

Vibrational Spectra of the Solid Solution of (Piperazine–Pinacol) Hexahydrate and Polarons

Isao Kanesaka,* Satomi Yonezawa and Mizuho Sakanaka

Faculty of Science, Toyama University, Gofuku, Toyama 930, Japan

Raman and infrared spectra of crystals obtained from an aqueous solution of piperazine and pinacol with an arbitrary molar ratio were observed and confirm the formation of a solid solution of (piperazine–pinacol) hexahydrate, for which the infrared and Raman bands due to piperazine molecules change as the molar fraction of piperazine, x , changes. The Raman spectra of the deuterated system with $x = 0.80$ were also observed in the temperature range 296–25 K. One of two N–D stretches, the lower wavenumber one, increased in intensity as the temperature decreases and was assigned to polarons. It was found that the Raman intensity of the polarons is stronger in the solid solution than the parent compound, which can be qualitatively explained in terms of the difference in structure between them. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

We have reported^{1,2} that the Raman spectra of deuterated piperazine hexahydrate shows a new band red shifted from the main N–D stretch by 38 cm^{-1} . The intensity of this band increases at low temperatures. This band has been assigned¹ to polarons, which result from the anharmonic coupling of N–D stretches with the acoustic modes on the basis of the Alexander and Krumhansl polaron model.³ However, since there is no acoustic mode which belongs to the totally symmetric species in piperazine hexahydrate, we have re-investigated the polarons² on the basis of the Scott polaron model,⁴ revealing coupling with optical modes at 95 cm^{-1} . The involvement of polarons in the H counterpart is not always clear,^{1,2} as has been found in deuterated acetanilide.^{5,6} Polarons in vibrational spectra were found for the first time in the amide I region in acetanilide.^{7,8} Hence, further investigations on polarons in the present system were desirable in order to clarify the properties of polarons and to confirm the assignment. In the present study, this was carried out using a solid solution of (piperazine–pinacol) hexahydrate.

The crystal structures of piperazine hexahydrate⁹ and pinacol hexahydrate¹⁰ are almost isomorphous with the space groups $P2_1/n$ and $P4_2/mnm$, respectively; the lattice constants are $a = 6.309$, $b = 6.323$, $c = 14.91\text{ Å}$ and $\beta = 94.96^\circ$ for piperazine hexahydrate, and $a = b = 6.398$ and $c = 15.926\text{ Å}$ for pinacol hexahydrate. In both the hydrates there are two-dimensional hydrogen-bonded networks consisting of five-membered rings involving water molecules. Piperazine molecules in the hydrate take the equatorial configuration of the NH groups and also partly the axial configuration² at room

temperature. Pinacol molecules in the hydrate take the *trans* form with the two equally populated positions, resulting in higher symmetry, and the polarized Raman spectra in the region of O–H stretches have been analysed.¹¹ Hence, since the vibrational spectra of both hydrates and the normal modes of piperazine¹² have been studied in detail, information about the formation and structure of the solid solution of (piperazine–pinacol) hexahydrate should be obtained from the vibrational spectra.

In this paper, we report the formation of the solid solution of (piperazine–pinacol) hexahydrate and discuss polarons, noting the difference in structures between the solid solution and the parent compound.

EXPERIMENTAL

The solid solution of (piperazine–pinacol) hexahydrate was obtained from aqueous solutions with the two compounds in an arbitrary molar ratio, by concentrating the aqueous solution at room temperature. The crystal initially precipitated from the solution was used for experiments. The molar fraction of piperazine, x , was determined by comparing the Raman spectra of the aqueous solution of the solid solution with calibrated solutions, using the intense Raman bands at 818 cm^{-1} for piperazine and 673 cm^{-1} for pinacol in the aqueous solution. The deuterated solid solution with $x = 0.80$ was also obtained from deuterated aqueous solutions.

Raman spectra were observed using a JASCO R800 spectrometer and an argon ion laser (514.5 nm excitation). Infrared spectra were recorded on a JASCO IR-B spectrometer using the Nujol mull method. Temperature was controlled using a cryostat (CTI Cryogenics) and a temperature controller (Lake Shore Cryotronics) over the range 296–25 K. The observed infrared and Raman wavenumbers were calibrated using of polystyrene, and indene or mercury lines,

* Correspondence to: I. Kanesaka.

respectively. They are believed to be accurate to within $\pm 2 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The Raman spectra in the fingerprint region of the solid solution at room temperature are given with that of the melt of piperazine hexahydrate ($x = 1.0$) at 51°C in Fig. 1. Some spectral changes in the solid solution are seen for the bands due to piperazine. For example, the intensity of the band at 1325 cm^{-1} increases with decreasing x , whereas that at 1302 cm^{-1} decreases. The spectral features in the region $1100\text{--}1000 \text{ cm}^{-1}$ also change, as can be seen in Fig. 1. The relative intensity of two bands, I_{1302}/I_{1325} , is plotted against $100x$ in Fig. 2. The fact that the relative intensity changes with x clearly indicates the formation of a solid solution because the relative intensity should be constant for the mixed crystal.

