FARADAY

Non-ideality of binary mixtures

Water–methanol and water–acetonitrile from the viewpoint of clustering structure

Akihiro Wakisaka,[a]* Hassan Abdoul-Carime,[a] Yoshitaka Yamamoto[b] and Yoshimichi Kiyozumi[c]

[a] *National Institute for Advanced Interdisciplinary Research, Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan*

[b] *National Institute for Resources and Environment, Onogawa 16-3, Tsukuba, Ibaraki 305, Japan*

[c] *National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan*

Water–methanol and water–acetonitrile, which show exothermic and endothermic mixing, respectively, represent good contrast in non-ideality of a binary mixture. The microscopic structure observed through the mass-spectrometric analysis of clusters isolated from solution also shows good contrast between these binary mixtures as follows: (1) methanol molecules have substitutional interaction with water clusters, while acetonitrile molecules have additional interaction with water clusters; (2) the clustering of methanol molecules are promoted in the presence of water; on the contrary, the acetonitrile clusters are disintegrated in the presence of water. Such findings could partially explain the non-ideality of these binary mixtures on the basis of the cluster structures.

The mixing of organic solvents with water is normally accompanied by a difference of enthalpy. This thermodynamic property is generally very different from that of an ideal binary mixture whose excess enthalpy of mixing is zero. The deviation from ideality is due to intermolecular interaction. When the mixing of two liquids, A and B, forms an ideal solution, the average A–B interactions must be the same as the average A–A and B–B interactions in the pure liquids; however, in real solutions A–A, B–B and A–B interactions are all different.[1]

For water–organic solvent mixtures, hydrogen-bonding, hydrophobic, dipole–dipole interactions *etc.* lead to the formation of clusters instead of free movement of the solvent.[2–8] As a typical example, special attention is paid here to water–methanol and water–acetonitrile mixtures. The excess enthalpies of mixing of these two mixtures indicate that their thermodynamic properties are far from ideality and contrary to each other: exothermic mixing for water–methanol mixtures and endothermic mixing for water–acetonitrile mixtures.[9–11] The reported excess enthalpies at 25 °C[10,11] are plotted in Fig. 1. Since exothermic and endothermic mixing correspond to an enthalpy-controlled and entropy-controlled process, respectively, the interaction of water with methanol should be quite different from that with acetonitrile. Therefore, it is very interesting to compare the microscopic structure between these binary mixtures.

The mass-spectrometric analysis of clusters isolated from water–methanol and water–acetonitrile binary mixtures provides an insight into the experimental approach to understanding non-ideal mixing.

Experimental

The specially designed mass spectrometer proposed by Nishi and Yamamoto[12,13] was used to measure mass-spectra of clusters generated from liquid droplets. As shown in Fig. 2,[7,8] this is composed of a heated nozzle, a quadrupole mass-filter and a four-stage differentially pumped vacuum system. A sample solution was injected into the first chamber through the heated nozzle (120 °C). When a part of the solution is vaporized in the nozzle, the resulting gas–liquid mixture forms a flow of liquid droplets. The temperature of the liquid droplets should be much lower than the nozzle temperature. This temperature difference was estimated to be 70–90 °C.[12] Owing to the pressure balance, the liquid droplets enter the second and the third chamber with lower pressures and they explode through adiabatic expansion, which leads to fragmentation of the liquid droplets into clusters. The mass spectra of the clusters were measured by the quadrupole mass-filter after electron-impact ionization.

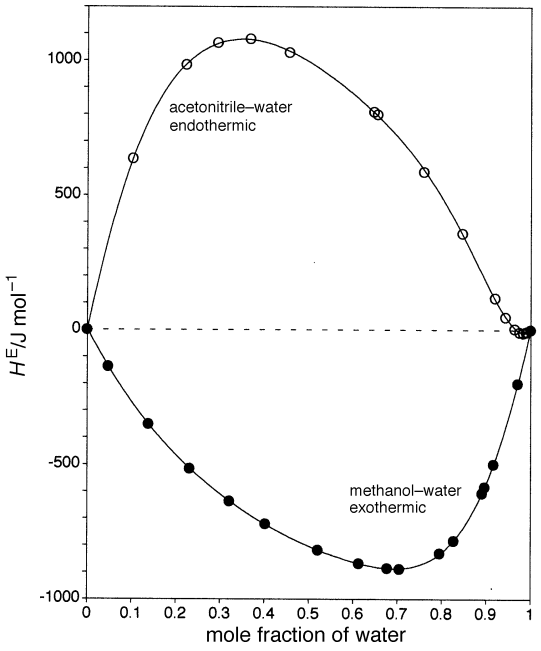

Fig. 1 Excess enthalpy of mixing at 25 °C for water–methanol[10] and water–acetonitrile[11] mixtures as functions of mole fraction of water. The dashed line corresponds to the ideal binary mixture whose excess enthalpy of mixing is zero.

