On the Origin of Microheterogeneity: Mass Spectrometric Studies of Acetonitrile−Water and Dimethyl Sulfoxide−Water Binary Mixtures (Part 2)

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The microscopic structures of acetonitrile−water and DMSO−water binary mixed solvents and their influence on the solvation for solutes (some alcohols and phenol) have been studied on the basis of the cluster structures observed through a specially designed mass spectrometer. In acetonitrile−water mixtures, the water clusters were observed at water mole fractions: $X_w > 0.2$; on the other hand, in DMSO−water mixtures, the water clusters were observed only at much higher water mole fractions: $X_w > 0.93$. In the mixing processes, the water clusters were stabilized in the acetonitrile−water mixtures, whereas the DMSO clusters were stabilized in the DMSO−water mixtures. It is demonstrated that these microscopic structures directly affect the solvation for alcohols and phenol in these binary mixed solvents.

Introduction

Water−organic solvent binary mixtures are powerful solvent systems used frequently in many branches of chemistry,[1] and their efficient application in chemical processes will contribute to reduce a global environmental impact.[2] Solvent effects in these mixtures depend nonlinearly on the mixing ratio, and a study of preferential solvation will offer important information.[3]

Even if an organic solvent is miscible with water at any mixing ratio, its binary mixture will be difficult to afford an ideal mixture because water−water, organic solvent−organic solvent, and water−organic solvent intermolecular interactions are different. The deviation from the thermodynamically ideal binary mixing system will be borne out as a microscopic structure, where water and organic solvent molecules are not homogeneously mixed at the cluster level.[4] When a solute is dissolved in such a nonideal binary mixture, the solvent composition in the solvation shell will not correspond to the mixing ratio of the binary solvent. As a consequence, preferential solvation takes place easily in these nonideal binary mixtures. Here we report how preferential solvation is controlled by the solvent−solvent and the solute−solvent interactions, on the basis of the mass spectrometric analysis of clusters generated from solutions.

Previously, we have already reported that preferential solvation of some hydrophobic solutes in dimethyl sulfoxide (DMSO)−water binary mixtures is controlled by the microheterogeneity (molecular clustering) of DMSO−water binary mixture observed through the specially designed mass spectrometer.[5] This was the first experimental evidence to show directly that the molecular clustering in the binary mixed solvent controlled the solvation of the added solutes. Moreover, we have also reported that preferential solvation in acetonitrile−water and alcohol (methanol, ethanol, or 1-propanol)−water binary

mixtures is a key factor for the solvent effect on several chemical reactions.[6] We note that our results on preferential solvation studied by the mass spectrometric technique was in good correlation with the molecular composition of the solvation shell, probed through intermolecular ¹H 2-D NOESY measurements as reported by Bagno et al.[3a−c]

Here we are focusing our attention on the solvation of several hydrophobic alcohols (cyclohexanol, 3-hexanol, etc.) and phenol in acetonitrile−water and DMSO−water binary mixed solvents. The solvation-controlling factors, that is, solute−solvent and solvent−solvent interactions have been systematically studied on the basis of the microscopic structures estimated through the mass spectrometric analysis of clusters isolated from solutions.

Experimental Section

The mass spectrometric analyses of clusters were carried out by means of the specially designed mass spectrometer, which consists of a four-stage differentially pumped vacuum chamber equipped with a nozzle for continuously injecting liquid sample and a quadrupole mass spectrometer (Extrel C50-4000) for analyzing the mass distribution of the clusters. A detailed description has been provided elsewhere.[7,8] Sample solutions were continuously introduced into the four-stage differentially pumped vacuum chamber with a flow rate of 0.08 mL/min by using a liquid chromatograph pump (Shimadzu, LC-10AD). The nozzle was heated electrically to form a flow of liquid droplets against the decrease of temperature due to the vaporization, and its temperature was monitored and controlled by two sets of thermocouples on the nozzle. The resulting liquid droplets were expanded adiabatically in the vacuum and fragmented into clusters. The resulting clusters were ionized by an electron impact at 25−30 eV and then analyzed by the quadruple mass spectrometer (Extrel C50-4000). The detected ion signals are averaged for 500 sweeps by a digital oscilloscope (IWATSU-LeCroy LT342).

