Physical Chemistry I
Written Qualifying Exam
June 2009
Professor Evans

Wakisaka, A., Abdoul-Carime, H., Yamamoto, Y., Kiyozumic, Y.; Non-ideality of binary mixtures; Water–methanol and water–acetonitrile from the viewpoint of clustering structure *J. Chem. Soc., Faraday Trans.*, 1998, 94(3), 369-374.

1. The authors state that ΔH of mixing is zero for an ideal binary solvent mixture. Define the properties of the two solvents that make up an ideal binary mixture.(1)

2. Is the formation of a hydrogen bond between solvent molecules exothermic or endothermic? Illustrate this concept with a potential energy vs. bond distance diagram.(1)

3. Exothermic reactions/processes are characterized as enthalpy driven. Endothermic reactions/processes are characterized as entropy driven. Explain.(2)

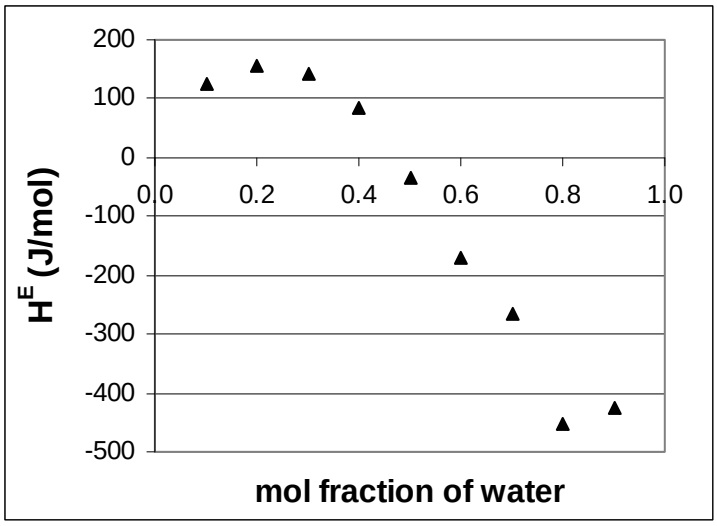
4. Does a chemical reaction occur when methanol and water are mixed? Describe on a molecular level what occurs when methanol and water are mixed in approximately equal mole ratios.(1)

5. Explain how the authors drew the following conclusion from the data presented in Figure 5. Acetonitrile molecules add to the water clusters at high water/acetonitrile ratios.(1)

6. How can the data in Figures 4 and 6 be interpreted to support the calorimetric data shown in Figure 1?(2)

7. The paper states that 1-butanol clusters in water/1-butanol mixtures are prominent species, even at very high water/1-butanol ratios (ie. 100:1). The authors suggest that the "hydrophobic effect" is responsible for this observation. What is the "hydrophobic effect" and why does it explain the prominence of the 1-butanol clusters? The driving force for hydrogen bond formation derives from the dipole moment of the solvent molecules. What is the driving force behind the hydrophobic effect?(1)

8. The data shown below is from a calorimetric experiment that measured the heat exchanged from mixing different mole ratios of water and 2-propanol. Use these data and the results of the Wakisaka paper to predict the relative level of clustering in pure 2-propanol and 80/20 2-propanol:water, and the relative clustering in pure water and 20/80 2-propanol:water.(1)



9. An isocratic HPLC method in the literature uses a 60:40 mixture of 2-propanol and methanol. It is found the using pure ethanol as the mobile phase provides a similar separation efficiency. Does it make sense from a green chemistry standpoint to switch to an ethanol-based mobile phase? Justify your answer.(2)

