.

The insert of two CH₂ units between the phenyl ring and the carbonyl group, on the other hand, causes only moderate increase in the magnitude of carbonyl group-solvent specific interaction enthalpy (Figure 2). The number of carbon atoms between the phenyl ring and the O atom is a measure of spatial accessibility, and existence of only one carbon atom

seems to yield virtually free interaction. Additional insert of carbon atoms secures more chance of hydrogen bond formation, but the effect is only marginal. It seems that the effect levels off (completely free interaction) when there exist more than two carbon atoms. In such an ordinary situation, the magnitude of hydroxyl group-solvent specific interaction enthalpy is larger than that of carbonyl group-solvent specific interaction enthalpy. For example, compare phenethylalcohol (Figure 1) with benzylacetone (Figure 2).

As for variation of functional group-solvent specific interaction with respect to solvent composition, its magnitude increases with increase of water content owing to the enhancement of solvent polarity, and such trends are more obvious for solutes of higher functional group-solvent accessibility. The magnitude of functional group-solvent interaction decreases as acetonitrile content increases, but above a certain limit, the magnitude increases again probably owing to enhancement of dipolar interaction between the solute functional group and acetonitrile despite weakening of hydrogen bond interaction.

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