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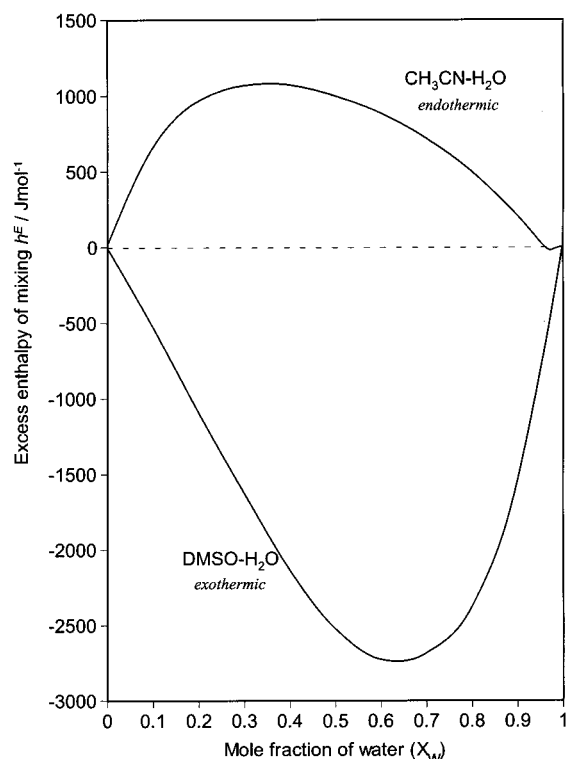‡ University of Groningen.

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Figure 1. Excess enthalpy of mixing for acetonitrile−water[4] and DMSO−water[9] as functions of mole fraction of water. The dashed line corresponds to the ideal binary mixture whose excess enthalpy of mixing is zero.

Figure 2. Mass spectra of acetonitrile−water mixtures at three different water mole fractions (X_w): (a) 0.06, (b) 0.21, and (c) 0.93. The clusters $H^+(CH_3CN)_m(H_2O)_n$ are labeled as (m, n), where each peak is also classified by symbols according to the number of acetonitrile molecules, m, within the clusters.

During the fragmentation of liquid droplets into clusters, the strongly interacting molecules, such as hydrogen bonding or dipole−dipole interacting molecules, remain in the clusters; however, relatively weak interactions such as the dispersive interactions do not contribute to the clustering. Therefore, it should be noted that the relatively weak intermolecular interactions cannot be observed by this mass spectrometric technique.

Acetonitrile (HPLC grade, Wako), DMSO (HPLC grade, Wako), 2-butanol (Wako), cyclopentanol (Wako), cyclohexanol (Wako), 3-hexanol (Wako), cycloheptanol (Aldrich), cyclooctanol (Wako), and phenol (Chromatography grade, Wako) were used without further purification. Millipore Milli-Q filtered water (resistivity > 18.3 MΩ cm at 25 °C) was used for all of the experiments.

Results and Discussion

Cluster Structures of Binary Mixtures: Acetonitrile−Water and DMSO−Water. Both acetonitrile and dimethyl sulfoxide (DMSO) are aprotic and dipolar solvents, and they are miscible with water at any mixing ratio. However, their thermodynamic properties for mixing with water are completely different: endothermic for acetonitrile−water[4] and exothermic for DMSO−water,[9] as shown in Figure 1. This suggests that the microscopic structures will be quite different in these aqueous binary mixtures. It is expected that the solvation of a solute in acetonitrile−water mixtures is also quite different from that in DMSO−water mixtures, if it is correlated with the microscopic structures in the binary mixtures.

Previous work has shown that the solvation in DMSO−water mixtures is predominantly controlled by the microheterogeneity of the DMSO−water mixture.[5] Here we have measured mass spectra of clusters generated from acetonitrile−water mixtures at varying mixing ratios. The microheterogeneity of the aceto-
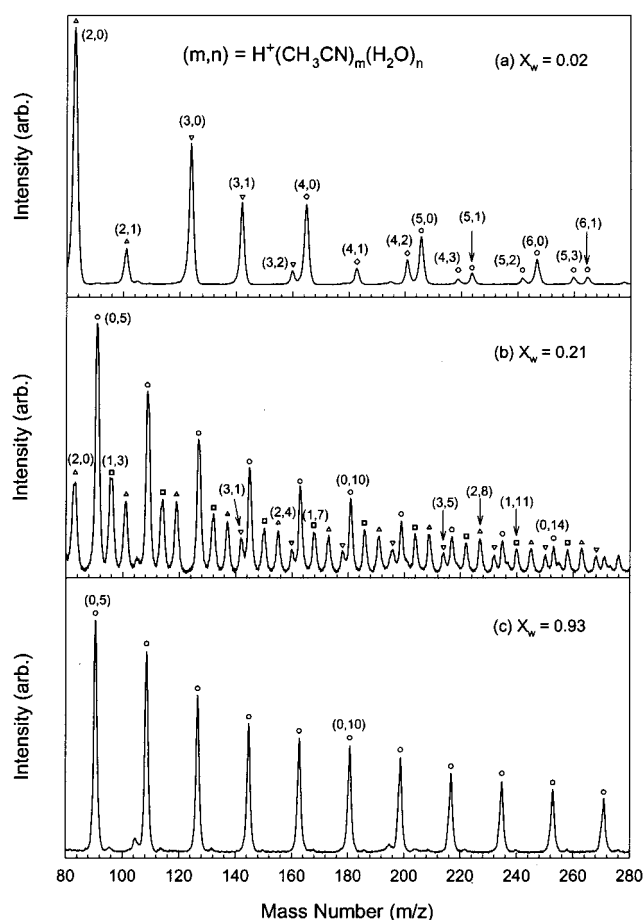
nitrile−water mixtures was evaluated on the basis of the observed peak intensities. The results are compared with those for the DMSO−water mixtures reported previously.[5]