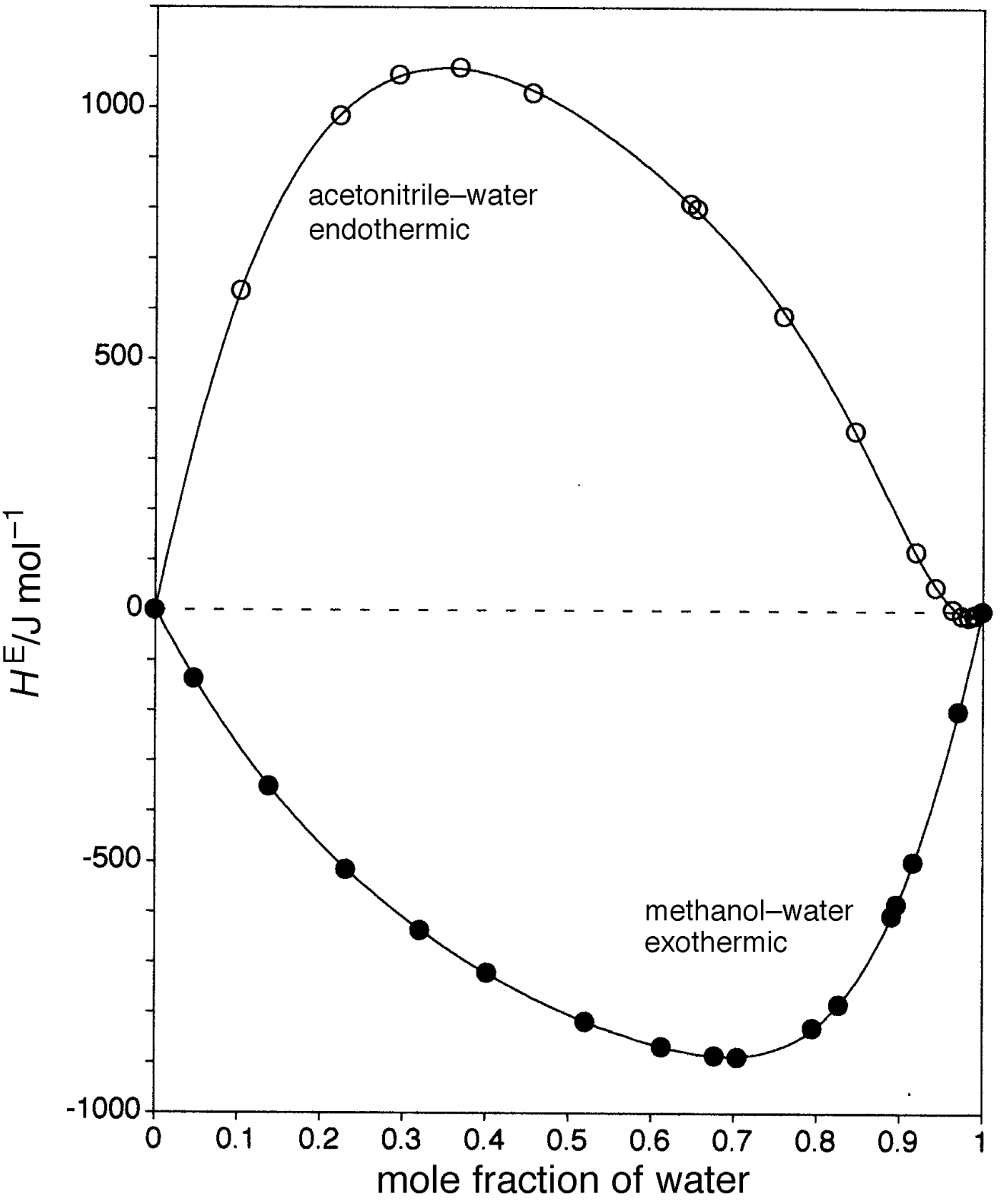


Fig. 1 Excess enthalpy of mixing at 25 °C for water–methanol[10] and water–acetonitrile[11] mixtures as functions of mole fraction of water. The dashed line corresponds to the ideal binary mixture whose excess enthalpy of mixing is zero.

