Reorganization of Clusters through Hydrophobic and Hydrogen-bonding Interaction in Pyridine–Phenol–Water Solution

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Clusters composed of pyridine and phenol molecules have been grown in aqueous solution by increasing the temperature.

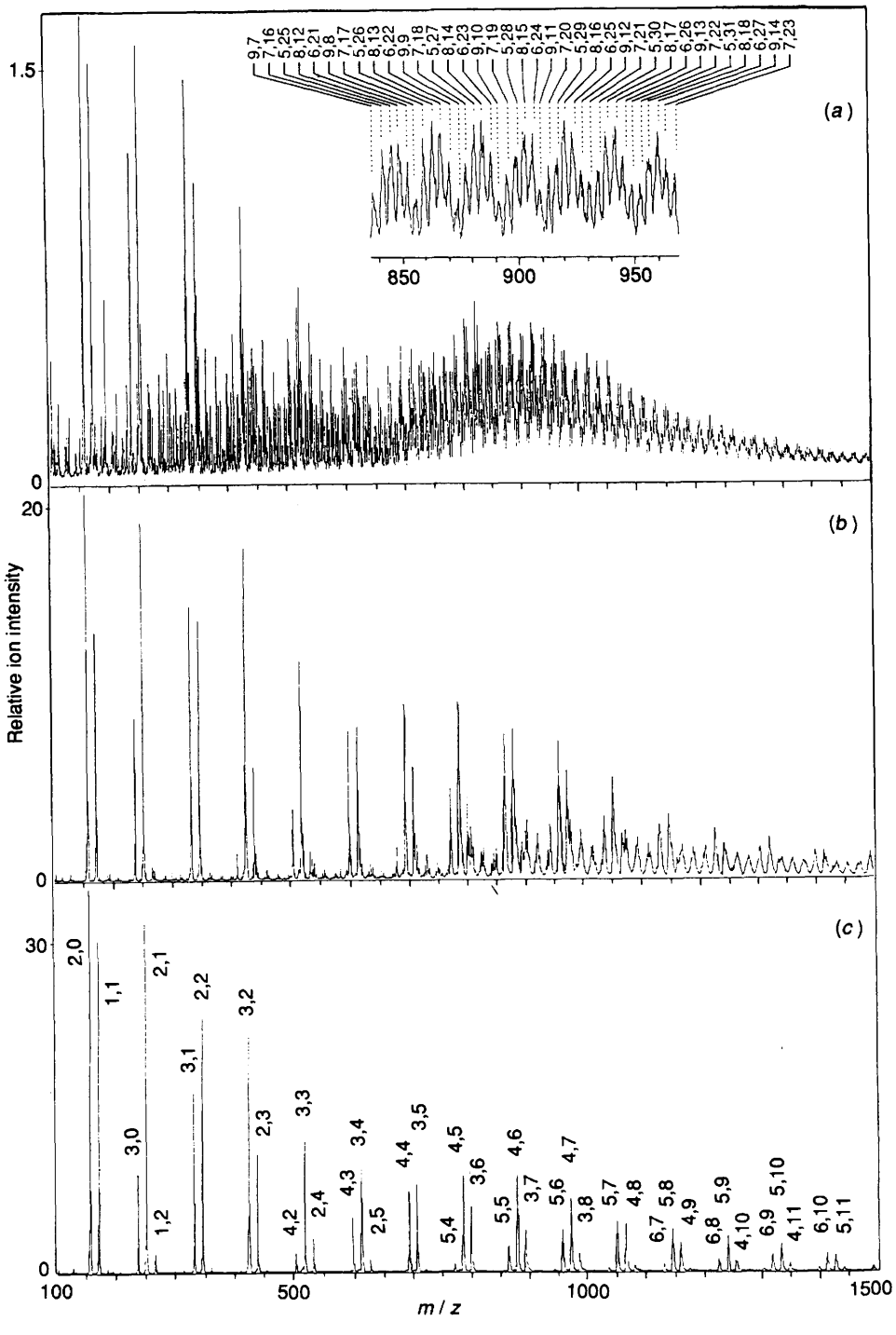

Fig. 1 Mass spectra of clusters generated from a solution containing pyridine, phenol and water in molar ratio 10 : 1 : 10. Temperatures of the liquid droplets are (*a*) 40, (*b*) 90 and (*c*) 110 °C. Insert in (*a*) is the expanded spectrum in the region from the mass number 836 to 968. The paired numbers numbers described in (*a*) and (*c*) represent *r*, *s* for $(C_5H_5N)_r(H_2O)_s$ and *p*,*q* for $(C_5H_5N)_p(C_6H_5OH)_q$, respectively.