Figure 2 shows mass spectra observed for the acetonitrile−water binary mixtures with mole fractions of water of X_w = 0.02, 0.21, and 0.93. Each peak observed in Figure 2 can be assigned to a cluster $H^+(CH_3CN)_m(H_2O)_n$. The clustering features are remarkably dependent on X_w. At lower water concentrations such as X_w = 0.02 (Figure 2a), acetonitrile clusters, which are composed only of acetonitrile molecules with (m, n) = (2, 0), (3, 0), (4, 0), ···, are observed as prominent peaks. A small number of water molecules are attached to these acetonitrile clusters. When X_w is increased to 0.21, the acetonitrile clusters almost disappear, and water clusters, composed of water molecules only with (m, n) = (0, 5), (0, 6), (0, 7), ···, become prominent at the expense of the acetonitrile clusters (Figure 2b). At this mixing ratio, the hydrogen-bonding network of water has been constructed, and the dipole−dipole interactions among acetonitrile molecules will be influenced by acetonitrile−water interactions. With further increase of X_w over 0.21, the observed cluster structures do not change essentially. Water clusters are observed as prominent species. The change of the cluster structures for X_w > 0.21 only involves a decrease of clusters including acetonitrile molecules. At X_w = 0.93 (Figure 2c), water clusters are observed predominantly, and the water clusters interacting with acetonitrile molecules show only weak peaks.
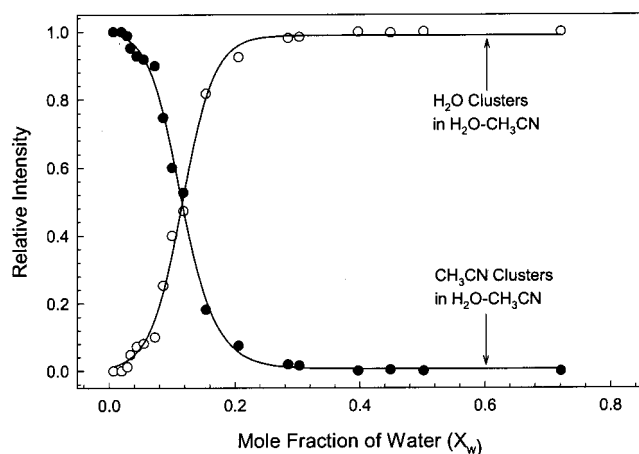
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Figure 3. Plots of the relative intensities of the acetonitrile cluster (R_A) and the water cluster (R_W) as a function of the mole fraction of water in the acetonitrile−water mixtures. The R_A and R_W were calculated from eqs 1 and 2 by using the mass-peak intensities observed at 100−500 amu.

To evaluate the microheterogeneity, the relative intensities of the acetonitrile cluster (R_A) and the water clusters (R_W) are calculated from eq 1 and 2 by using the peak intensities, and they were plotted in Figure 3 as functions of the X_w.

$$R_A = \frac{\sum_m H^+(CH_3CN)_m}{\sum_m H^+(CH_3CN)_m + \sum_n H^+(H_2O)_n} \quad (1)$$

$$R_W = \frac{\sum_m (H_2O)_n}{\sum_m H^+(CH_3CN)_m + \sum_n H^+(H_2O)_n} \quad (2)$$

Figure 3 clearly indicates that the microheterogeneity of the acetonitrile−water mixture is not linearly dependent on the mixing ratio, and drastically changes around $X_w = 0.1$. Acetonitrile clusters appear predominantly up to $X_w = 0.08$. At $X_w > 0.08$, the acetonitrile clusters formed through dipole−dipole interaction are rapidly broken. At the same time, water clusters are generated with increasing intensities. At $X_w > 0.2$, the water clusters become the prominent species.

To compare the microheterogeneity of the acetonitrile−water with the DMSO−water binary mixtures, the microheterogeneity curve for the DMSO−water mixtures, reported previously,[5] is shown in Figure 4. Figure 4 indicates that the cluster structure of the DMSO−water binary mixture also changes nonlinearly with X_w, but its X_w dependence is quite different from that shown in Figure 3. The relative intensity of the water cluster becomes predominant at much higher water mole fractions: $X_w > 0.93$, and the DMSO clusters are formed prominently at $X_w < 0.91$ instead of the water clusters. The microscopic structure in the DMSO−water mixture also changes drastically and nonlinearly at a critical value of X_w. It is apparent that the critical X_w is quite different between the acetonitrile−water and the DMSO−water binary mixtures (Figures 3 and 4).