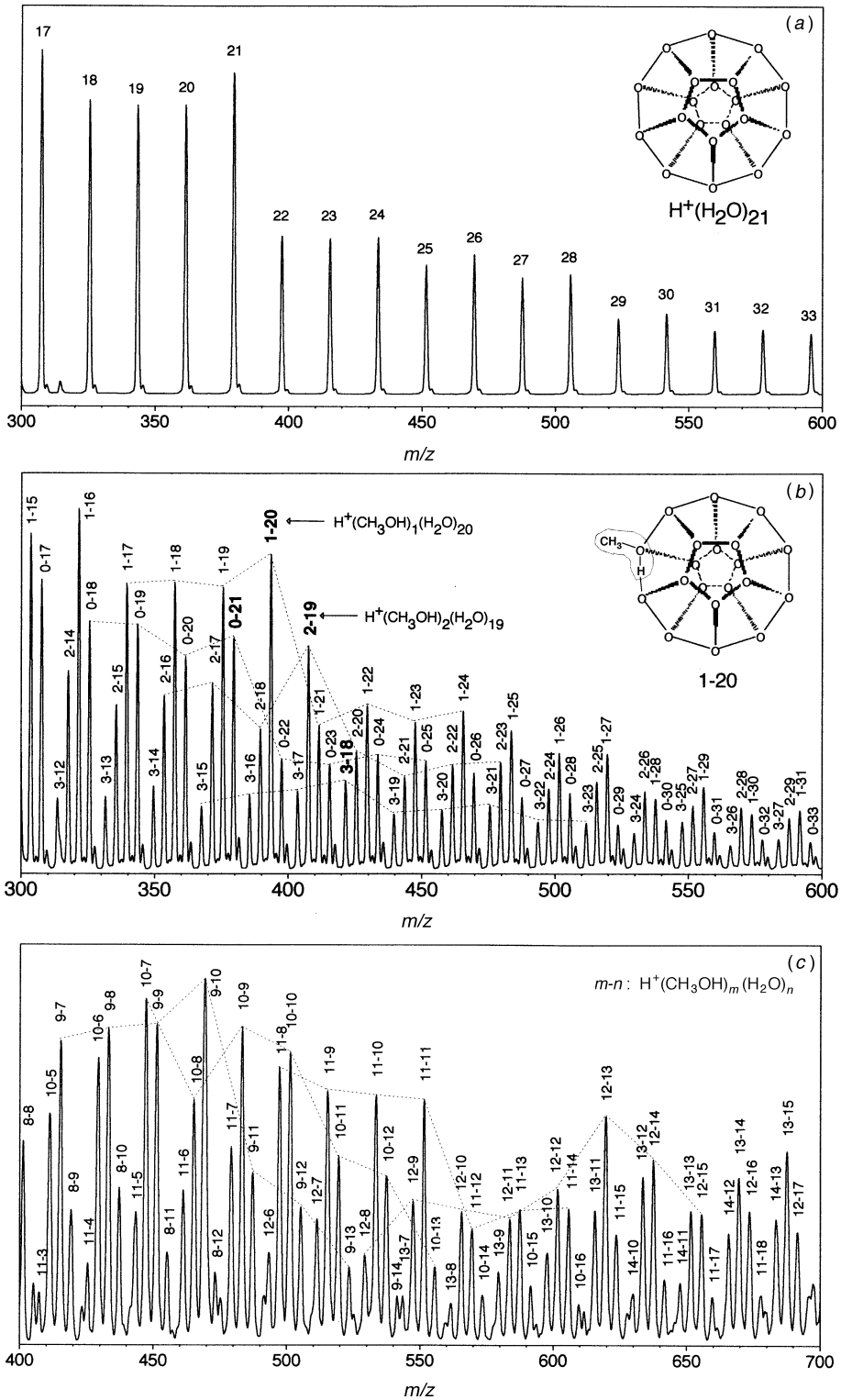


Fig. 3 Mass spectra for clusters generated from pure water and water–methanol mixtures. (*a*) Pure water; the numbers written on the peaks represent n for $H^+(H_2O)_n$; the insert shows a magic-number cluster $H^+(H_2O)_{21}$ which has a dodecahedral structure. (*b*) Water–methanol mixture with a molar 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 $H^+(CH_3OH)_m(H_2O)_n$.