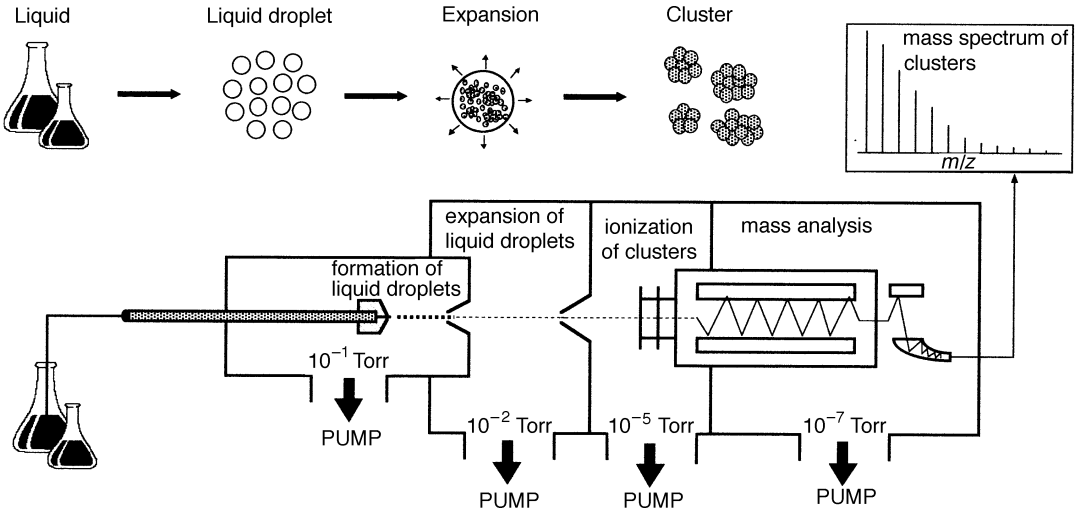

Fig. 2 Schematic of the specially designed mass spectrometer for clusters isolated from liquid droplets. A sample solution is injected into a four-stage differentially pumped vacuum system at 0.08 ml min^{-1}. The sample solution is fragmented from liquid droplets into clusters through vacuum adiabatic expansion. The resulting clusters are analysed by a quadrupole mass spectrometer after electron impact ionization.[7,8]

Results and Discussion

1 Water–methanol mixtures

'Substitutional' interaction of methanol with water clusters. The mass spectra of clusters generated from water–methanol mixtures provide information on the microscopic structure in the solution. The resulting clusters changed markedly with increasing methanol concentration in water (Fig. 3) and reflected an intermolecular interaction dependent on the mixing ratio.

The mass spectrum of clusters generated from pure water is shown in Fig. 3(*a*). The clusters composed of water molecules are observed as a series of peaks. In this series of water clusters, the peak intensities decrease with increasing cluster size; however, the peak corresponding to $H^+(H_2O)_{21}$ is observed as a prominent peak in comparison with its neighbouring peaks: [$H^+(H_2O)_{20}$ and $H^+(H_2O)_{22}$]. It is well known that the $H^+(H_2O)_{21}$ is a magic-numbered species with dodecahedral structure.[14–16] Twenty water molecules make the cage structure and H_3O^+ is included inside the cage.

At first, we focus on how the hydrogen-bonding network of water is influenced by the addition of a small amount of methanol into water. In a mass spectrum of clusters isolated from a water–methanol mixture (molar ratio of $H_2O : CH_3OH = 100 : 1$), a series of water clusters and methanol hydrate clusters, $H^+(CH_3OH)_m(H_2O)_n$, are observed [Fig. 3(*b*)]. A series of clusters with the same number of methanol molecules, $m = 0$–3, are connected by dotted lines. A series of clusters with $m = 0$, that is, water clusters, has the same mass distribution as in pure water [Fig. 3(*a*)], including the magic number $H^+(H_2O)_{21}$.

In a series of methanol hydrate clusters, $H^+(CH_3OH)_m(H_2O)_n$, with $m = 1$–3, the peaks observed as prominent species are *m*–*n*: 1–20, 2–19 and 3–18, respectively. All these clusters contain 21 molecules in total. The clusters including 21 water molecules such as 1–21, 2–21, *etc.* are not prominent species. The interaction of $H^+(H_2O)_{21}$ with methanol is found to proceed through the substitution of water with methanol. This substitutional interaction of CH_3OH with $H^+(H_2O)_{21}$ is illustrated schematically in the insert of Fig. 3(*b*). As mentioned above, when the dodecahedral cage structure is composed of 20 water molecules through their hydrogen-bonding network, *i.e.* 20 oxygen atoms located on the vertices and each oxygen is connected by a hydrogen bond, 10 hydrogen atoms do not contribute to the hydrogen-bonding network. Theoretically, 10 water molecules in $H^+(H_2O)_{21}$ can be substituted with 10 methanol molecules. With increasing methanol concentration, the dodecahedral cluster substituted with eight methanol molecules could be confirmed; however, the substitutional interaction was difficult to observe because of the overlap with other peaks and change in the water–cluster structure.