In solution, it is easy for molecules to make cluster structures through hydrogen-bonding, hydrophobic interaction, *etc.*[1–3] Such clusters in solution are expected to be reorganized with changes in temperature, which will finally lead to macroscopic changes such as vaporization, crystallization, phase separation, *etc.* However, there is very little direct experimental evidence for the reorganization of the cluster structures in solution. We have observed cluster structures, indicating the reorganization of molecules as the intermolecular interaction in solution is changed, by the measurement of mass spectra of clusters in a solution containing pyridine, phenol and water.

Mass spectra of the clusters in the solution were measured using vacuum adiabatic expansion of liquid droplets.[1–3] The sample solution was injected into a four-stage differentially pumped vacuum system through a heated nozzle. Liquid droplets (mist particles) were formed in the first chamber at a pressure of 0.2 Torr, and were expanded to be disintegrated into clusters in the second chamber at 0.01 Torr. The resulting clusters were ionized by an electron impact with 30 eV in the third chamber at 1×10^{-5} Torr and analysed by a quadrupole mass spectrometer in the fourth chamber at 1×10^{-7} Torr. The mass spectra obtained reflect the size distribution of the clusters in the solution. The lifetime that a given cluster maintains in solution is very short due to thermal motion,[4] but the size distribution of the cluster obtained in the spectrum is thought to be representative of the steady state of the clustering structure in the original solution, albeit under different physical conditions.

Figs 1(*a*), (*b*) and (*c*) show the mass spectra of clusters generated from a solution containing pyridine, phenol and water in a molar ratio 10:1:10; temperature of the liquid droplets are 40, 90 and 110 °C, respectively. At 40 °C [Fig. 1(*a*)], the prominent peaks observed with *m/z* numbers lower than *ca.* 600 are assigned to $(C_5H_5N)_p(C_6H_5OH)_q$, and other smaller peaks correspond to $(C_5H_5N)_p(C_6H_5OH)_q(H_2O)_m$, $(C_5H_5N)_r(H_2O)_s$ and $(H_2O)_n$. On the other hand, most peaks with *m/z* numbers higher than *ca.* 600 corresponds to the sequences of $(C_5H_5N)_r(H_2O)_s$, as shown in Fig. 1(*a*). As the temperature of the liquid droplets increases, the $(C_5H_5N)_r(H_2O)_s$ clusters are reduced, while larger $(C_5H_5N)_p(C_6H_5OH)_q$ clusters grow remarkably. At 110 °C [Fig. 1(*c*)], every observed peak corresponds to the cluster composed of pyridine and phenol molecules $(C_5H_5N)_p$-$(C_6H_5OH)_q$. This temperature effect indicates that with increasing temperature, the interaction of pyridine with water is disturbed and the interaction of pyridine with phenol becomes favourable. As a result, the cluster structure is reorganized in the liquid state with increasing temperature.

Water is the most volatile species in this mixed solution; therefore, with increasing temperature the water molecules are likely to become free from hydrogen-bonding interactions with pyridine because of their relative volatility and mobility. By comparing the mass spectra for the solutions with and without water, it was shown that these free water molecules played an important role in the cluster structure of pyridine and phenol. In the mass spectra of a solution containing pyridine and phenol in the molar ratio 10:1 (in the absence of water), $(C_5H_5N)_1(C_6H_5OH)_1$ was the only species observed as a cluster. It is surprising that when the water molecules become free from the cluster with pyridine at higher temperatures, the residual molecular interaction, *i.e.* the clustering of pyridine and phenol molecules, is accelerated.

The formation or nucleation process for $(C_5H_5N)_p$-$(C_6H_5OH)_q$ clusters is an entropy-decreasing process. On the other hand, as the water molecules become free from the hydrogen-bonding interaction with pyridine at higher temperatures, this process is accompanied by an increase of entropy. As a model for the ordered-structure making process, some attention needs to be paid to the thermodynamics involved in the reorganization of clusters in aqueous solution.

Thus all the results obtained to date suggest that the reorganization process of clusters in this three-component solution, and perhaps others, can be observed using this mass spectral approach.

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