The Raman spectra in the region of the N–H and O–H stretches of the solid solution at room temperature are given in Fig. 3. The two bands at 3291 and 3258 cm^{-1} , which are assigned to N–H stretches, change in relative intensity as x changes. This is shown in Fig. 4, and also supports the formation of the solid solution. It should be noted that the value of x in the solid solution differs from that in the initial aqueous solution. For example, a solid solution with $x = 0.47$ is obtained when the molar fraction of piperazine is 0.70

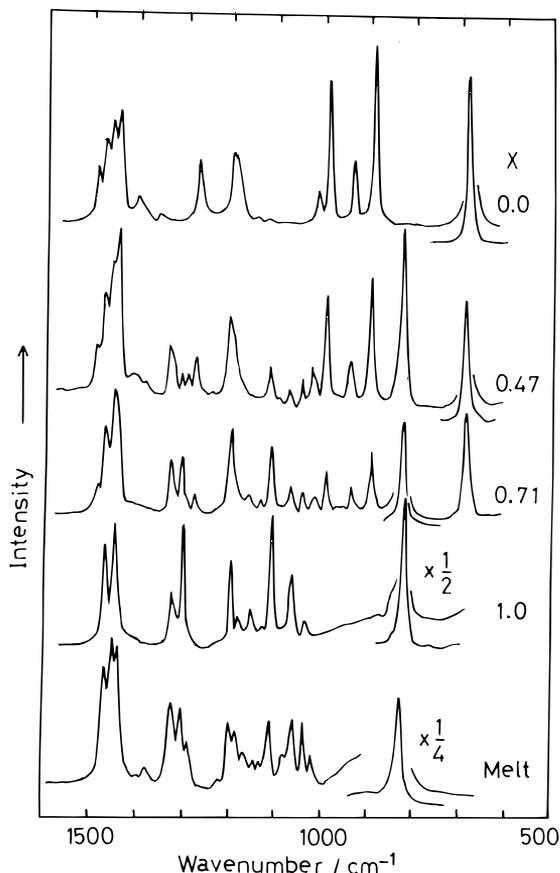


Figure 1. Raman spectra of the solid solution at room temperature and the melt of piperazine hexahydrate at 51°C .

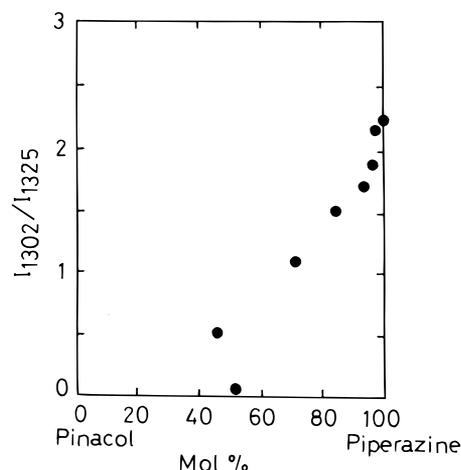


Figure 2. Plot of relative intensity, I_{1302}/I_{1325} , vs. $100x$.

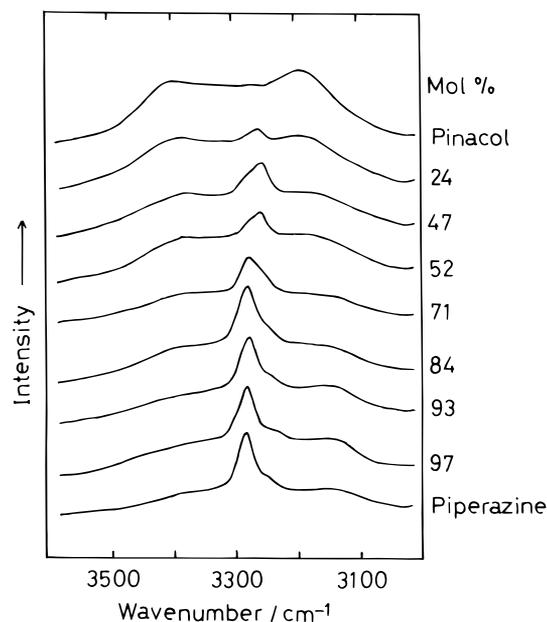


Figure 3. Raman spectra in the region of O–H and N–H stretches of the solid solution at room temperature.