A similar substitutional interaction is also confirmed for the clusters composed of 28 molecules in total (0–28, 1–27, 2–26 and 3–25) showing magic-number properties. This suggests that when a small amount of methanol was added into water, a part of the hydrogen-bonding network of water is easily substituted with OH groups of CH_3OH.

Such a substitutional interaction was observed only at water mole fractions $X_w \geqslant 0.95$. At $X_w = 0.7$, *m*–*n*: 10–10, 11–11, *etc.* were observed as stable species, as shown in Fig. 3(*c*). In this mixing ratio, the magic-number water clusters substituted with methanol molecules are not observed. This means that the water hydrogen-bonding network inherent in pure water has been changed with the interaction with methanol.

Enthalpy-controlled mixing. Fig. 3 indicates that the interaction of methanol with water is strongly dependent on the mixing ratio. At lower concentrations of methanol, the methanol molecules have substitutional interaction with water clusters; therefore, each methanol molecule exists as a monomeric molecule having a hydrogen-bonding interaction with water. With increasing methanol concentration, the methanol molecules contact with each other to form larger methanol clusters (Fig. 3).

However, the clusters generated from pure methanol were very small. As shown in Fig. 4(*a*), methanol clusters larger than the tetramer are difficult to form from pure methanol. When a small amount of water was added to pure methanol, the methanol clustering was found to be promoted markedly. At the molar mixing ratio $CH_3OH : H_2O = 95 : 5$, the methanol heptamer and octamer were clearly observed [Fig. 4(*b*)].

The correlation between the cluster structure and the excess enthalpy of mixing should be noted here. As shown in Fig. 1, methanol mixes with water exothermically at all mixing ratios. This means that the interaction of methanol with water is energetically favourable and forms a stable structure (cluster). From the viewpoint of cluster structure, when methanol is