In acetonitrile−water binary mixtures, the critical X_w is low (around 0.1), which means that the acetonitrile cluster structure is preferentially broken (or reorganized) for miscibility with water clusters. On the contrary, in the DMSO−water mixtures,
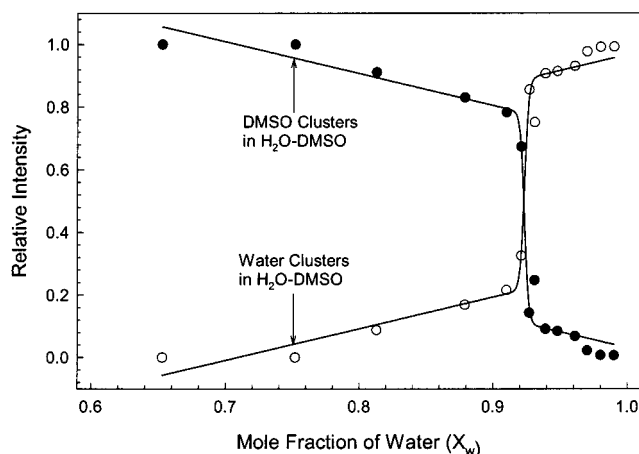

Figure 4. Plots of the relative intensities of the DMSO cluster (R_A) and the water cluster (R_w) as a function of the mole fraction of water in the DMSO−water mixtures. (Taken from ref 5.)

the critical X_w is high (around 0.92), which means that the water cluster structure is preferentially broken (or reorganized) to allow miscibility with DMSO clusters. This difference may be related to hydrophobicity.[10] The DMSO molecules are forced to form self-aggregating clusters to reduce the interface with water, whereas acetonitrile can coexist with water clusters but with decreasing the size of acetonitrile clusters.

The striking contrasts in the excess enthalpies of mixing, shown in Figure 1, can be related to the difference in the observed molecular clustering. As described above, acetonitrile clusters were broken and DMSO clusters were promoted when these organic solvents were mixed with water. The dipole−dipole interactions among acetonitrile molecules are weakened, whereas ones among DMSO molecules are enhanced after the mixing with water. This leads to endothermic and exothermic mixing for an acetonitrile−water and a DMSO−water binary mixing, respectively.

Solvation-Controlling Factors in Acetonitrile−Water and DMSO−Water Binary Mixed Solvents. *(i) Solvation in Acetonitrile−Water Mixtures.* As for the solvation in DMSO−water binary mixtures, we have already reported that the solvation for 2-butanol, cyclopentanol, cyclohexanol, and phenol is mainly controlled by the microheterogeneity of the DMSO−water binary mixtures, as shown in Figure 4.[5] To compare the solvation in the DMSO−water system with that in the acetonitrile−water system, we measured mass spectra of the acetonitrile−water solutions containing alcohol (cyclopentanol, 3-hexanol, or cyclooctanol) or phenol as a solute.

Figure 5 shows mass spectra for the acetonitrile−water systems with cyclopentanol as a solute at varying the acetonitrile−water mixing ratios ($X_w = 0.05, 0.15, 0.40$). At $X_w = 0.05$ (Figure 5a), the clusters containing cyclopentanol are mainly composed of acetonitrile molecules, which indicates that the cyclopentanol is solvated by the acetonitrile. At $X_w = 0.15$ (Figure 5b), the interactions of cyclopentanol with acetonitrile become comparable with those with water. Upon further increasing X_w, at $X_w = 0.40$ (Figure 5c), cyclopentanol is mainly interacting with water, and hydrated cyclopentanol is observed as a series of clusters with varying number of water molecules. When 3-hexanol and cyclooctanol are used as a solute instead of the cyclopentanol, the same kind of X_w dependence of the cluster structure was found.