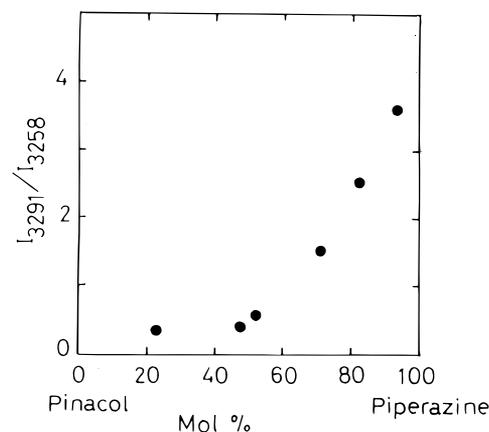


Figure 4. Plot of relative intensity, I_{3291}/I_{3258} , vs. $100x$.

in the initial aqueous solution. Although this means that x is not a unique value but an averaged one, the deviation from the average may be small, because we used the crystal initially precipitated. This can also be realized from Figs 1–4, where the spectral changes are clear and continuous as x changes.

The infrared spectra in the fingerprint region of the solid solution at room temperature are shown in Fig. 5, from which one can see the changes in the bands due to piperazine. These are consistent with the results in Figs 1–4. For example, the strong band at 1129 cm^{-1} for $x = 1.0$ decreases for $x = 0.52$ and a new band at 1037 cm^{-1} appears in the solid solution. Three bands at 1173 , 1140 and 1116 cm^{-1} are observed with almost the same intensity for $x = 0.0$, whereas the intensity of the lowest wavenumber band decreases relatively as x increases, as seen in Fig. 5. These observations also support the formation of the solid solution.

In Fig. 1, it can be seen that the Raman bands due to piperazine in the solid solution with $x = 0.71$ correspond well to those of the melt of piperazine hexahydrate at 51°C , the spectrum of which is complex because of overlapping with bands of piperazine with axial configurations of NH groups. A similar situation has been discussed for deuterated piperazine hexahydrate² and related to the enthalpy difference between the equatorial and axial configurations (one site) of 8.1 kJ mol^{-1} in the solid state. The bands at 1319 and 1031 cm^{-1} in the melt are attributed to the axial configuration (one site) of piperazine, whereas the bands at 1011 and 1319 cm^{-1} are attributed to the axial

configuration (both sites). Hence, it is concluded that the spectral changes in the solid solution result from an increase in piperazine with axial configurations (from one to both sites) as x decreases. The relative intensities, I_{1302}/I_{1325} and I_{3291}/I_{3258} , decrease almost linearly in the range $0.5 \lesssim x \lesssim 1.0$ and are constant for $x \lesssim 0.5$, as seen in Figs 2 and 4, respectively. This suggests that the crystal structure is tetragonal at $x \lesssim 0.5$ and monoclinic at $x \gtrsim 0.5$.

The Raman spectra in the region of the N–D and O–D stretches of the deuterated solid solution with $x = 0.80$ are given for various temperatures in Fig. 6, where the bands denoted A and B are attributed to the ND groups and those denoted C and D to water networks.^{1,2} It is seen that the Raman intensity of band B increases with decreasing temperature. The peak wavenumbers of bands A and B are 2461 and 2423 cm^{-1} at room temperature, respectively, and 2459 and 2423 cm^{-1} at 25 K . A similar feature has been found in the deuterated system with $x = 1.0$ and band B assigned to polarons.^{1,2} The intensity change between bands A and B cannot be explained in terms of the equatorial–axial equilibrium in ND groups, the phase transition at 170 K^2 and Fermi resonance. Hence it is clear that band B is due to polarons.

The relative intensity, $I_R(T) = I_B/(I_A + I_B)$, of the solid solution with $x = 0.80$ is given with that for $x = 1.0$ in Table 1 and plotted relative to $I_R(100)$ against T^2 in Fig. 7, where the plot reported for the deuterated system with $x = 1.0$ ² is also shown (broken line) on the basis of the Scott polaron model.⁴ The fact that $I_R(T)$