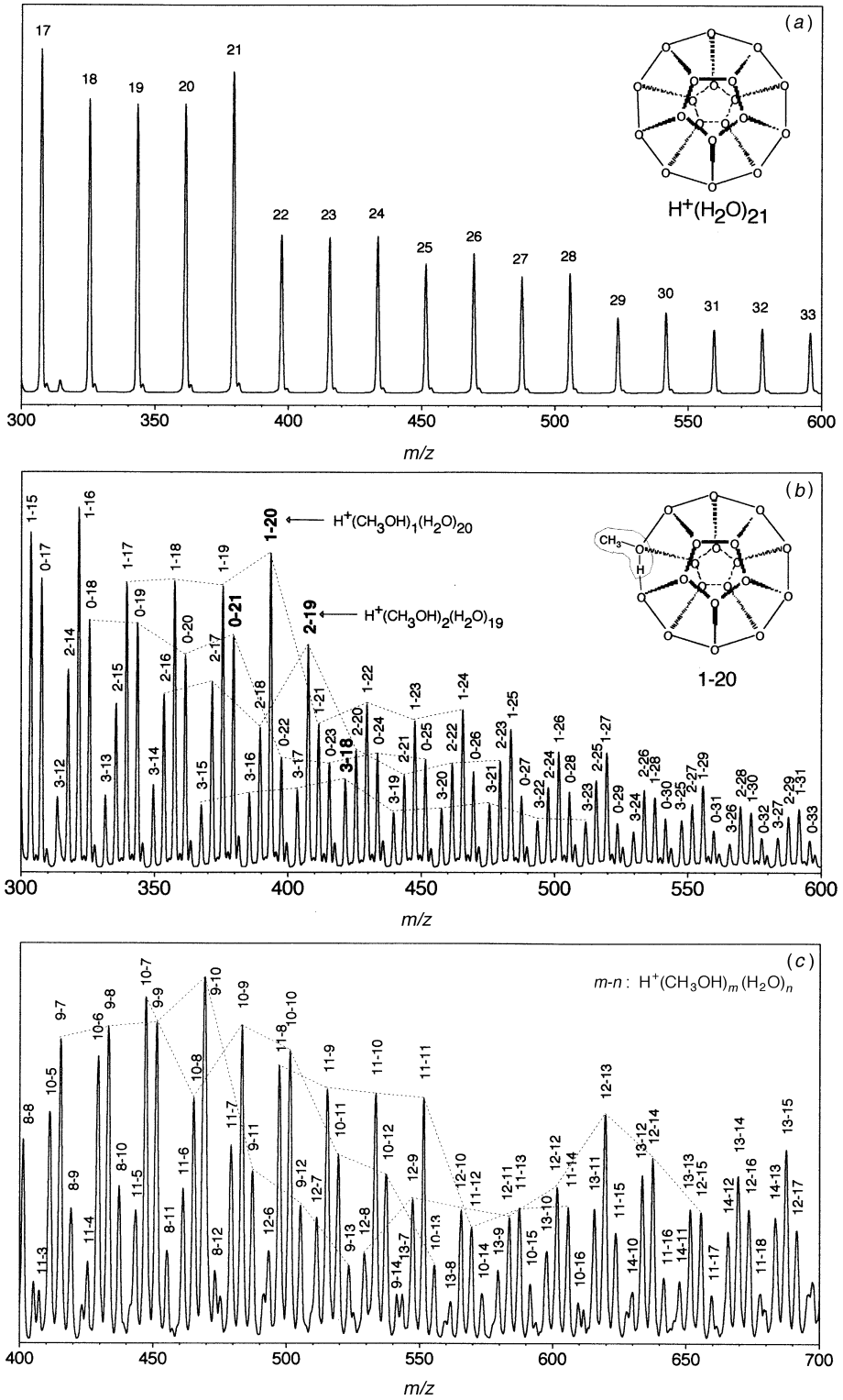

Fig. 3 Mass spectra for clusters generated from pure water and water–methanol mixtures. (*a*) Pure water; the numbers written on the peaks represent n for $H^+(H_2O)_n$; the insert shows a magic-number cluster $H^+(H_2O)_{21}$ which has a dodecahedral structure. (*b*) Water–methanol mixture with a molar ratio of $H_2O : CH_3OH = 100 : 1$; the paired numbers represent m–n for $H^+(CH_3OH)_m(H_2O)_n$; the peaks with the same number of m are connected by the dotted lines; the insert shows a schematic for 'substitutional interaction' of a methanol molecule with the $H^+(H_2O)_{21}$ cluster to form $H^+(CH_3OH)_1(H_2O)_{20}$. (*c*) Water–methanol mixture with a molar ratio of $H_2O : CH_3OH = 7 : 3$; the paired numbers represent m–n for $H^+(CH_3OH)_m(H_2O)_n$.

added to water, each methanol molecule makes a hydrogen bond with water, substituting the hydrogen-bonding network of water; on the contrary, when water is added to methanol, the methanol–methanol interaction is stabilized as a result of the cooperative effect of the hydrophobic interaction and the hydrogen-bonding interaction.[3] Accordingly, the number of hydrogen bonds is increased by the mixing of methanol and water, which is observed as exothermic mixing. The excess enthalpy shows a minimum around the water mole fraction 0.7, which may correspond to the maximum hydrogen-

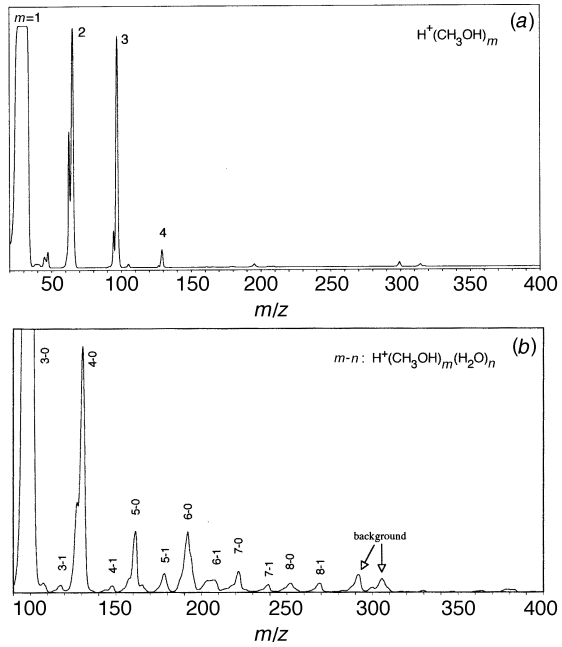

Fig. 4 Clustering of methanol influenced by a small amount of water. (*a*) Mass spectrum for pure methanol. The methanol clusters smaller than the tetramer are observed: $H^+(CH_3OH)_m$, $m \leqslant 4$. (*b*) Mass spectrum for methanol in the presence of a small amount of water ($CH_3OH : H_2O = 95 : 5$). The paired numbers represent m–n for $H^+(CH_3OH)_m(H_2O)_n$.

bonding interaction, since the large methanol hydrate clusters were formed around this mixing ratio.