To further evaluate the microscopic environment around the solute in acetonitrile−water mixtures on the basis of the
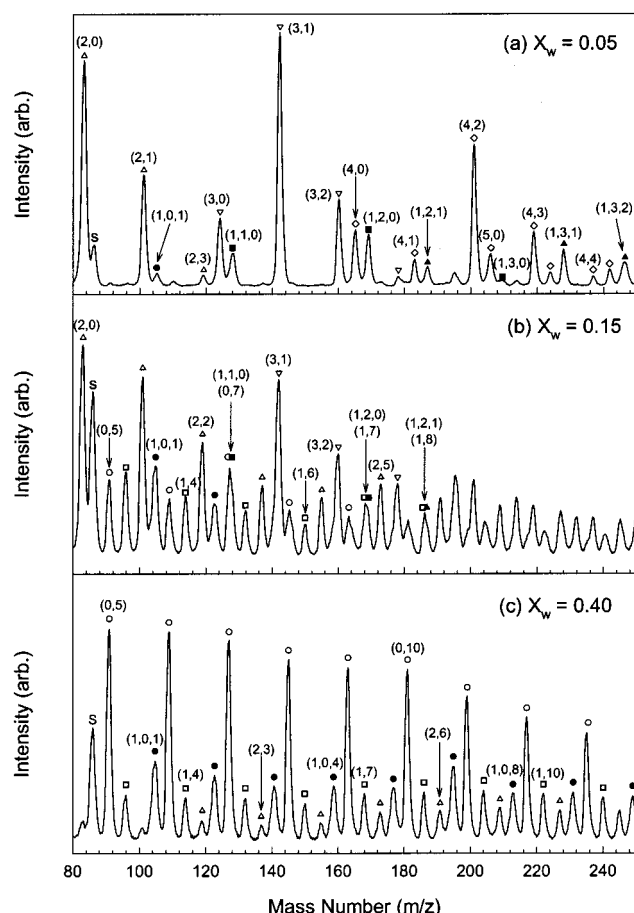
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Figure 5. Mass spectra of acetonitrile−water mixtures containing cyclopentanol (mole fraction: 0.002) at three different water mole fractions (X_w): (a) 0.05, (b) 0.15, and (c) 0.40. The clusters $H^+(CH_3CN)_m(H_2O)_n$ and $H^+(cyclpentanol)_l(CH_3CN)_m(H_2O)_n$ are labeled as (m, n) with open symbols and (l, m, n) with closed symbols, respectively. "S" designates peaks for the cyclopentanol ion.

observed cluster structure, the relative intensities of the solute solvated by acetonitrile (S_A) or water (S_W) were calculated from eqs 3 and 4 by using the peak intensities, and they are plotted in Figure 6 as functions of X_w.

$$S_A = \frac{\sum_m H^+(solute)(CH_3CN)_m}{\sum_m H^+(solute)(CH_3CN)_m + \sum_n H^+(solute)(H_2O)_n} \quad (3)$$

$$S_W = \frac{\sum_n H^+(solute)(CH_3CN)_m}{\sum_m H^+(solute)(CH_3CN)_m + \sum_n H^+(solute)(H_2O)_n} \quad (4)$$

It is obvious that the three alcohols used as solutes exhibit the same solvation behavior against the acetonitrile−water mixing ratio (X_w). These alcohols are solvated by acetonitrile at X_w < 0.08, and interaction of these alcohols with water clusters becomes prominent at X_w > 0.2. Interestingly, the resulting solvation curve shown in Figure 6 is in good agreement with the solvent microheterogeneity curve shown in Figure 3. This indicates that the solvation of the alcohol in the acetonitrile−water mixture is strongly related to the mixed solvent cluster structure.
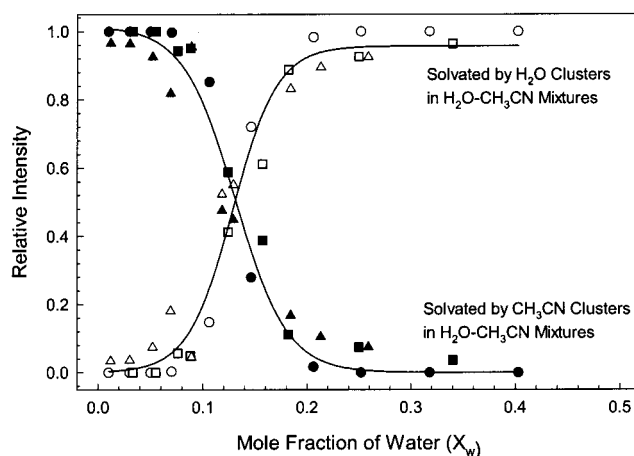

Figure 6. Plots of the relative intensities of solute alcohols solvated by acetonitrile (S_A) and water (S_W) in acetonitrile−water mixed solvents, calculated from eq 3 and 4 by using the peak intensities observed at 100−500 amu as a function of X_w. Solute alcohols are cyclopentanol (circle), 3-hexanol (triangle), and cyclooctanol (square).
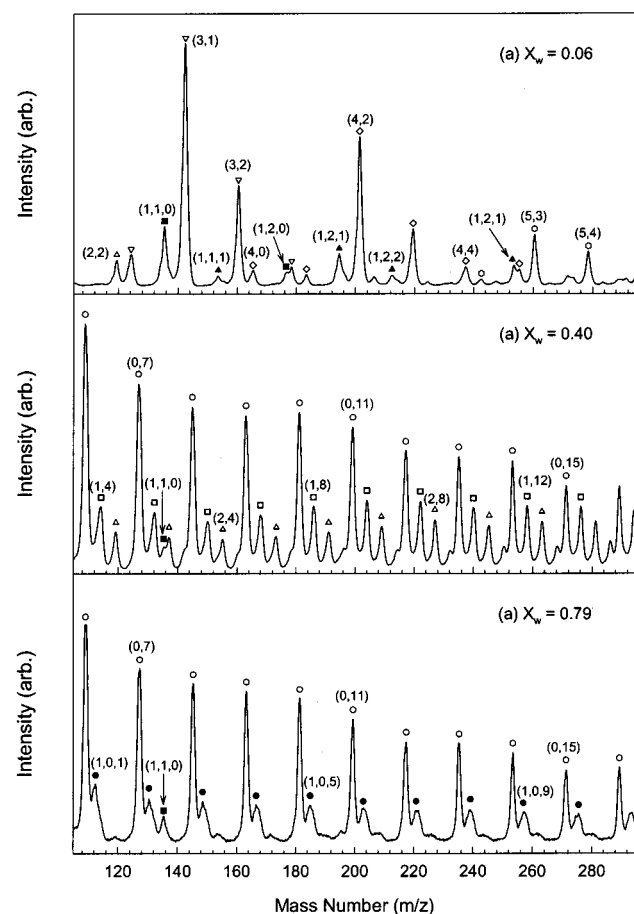