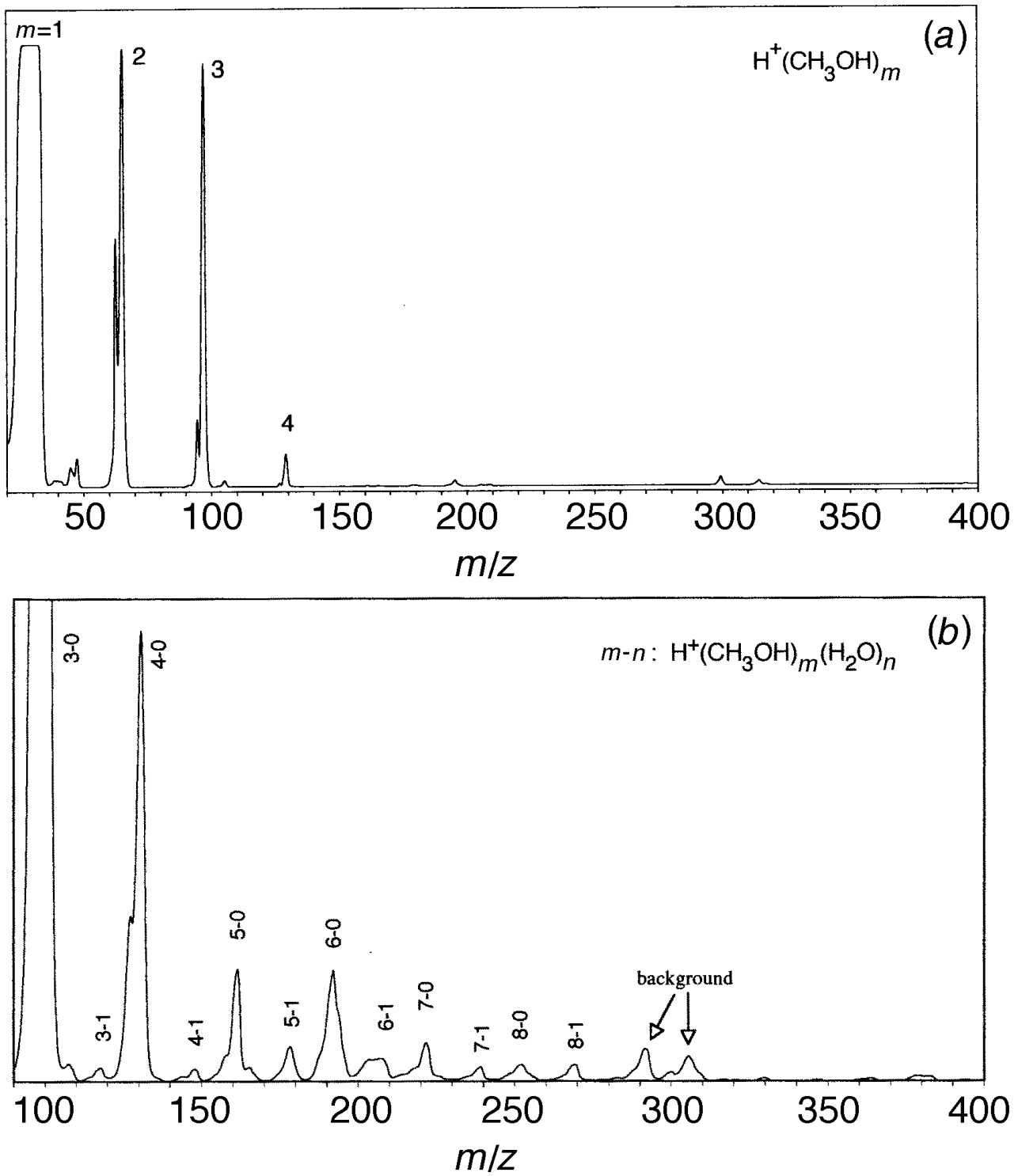


Fig. 4 Clustering of methanol influenced by a small amount of water. (*a*) Mass spectrum for pure methanol. The methanol clusters smaller than the tetramer are observed: $H^+(CH_3OH)_m$, $m \leqslant 4$. (*b*) Mass spectrum for methanol in the presence of a small amount of water ($CH_3OH : H_2O = 95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

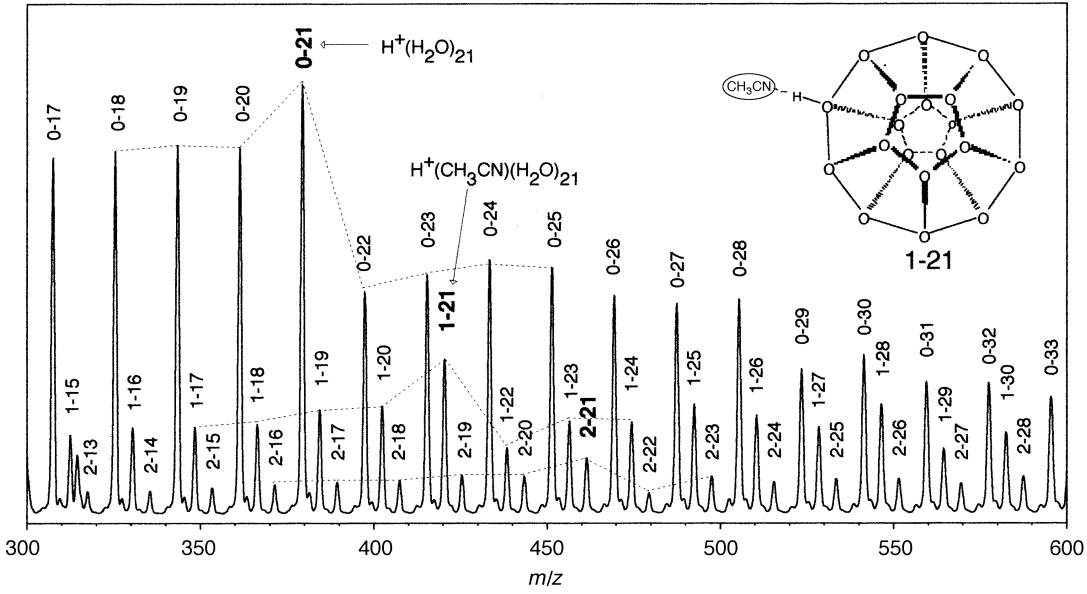


Fig. 5 Mass spectrum for water–acetonitrile mixture with a molar ratio of $H_2O : CH_3CN = 7 : 3$. The paired numbers represent p–q for $H^+(CH_3CN)_p(H_2O)_q$. The peaks with the same number of p are connected by the dotted lines. The insert shows a schematic picture for 'additional interaction' of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

