Clustering of a Hydrogen-bonding Complex between Pyridine and Pyrrole: Correlation with Nucleation of Intermolecular Compounds

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A hydrogen-bonding complex between pyridine and pyrrole aggregates in aqueous solution.

Upon crystallization from mixtures containing five- and six-membered nitrogen heteroaromatic compounds, intermolecular compounds of 1 : 1 molar ratio are isolated as crystals in which hydrogen bonding occurs between the two molecules. Examples include indole–isoquinoline,[1] indole–2-methylquinoline[2] *etc.* However, there is very little direct experimental evidence to show how crystals of the intermolecular compounds are formed through the hydrogen-bonding interaction. We have observed by mass spectrometry that the hydrogen-bonding complex of pyridine and pyrrole is a definate species which forms clusters in solution composed of pyridine and pyrrole molecules. This model system demonstrates the primary process for the nucleation of the intermolecular compounds.

The mass spectra of clusters in solutions containing pyridine and pyrrole were measured by using the liquid adiabatic expansion technique.[3] The sample solution was injected into four-stage differentially pumped vacuum system through a heated nozzle. Liquid droplets (aerosol) were formed in the first chamber (0.2 Torr), and were disintegrated into clusters by adiabatic expansion in the second chamber. The resulting clusters were ionized by electron impact (30 eV) in the third chamber, and analysed by a quadrupole mass spectrometer in the fourth chamber.

Figs. 1(*a*) and (*b*) show the mass spectra of clusters generated from pyrrole–pyridine mixed solutions of 1 : 1 and 2 : 1 molar ratios respectively. Observed peaks at *m/z* 134 and 146 correspond to the pyrrole dimer $[(C_4H_5N)_2{\cdot}^+]$ and the 1 : 1 pyrrole–pyridine complex $[(C_4H_5N)(C_5H_5N){\cdot}^+]$, respectively. Other complexes of pyrrole–pyridine such as 2 : 1 or 1 : 2 species were not observed. The relative signal intensity of the pyrrole–pyridine hydrogen-bonding complex to the pyrrole dimer is increased upon increasing the pyridine concentration. The 1 : 1 pyrrole–pyridine complex was observed over a wide range of mixing ratios. This is in good correlation with the fact that the crystal of the 1 : 1 indole–isoquinoline intermolecular compound is formed over a wide range of mixtures. The solid–liquid phase diagram of the indole–isoquinoline system is shown in Fig. 1 (inset). No complex could be observed for the *N*-methylpyrrole–pyridine system. These results indicate that the formation of pyrrole dimer and pyrrole–pyridine complex arise from hydrogen-bonding interactions between these molecules in solution.

To accelerate the clustering of the pyrrole–pyridine system *via* hydrophobic interactions, a small amount of water was added. As Fig. 2 shows, a variety of clusters composed of pyrrole and pyridine molecules are generated in the presence of water. If signals corresponding to species with the same number of pyrrole molecules are connected by dashed lines, as shown in Fig. 2, it is found that clusters composed of equimolecular amounts of pyrrole and pyridine *e.g.* (pyrrole)(pyridine)$^{\cdot+}$, (pyrrole)$_2$(pyridine)$_2{\cdot}^+$ and (pyrrole)$_3$(pyridine)$_3{\cdot}^+$, predominate. This fact suggests that the hydrogen-bonding complex of pyrrole–pyridine is the basic unit for the clustering in pyrrole–pyridine mixtures.

If nuclei for crystallization are produced through the aggregation of the stable clusters in the liquid state, the observed mass spectra of Figs. 1 and 2 demonstrate a model

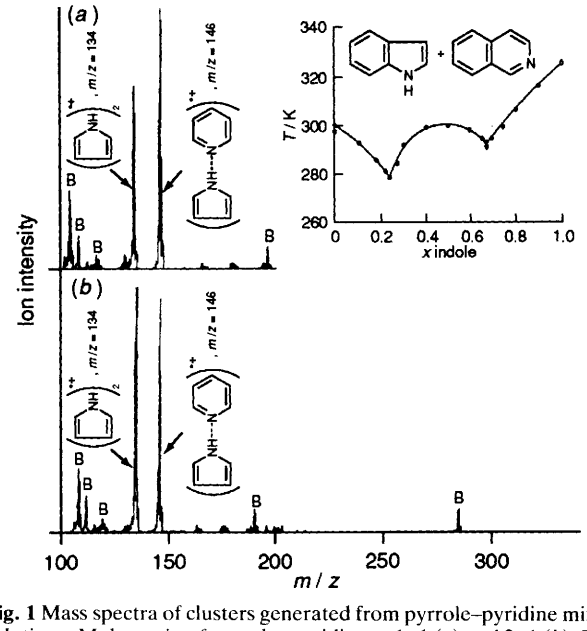

Fig. 1 Mass spectra of clusters generated from pyrrole–pyridine mixed solutions. Molar ratio of pyrrole : pyridine = 1 : 1 (*a*) and 2 : 1 (*b*). The liquid droplets are at 70 °C. (B represents background peaks from vacuum oil). The insert shows the solid–liquid phase diagram of the indole–isoquinoline system.

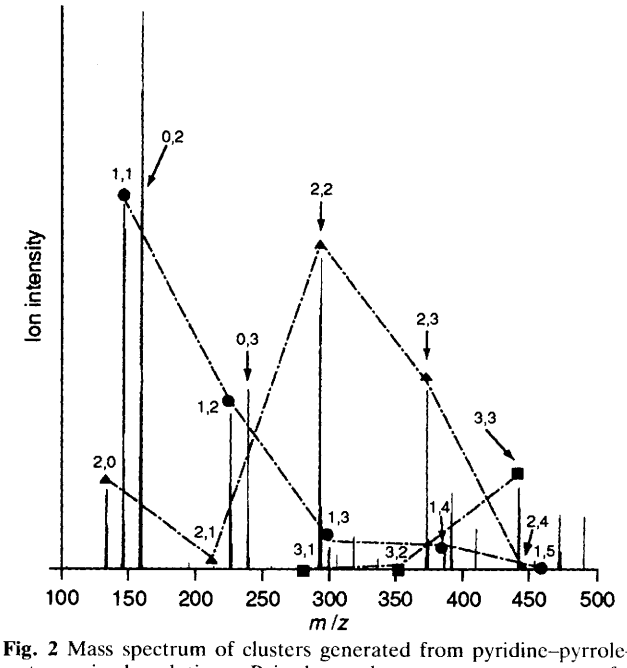

Fig. 2 Mass spectrum of clusters generated from pyridine–pyrrole–water mixed solution. Paired numbers represent *m*, *n* for (pyrrole)$_m$(pyridine)$_n{\cdot}^+$. (●) (pyrrole)$_1$(pyridine)$_n{\cdot}^+$ (n = 1–5), (▲) (pyrrole)$_2$(pyridine)$_n{\cdot}^+$ (n = 0–4), (■) (pyrrole)$_3$(pyridine)$_n{\cdot}^+$ (n = 0–3).

system in which clustering of hydrogen-bonding complexes affords the nucleus for the crystal of the resulting 1:1 intermolecular compounds.

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