Figure 7. Mass spectra of acetonitrile−water mixtures containing phenol (mole fraction: 0.002) at three different water mole fractions (X_w): (a) 0.06, (b) 0.40, and (c) 0.79. The clusters $H^+(CH_3CN)_m(H_2O)_n$ and $H^+(phenol)_l(CH_3CN)_m(H_2O)_n$ are labeled as (m, n) with open symbols and (l, m, n) with closed symbols, respectively.

For phenol as the solute in acetonitrile−water mixtures, the dependence of solvation of the phenol on the acetonitrile−water mixing ratio was quite different from that for the alcohol. Figure 7 shows mass spectra of acetonitrile−water mixtures in the presence of phenol. At X_w = 0.06 (Figure 7a), the pure acetonitrile clusters are disintegrated by the interaction with water molecules, and resulting small acetonitrile clusters
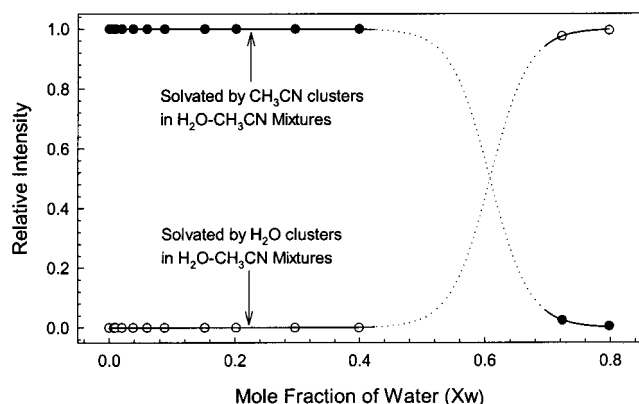
Figure 8. Plots of the relative intensities of solute phenol solvated by acetonitrile (S_A) and water (S_W) in acetonitrile−water mixed solvent, calculated from eqs 3 and 4 using the peak intensities observed at 100−500 amu as a function of X_w. In the region $0.4 < X_w < 0.7$, water cluster−acetonitrile interaction is the most favorable; accordingly, the phenol−solvent interaction is too weak to be detectable.

interacting with water molecules solvate the phenol preferentially. Upon increase of X_w to 0.40 (Figure 7b), water clusters and their interacting with acetonitrile molecules are observed as prominent species; however, these clusters do not contain phenol. At $X_w = 0.4$, the hydrogen-bonding network of water has been constructed, and the acetonitrile molecules are surrounding the water clusters, whereas the acetonitrile−acetonitrile interactions are considerably reduced. Apparently, phenol cannot interact with these water clusters, because the water−acetonitrile interactions dominate. Perhaps phenol could interact with the acetonitrile surrounding the water clusters, but its interaction is too weak to be detectable. With a further increase of X_w, at $X_w = 0.79$ (Figure 7c), the phenol is mainly interacting with water clusters. In this high X_w region, the number of acetonitrile molecules surrounding the water clusters is not enough to restrict the interaction between the phenol and the water clusters.

To evaluate the microscopic environment around the phenol in the acetonitrile−water mixtures, the S_A and S_W values were also calculated through eqs 3 and 4 for the phenol−acetonitrile−water system, and a plot is shown in Figure 8. The data in Figure 8 clearly show that the phenol is preferentially solvated by the acetonitrile at lower water contents, and that the interaction of the phenol with the water cluster is promoted at $X_w \geq 0.7$. At $0.4 < x_w < 0.7$, the water cluster−acetonitrile molecule interaction predominates over the water−phenol and the acetonitrile−phenol interactions; therefore, the solvated phenol will be easily fragmented into phenol molecules and solvent molecules.

