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# Proton and Nitrogen-14 Nuclear Magnetic Resonance Study of Pyridine - Water System

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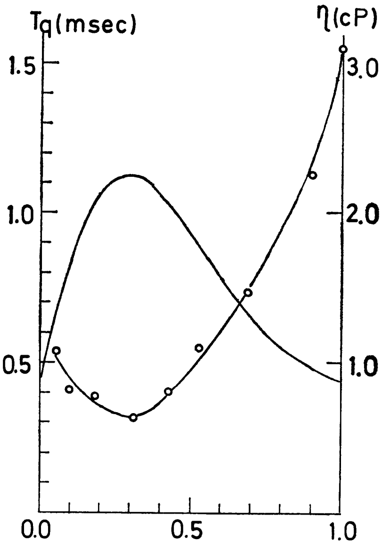
This note reports the results of $^1$H and $^{14}$N Nuclear Magnetic Resonance (NMR) study of the pyridine-water system. Using $^1$H and $^{14}$N line width data for pyridine, the anomalous concentration dependence of macroscopic quantities such as viscosity and density is discussed in terms of the formation of hydrogen-bonding.

Proton and $^{14}$N NMR spectra were collected at room temperature using JEOLCO JNM 4H-100 and Varian VF-16 spectrometers operating at 100 MHz and 4.15 MHz, respectively. Proton NMR samples were vacuum degassed by repeated freeze-pump cycles.

A remarkable dependence on concentration was observed for the line widths of the α protons and $^{14}$N of pyridine. The line width of the α protons for the neat pyridine sample is about 1.5 Hz. On adding water, the line width of the α protons decreases until it becomes minimum at $M=0.3$, where $M$ denotes the mole fraction for pyridine, increasing again with further addition of water. In parallel with the behavior of the $^1$H line widths, the line width for $^{14}$N has its maximum at $M=0.3$. Figure 1 shows the change of the $^{14}$N relaxation time calculated from the line width by assuming that the line shape is Lorentzian. The variation of viscosity with concentration[1] is also given in Fig. 1, which shows that the viscosity has a maximum at $M=0.3$.

It has been suggested from infrared [2,3] and Raman[4] data that hydrogen-bonded complexes are formed between pyridine and water molecules. When the amount of pyridine is much smaller than that of water, the dominant species is supposed to be [pyridine·$H_2O$] for which the formation constant has been estimated at 2.8 *l*/mol.[4]



mole fraction, pyridine

Fig. 1. Concentration dependence of the viscosity and the relaxationtime of $^{14}$N.
—○—: Relaxation time of $^{14}$N.
———: Viscosity (Ref. 1).

Over the whole range examined, a single line is observed in the $^{14}$N spectra, which suggests that there is a rapid exchange of pyridine molecules between free and hydrogen-bonded (to water) sites. In this case, the line width $\Delta H$ may be given by

$$\Delta H = p\Delta H_{\mathrm{coord}} + (1-p)\Delta H_{\mathrm{free}}, \qquad \text{(A)}$$

where $p$ is the fractional population of the hydrogen-bonded pyridine molecules, and $\Delta H_{\mathrm{coord}}$ and $\Delta H_{\mathrm{free}}$ are the line widths for the hydrogen-bonded and free pyridine molecules, respectively. The fractional population $p$ was calculated with the use of the equilibrium constant $K=2.8$ *l*/mol;[4] $\Delta H_{\mathrm{free}}$ was taken as the line width of neat pyridine, and $\Delta H_{\mathrm{coord}}$ from the region $M \leqq 0.1$ of the mixture. The line widths $\Delta H_{\mathrm{coord}}$ and $\Delta H_{\mathrm{free}}$ were divided by the viscosity to eliminate any effect due to viscosity. In Fig. 2, $\Delta H$ thus obtained is compared with the observed line width (corrected with respect to the viscosity). Thus in the region $M < 0.5$, the gross features of the line width are well reproduced by the assumption of the formation of [pyridine·$H_2O$] complex. These results suggest that the formation of the hydrogen-bonded complex is responsible for the anomalous concentration dependence of the vis-

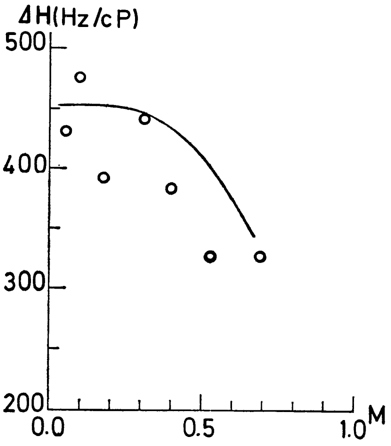


Fig. 2. Calculated and observed line width.
——: Line width calculated from the expression (A).
○: Observed line width corrected for viscosity.

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cosity and density. For the region where *M* is sufficiently large, complexes other than [pyridne$\cdot H_2O$] will be formed and the above assumption does not hold.

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