2 Water–acetonitrile mixtures

'Additional interaction' of acetonitrile with water clusters. The excess enthalpy of mixing of water–acetonitrile binary mixtures also deviates from ideality, and this thermodynamic property is quite opposite to that of water–methanol mixtures, as shown in Fig. 1. The observed clustering of water–acetonitrile mixtures was also in good contrast with that of water–methanol mixtures in all mixing ratios. The acetonitrile–water interaction is much smaller than the methanol–water interaction; therefore, the water–cluster structure was conserved even at a molar ratio of $H_2O : CH_3CN = 7 : 3$. Fig. 5 shows the mass spectrum for $H_2O : CH_3CN = 7 : 3$. The paired numbers correspond to p–q of $H^+(CH_3CN)_p(H_2O)_q$. A series of clusters including the same number of acetonitrile molecules, $p = 0$–2, are connected by the dotted lines. As mentioned above, the water clusters, *i.e.* a series of clusters with $p = 0$, are clearly observed as for the clusters generated from pure water. In the series of acetonitrile hydrates with $p = 1$ and 2, the peaks p–q: 1–21 and 2–21 are observed as prominent species. The clusters including 21 water molecules are observed as magic-number species. The magic number $q = 28$ can also be confirmed on the mass spectrum for all the series of $p = 0$–2, *i.e.* 0–28, 1–28 and 2–28. In other words, the magic-number species are controlled by the number of water molecules (q), irrespective of the number of including acetonitrile molecules (p).

This is in contrast with the $H^+(CH_3OH)_m(H_2O)_n$ clusters, in which the clusters with the sum of the number of composed molecules: $m + n = 21$ or 28 show the magic-number property. Accordingly, if we call the methanol–water mixing 'substitutional mixing', we will be able to call the acetonitrile–water mixing 'additional mixing'. A schematic illustration of 'additional mixing' is shown in the insert of Fig. 5.

Entropy-controlled mixing. The excess enthalpy of mixing of the water–acetonitrile binary system shown in Fig. 1 shows that this mixing is an endothermic process. Furthermore, as shown in Fig. 5, after the mixing of acetonitrile and water, the acetonitrile clusters are hardly formed and the water conserves its own cluster structure. In general, an endothermic process should accompany an increase of entropy; therefore, it is reasonably deduced that the structure of acetonitrile after the mixing with water becomes more disordered than that before the mixing, on the basis of the clustering structure.

Fig. 6(*a*) shows the mass spectrum of clusters generated from pure acetonitrile. The acetonitrile clusters, $H^+(CH_3CN)_p$: $p = 1, 2, 3, \ldots$, composed of more than 20 molecules are clearly observed. The acetonitrile molecules form

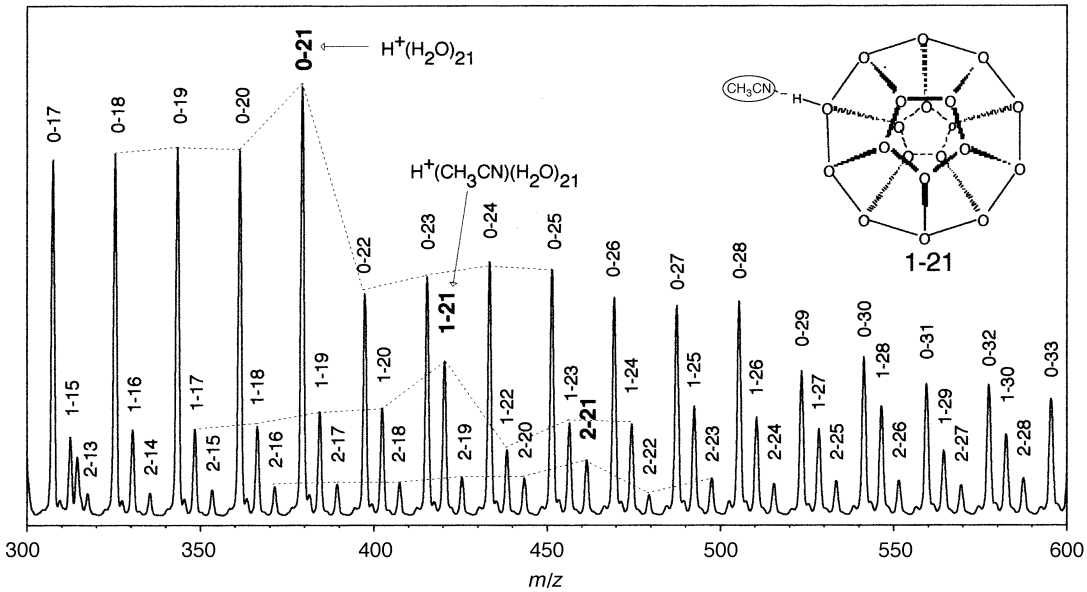

Fig. 5 Mass spectrum for water–acetonitrile mixture with a molar ratio of $H_2O : CH_3CN = 7 : 3$. The paired numbers represent p–q for $H^+(CH_3CN)_p(H_2O)_q$. The peaks with the same number of p are connected by the dotted lines. The insert shows a schematic picture for 'additional interaction' of an acetonitrile molecule with the $H^+(H_2O)_{21}$ cluster to form $H^+(CH_3CN)_1(H_2O)_{21}$.