There is a clear contrast between the solvation of the alcohol and of the phenol in the acetonitrile−water mixtures. The solvation curve for phenol (Figure 8) is quite different from the mixed-solvent microheterogeneity curve shown in Figure 3. This means that the phenol prefers acetonitrile molecules even when the water clusters are stabilized in the mixed solvent. On the other hand, the solvation curve for the alcohols (Figure 6) is in good agreement with Figure 3. This indicates that the alcohols preferentially interact with the water clusters when the water clusters are stabilized in the mixed solvent. In other words, the alcohols easily interact with water clusters, whereas the phenol is much less eager to interact with water clusters.

The difference in the interactions of alcohol and phenol with water clusters is confirmed by mass spectrometric analysis of these aqueous solutions. Figure 9 shows mass spectra of aqueous alcohol solutions (a: cyclopentanol, b: cyclohexanol, c: cyclo-
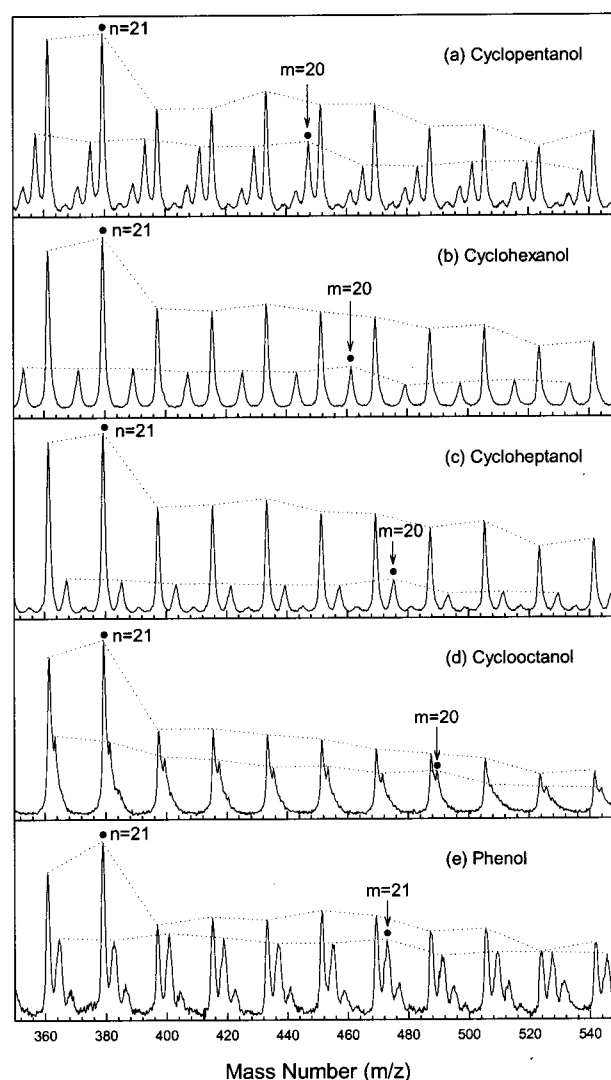

Figure 9. The mass spectra of aqueous solutions containing alcohol ((a) cyclopentanol, (b) cyclohexanol, (c) cycloheptanol, (d) cyclooctanol) and (e) phenol. Water clusters $H^+(H_2O)_n$ and the hydrated solute $H^+(solute)(H_2O)_m$ observed as a series of clusters are connected by the dotted line. The magic-number clusters are identified by $n = 21$ and $m = 20$.

heptanol, d: cyclooctanol) and an aqueous phenol solution (e). In each spectrum, water clusters, $H^+(H_2O)_n$, and hydrated solute, $H^+(solute)_m(H_2O)_n$, are observed as a series of clusters. In the water clusters, the peak $H^+(H_2O)_{21}$ is observed as a magic-number species in each spectrum.[4,11] The magic-number property is also observed for the hydrated clusters, which is clearly different between alcohol and phenol. For the aqueous alcohol solutions (Figure 9 a−d), the clusters composed of one alcohol molecule and twenty water molecules have the magic-number property, whereas for the aqueous phenol solution (Figure 9e), the cluster composed of one phenol molecule and twenty-one water molecules shows the magic-number property.[4]

In consideration of the difference in the magic number properties and taking into account the similarity of mass distribution for each series of clusters, the difference in the interactions of alcohol and phenol with water clusters may be rationalized as follows. Alcohol has substitutional interaction with water clusters, that is, a hydrogen-bonding H_2O in a water cluster is replaced by the alcohol, ROH. On the other hand, phenol cannot work as a part of the hydrogen-bonding network of water; accordingly, phenol undergoes additional interaction
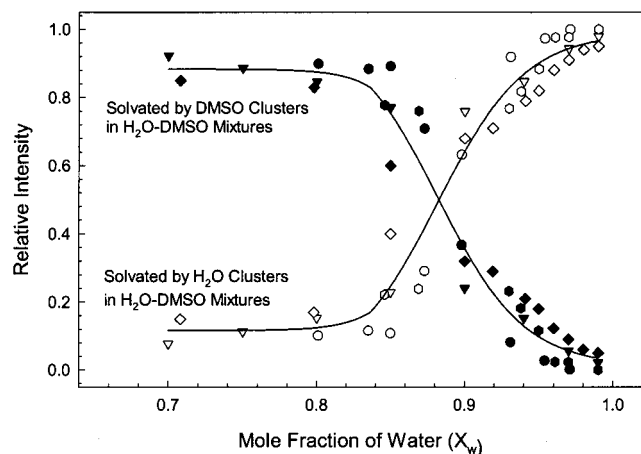
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Figure 10. Plots of the relative intensities of solute solvated by DMSO (S_A) and water (S_W) in DMSO−water mixed solvents. The solutes are 2-butanol (hexagon), cyclopentanol (circle), cyclohexanol (triangle), and phenol (diamond). (Taken from ref 5.)