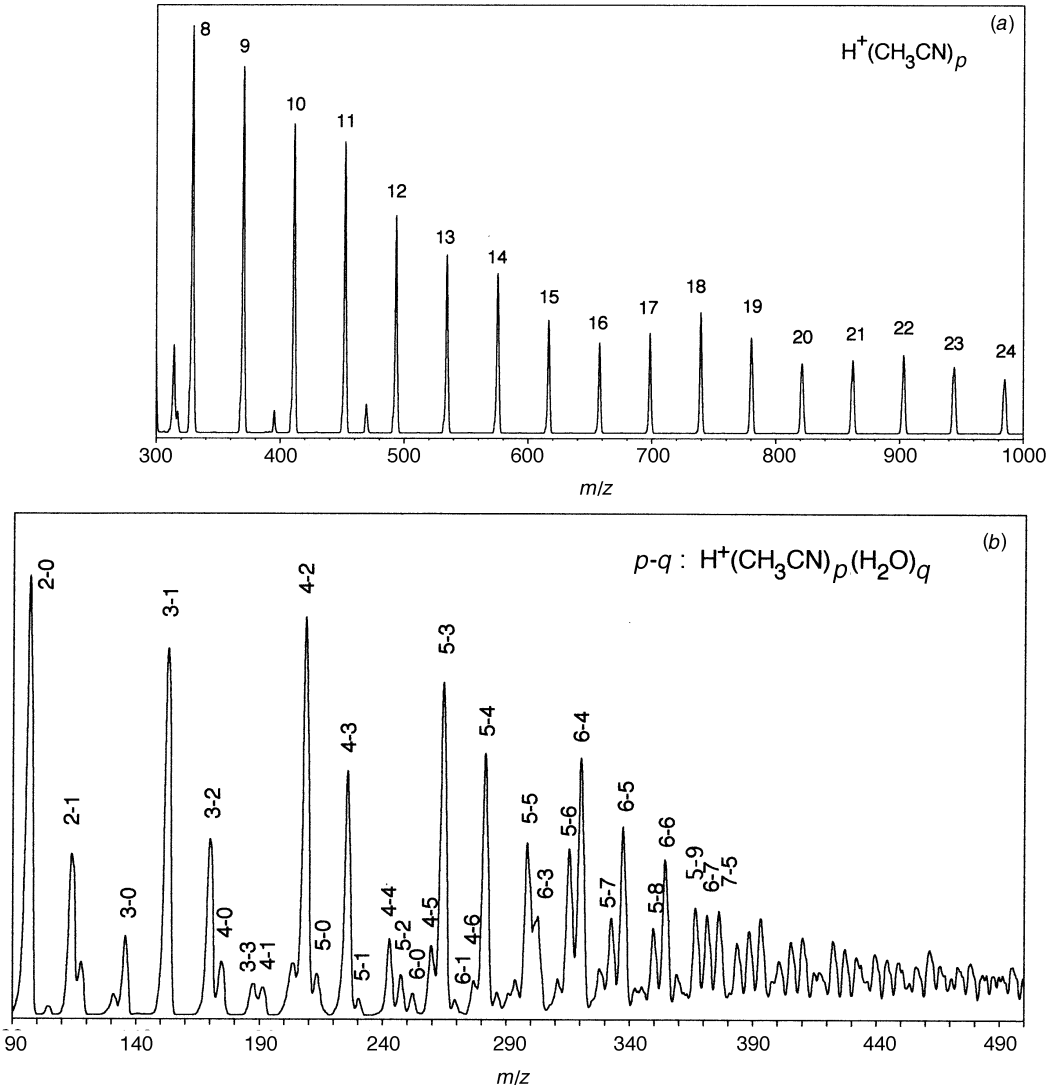


Fig. 6 Clustering of acetonitrile influenced by a small amount of water. (*a*) Mass spectrum for pure acetonitrile. The numbers 8, 9, 10, … represent p for $H^+(CH_3CN)_p$. The large clusters are observed clearly. (*b*) Mass spectrum for acetonitrile in the presence of a small amount of water ($CH_3CN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