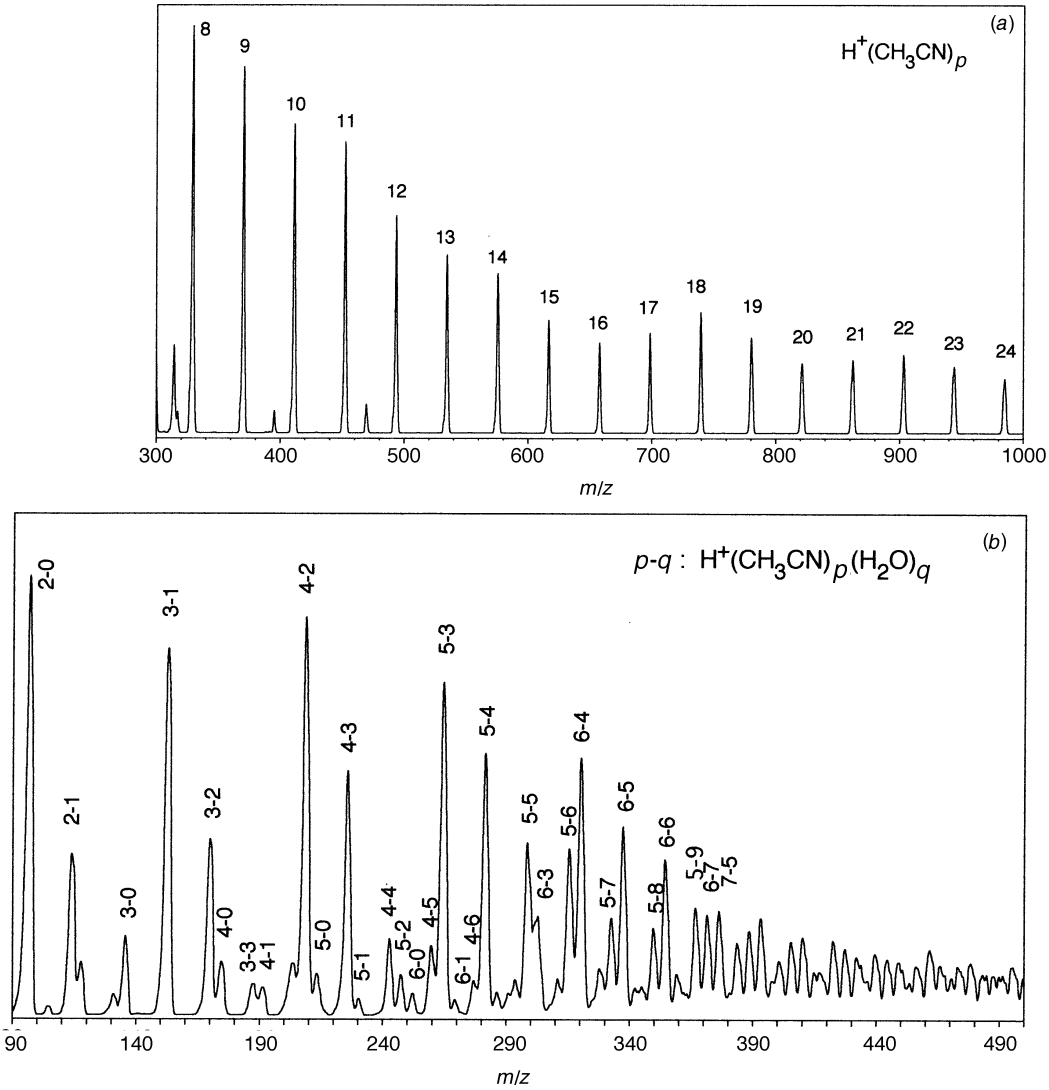

Fig. 6 Clustering of acetonitrile influenced by a small amount of water. (*a*) Mass spectrum for pure acetonitrile. The numbers 8, 9, 10, ... represent p for $H^+(CH_3CN)_p$. The large clusters are observed clearly. (*b*) Mass spectrum for acetonitrile in the presence of a small amount of water ($CH_3CN : H_2O = 95 : 5$). The paired numbers represent p–q for $H^+(CH_3CN)_p(H_2O)_q$.