with water clusters. The alcohol and water molecules form clusters cooperatively, whereas the phenol is excluded from clustering of water molecules. As in the case of water, the OH group of the alcohol can work as both a hydrogen-bond donor and a hydrogen-bond acceptor. On the other hand, the OH of phenol works as a hydrogen-bond donor rather than an acceptor, because of its more acidic character in water. This difference will be related to the interaction of the solute molecules with water in the acetonitrile−water mixtures.

(ii) Solvation in DMSO−Water Binary Mixtures. As shown in Figures 3 and 4, the microheterogeneity in acetonitrile−water mixture is quite different from that in DMSO−water mixture. Consequently, the solvation features in DMSO−water mixtures are also different from those in acetonitrile−water mixtures. Figure 10 shows the solvation curve for the alcohol and phenol in DMSO−water mixtures, and a comparison can be made with Figures 6 and 8. In the DMSO−water mixtures, alcohols and phenol possess the same solvation characteristics, irrespective of the nature of the solutes. At water mole fractions beyond $X_w \approx 0.9$, the solute is strongly interacting with water clusters, whereas below $X_w \approx 0.9$, it is preferentially solvated by DMSO clusters. It is obvious that the solvation structure of the solutes is also nonlinearly related to the mixing ratios of DMSO−water mixtures. Furthermore, the solvation curve is in good correlation with the cluster structure of the DMSO−water mixture shown in Figure 4. This indicates that the factor governing solvation of solutes is immediately related to microscopic solvent structures of the DMSO−water mixtures. As a consequence, the nature of the preferential solvation will originate from the propensity that the solute molecules dissolved in a DMSO−water mixture interact with already established solvent clusters, rather than individual solvent molecules.

(iii) Comparison with Other Experimental Approaches. Bagno et al. reported a study of the solvation shell by means of the ^{1}H NOESY technique.[3a−c] A part of the results presented here can be directly compared with Bagno's results. As for the solvation for phenol in acetonitrile−water and DMSO−water binary solvent mixtures, the local solvent compositions of the solvation shell were obtained at various bulk solvent compositions. For acetonitrile−water mixtures with bulk water mole fractions (X_B) 0.5, 0.8, and 0.9, the local mole fractions of water around phenol (X_B') were decreased to 0.4, 0.5, and 0.7, respectively. For DMSO−water mixtures with $X_B = 0.1$, 0.5, and 0.9, the values of X_B' were 0.1, 0.4, and 0.8, respectively. These results indicate

that phenol shows preference for the organic solvent even at higher X_B.

In our mass spectrometric analysis of clusters presented here, it was confirmed that phenol was preferentially solvated by the organic solvent component at widely different mixing ratios; however, the preference for the organic solvent component seems to disappear at higher water mole fractions, as shown in Figures 8 and 10. This difference will be characteristic of the experimental method. As described in the Experimental Section, the weakly interacting molecules such as the dispersive force cannot be observed as clusters. On the contrary, ^{1}H NOESY studies revealed such weak intermolecular interactions. Therefore, the difference between the ^{1}H NOESY and the mass spectrometric data at higher water content regions suggests that the preference of phenol for the organic solvent component will be due to relatively weak dispersive force. In consideration of the difference in the experimental method, the obtained results from both experiments show a good correlation. Bagno's results also shows that the water−phenol interaction in these binary mixed solvents is of substantial importance at higher water contents.

Conclusion

When water and acetonitrile are mixed, water can form clusters but acetonitrile molecules cannot, especially at $X_w > 0.2$. In the resulting mixed solvents, alcohol and phenol, added as a solute, have preferential interaction with the water and the acetonitrile, respectively. On the other hand, when water and DMSO are mixed, water clusters and DMSO clusters are disintegrated and constructed, respectively, in the wide mixing region of $X_w < 0.91$. In the resulting DMSO−water mixed solvents, both alcohol and phenol, added as a solute, have preferential interaction with the DMSO clusters. The relation between the solvation behavior and the cluster structures of the binary mixed solvents has been elucidated in some detail.

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