clusters through their dipole–dipole interaction.[17] To see the effect of water on the clustering of acetonitrile, a small amount of water was added to pure acetonitrile. Even in the presence of a small amount of water (a mixing ratio of $CH_3CN : H_2O = 95 : 5$) the clustering of acetonitrile was found to be influenced markedly, as shown in Fig. 6(*b*). The large acetonitrile clusters, as observed for pure acetonitrile [Fig. 6(*a*)], are hardly observed, and some acetonitrile hydrate clusters are generated instead. In the acetonitrile hydrate clusters, the peaks p–q for $H^+(CH_3CN)_p(H_2O)_q$: 2–0, 3–1, 4–2, 5–3, 6–4, 7–5 *etc.* are observed as prominent species. The general formula for these clusters with q water molecules is described by $H^+(CH_3CN)_{q+2}(H_2O)_q$, which corresponds to clusters containing q water molecules and the maximum number of acetonitriles interacting with q water molecules, as shown in Fig. 7. This is in good agreement with the model reported by Meot-Ner and co-workers.[18,19] This indicates that the dipole–dipole interaction, which maintains the clustering of acetonitrile, is reduced in the presence of water. Before the mixing of acetonitrile and water, both of them readily form clusters in their pure liquids. However, when acetonitrile and water are mixed, the acetonitrile clusters disintegrate due to the interaction with water. This process corresponds to the endothermic process.

3 Substitutional mixing and additional mixing

As described above, the thermodynamic properties for the mixing of water and methanol are quite opposite to those for the mixing of water and acetonitrile. Furthermore, the difference in the thermodynamic properties between water–methanol and water–acetonitrile is related to the clustering structure observed by mass spectrometry. The difference in the clustering structure between water–methanol and water–

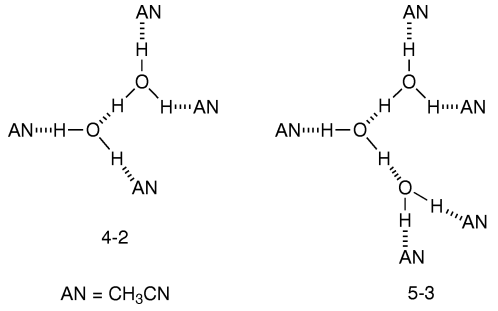

Fig. 7 Schematic illustration of acetonitrile–water clusters including the maximum number of acetonitrile molecules

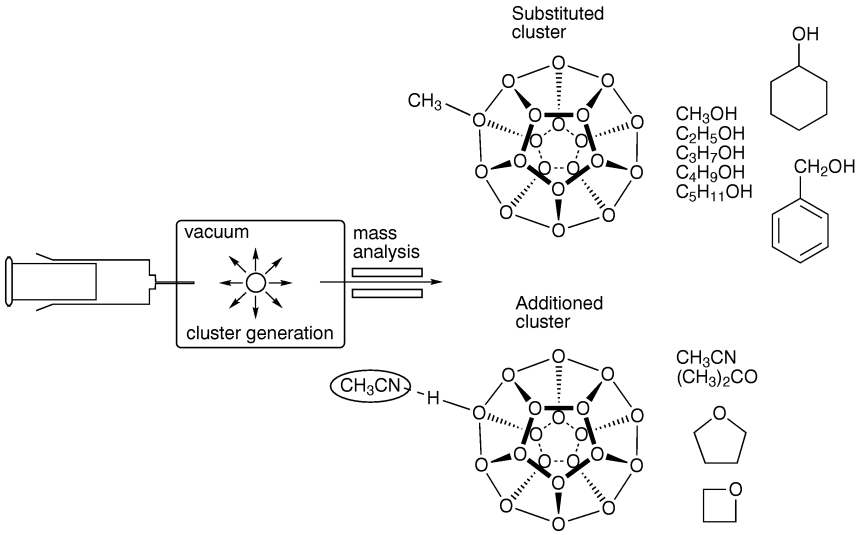

Fig. 8 'Substitutional' and 'additional' interaction of organic molecules with water clusters. For 11 kinds of organic molecules, the type of interaction of the organic molecules with water clusters is classified into 'substitutional' and 'additional' interactions.

acetonitrile is thought to be mainly due to hydrogen bonding, *i.e.* the OH group of methanol works as both a hydrogen-bond donor and an acceptor, while the CN group of acetonitrile works only as a hydrogen-bond acceptor. Therefore, part of the hydrogen-bonding network of water can be substituted by the methanol but not by the acetonitrile. In other words, methanol has a substitutional interaction with the water clusters, while the acetonitrile is forced to have an additional interaction. Such substitutional and additional interactions were observed for the various water–organic solvent mixtures, and it was confirmed that these interactions are dependent on the hydrogen-bond donor–acceptor properties. The mass spectra of clusters for 11 water–organic solvent binary mixtures were measured, and these binary mixtures classified into 'substitutional' and 'additional' mixing systems (Fig. 8).

Seven alcohols (methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, cyclohexanol and benzyl alcohol) showed 'substitutional mixing' with water. The mass spectra of these binary mixtures with water were the same type as in Fig. 3(*b*). However, with increasing size of the hydrophobic group of alcohols, methyl → ethyl → propyl → butyl …, the alcohol–alcohol interactions occurred easily. For example, the water–butan-1-ol system with a molar ratio of $H_2O : C_4H_9OH = 300 : 1$ showed the same type of mass spectrum as the water–methanol system with $H_2O : CH_3OH = 100 : 1$, but at $H_2O : C_4H_9OH = 100 : 1$, clusters composed of butan-1-ol molecules, $H^+(C_4H_9OH)_n$: $n = 1, 2, 3 \ldots$, were observed as prominent species. This is due to the so-called hydrophobic effect. Note that each alcohol has a 'substitutional' with water at lower concentrations, and that the alcohol–alcohol interaction occurs more easily for the alcohols with a larger hydrophobic group. This is related to the phase separation process.

On the other hand, acetonitrile, acetone, oxetane and tetrahydrofuran exhibited 'additional mixing' with water. The mass spectra of these binary mixtures were the same as that in Fig. 5. Since all these organic molecules work only as hydrogen-bond acceptors, these organic molecules cannot work as a part of the hydrogen-bonding network of water. The 'additional mixing' with water means that the organic molecules exist in the space between water clusters.

Conclusion

The cluster structure of water–methanol mixtures was found to be in remarkable contrast with that of water–acetonitrile mixtures. The excess enthalpy of mixing for the water–methanol system also contrasted with that for water–acetonitrile mixtures. This difference in the thermodynamic properties and the deviation from ideality for these two binary mixtures could be partially explained by the clustering process observed here. It is well known that the excess enthalpy of mixing is dependent on the temperature. It should also be related to the cluster structure. Owing to experimental difficulties, we could not have a precise discussion on this temperature effect.

Although the water–organic solvent mixtures, especially at low concentrations of organic solvent, were classified 'substitutional' and 'additional' mixing systems, their thermodynamic properties are still not perfectly explained by the observed cluster structure.

References

1 P. W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 1986, p. 169.
2 N. Nishi, *Z. Phys. D*, 1990, **15**, 239.
3 S. Okazaki, H. Touhara and K. Nakanishi, *J. Chem. Phys.*, 1984, **81**, 890.
4 A. Wakisaka, Y. Shimizu, N. Nishi, K. Tokumaru and H. Sakuragi, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1129.
5 A. Wakisaka, S. Takahashi and N. Nishi, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 4063.
6 A. Wakisaka, Y. Yamamoto, Y. Akiyama, H. Takeo, F. Mizukami and K. Sakaguchi, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3339.
7 A. Wakisaka, Y. Akiyama, Y. Yamamoto, T. Engst, H. Takeo, F. Mizukami, K. Sakaguchi and H. Jones, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3539.
8 A. Wakisaka, *J. Org. Syn. Chem. Jpn.*, 1994, **52**, 478.
9 D. A. Armitage, M. J. Blandamer, M. J. Foster, N. J. Hidden, K. W. Morcom, M. C. R. Symons and M. J. Wootten, *Trans. Faraday Soc.*, 1968, **64**, 1193.
10 L. Benjamin and G. C. Benson, *J. Phys. Chem.*, 1963, **67**, 858.
11 K. W. Morcom and R. W. Smith, *J. Chem. Thermodyn*, 1969, **1**, 503.
12 N. Nishi and K. Yamamoto, *J. Am. Chem. Soc.*, 1987, **109**, 7353.
13 N. Nishi and K. Yamamoto, *J. Am. Chem. Soc.*, 1990, **112**, 549.
14 S. Wei, Z. Shi and A. W. Castleman Jr., *J. Chem. Phys.*, 1991, **94**, 3268.
15 X. Yang and A. W. Castleman Jr., *J. Am. Chem. Soc.*, 1989, **111**, 6845.
16 U. Nagashima, H. Shinohara, N. Nishi and H. Tanaka, *J. Chem. Phys.*, 1986, **84**, 209.
17 G. D. Mistro and A. J. Stace, *J. Chem. Phys.*, 1993, **99**, 4656.
18 C. A. Deakyne, M. Meot-Ner, C. L. Campbell, M. J. Hughes and S. P. Murphy, *J. Chem. Phys.*, 1986, **84**, 4958.
19 M. Meot-Ner, *J. Am. Chem. Soc.*, 1986, **108**, 6189.

Paper 7/05777F; *Received* 7*th August*, 1997