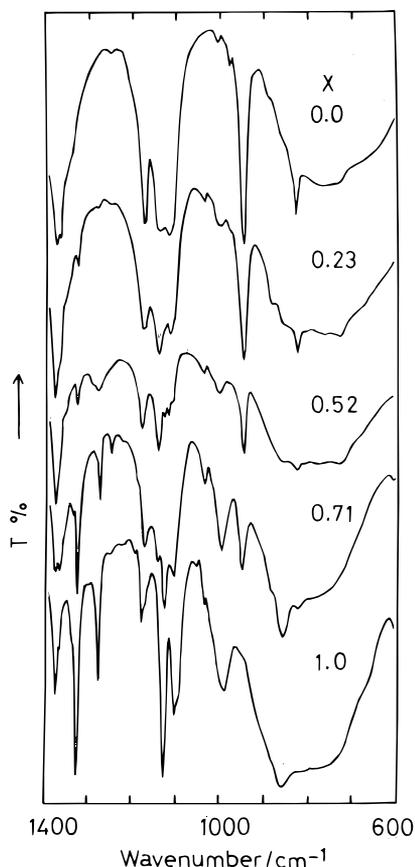


Figure 5. Infrared spectra of the solid solution at room temperature.

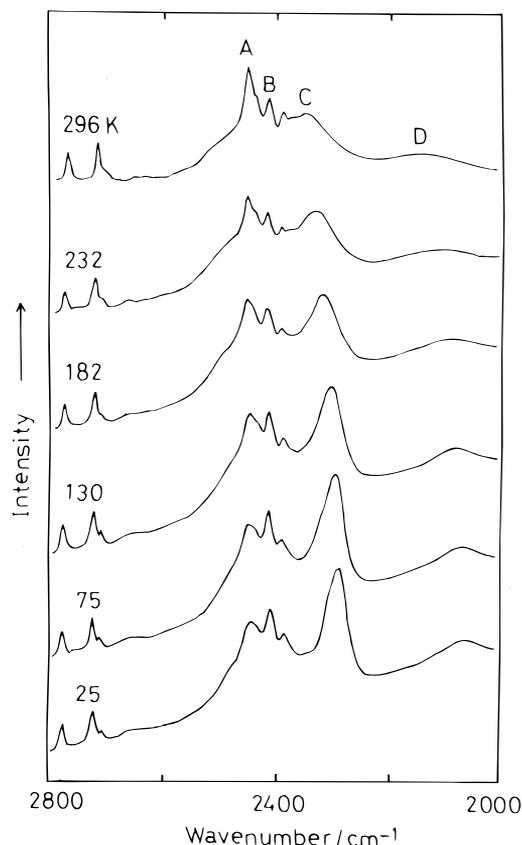


Figure 6. Raman spectra in the region of N–D stretches of the deuterated solid solution with $x = 0.80$.

Table 1. Integrated intensity ratios for bands A and B in the deuterated solid solution with $x = 0.80$ and 1.0^a

T/K	$x = 0.8$		$x = 1.0$	
	I_A/I_B	$I_B/(I_A+I_B)$	T/K	$I_B/(I_A+I_B)^a$
296	1.9	0.34	293	0.20
270	1.8	0.35	248	0.23
251	1.6	0.37	220	0.27
232	1.8	0.35	209	0.25
208	1.6	0.38	178	0.31
182	1.3	0.44	165	0.33
156	1.1	0.46	159	0.35
130	1.1	0.46	143	0.36
103	1.0	0.51	125	0.44
75	0.92	0.52	100	0.47
52	0.92	0.52	77	0.49
25	0.69	0.59	50	0.52
			29	0.53

^a Taken from Refs 1 and 2.

for $x = 0.80$ is larger than that for $x = 1.0$ in Table 1 indicates that polarons are formed more in the solid solution than in the parent compound. As discussed by Careri and co-workers,^{7,8} the oscillator in a polaron state does not couple with the surrounding oscillators of the same kind but interacts with neighbouring species so as to distort them. In the present system, the interaction will be with water networks. Hence, a similar isolated state, that is, a polaron, may be newly formed in the solid solution because of the mixing of pinacol molecules, explaining qualitatively the observations in Table 1. As reported recently,¹³ the decoupled N–D stretches in anilinium bromide behave like polarons in

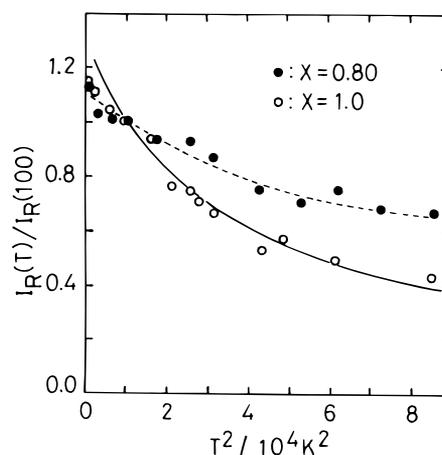


Figure 7. Plot of $I_R(T)$ vs. T^2 in the deuterated system with $x = 0.80$. Those with $x = 1.0$ and the simulation are given by the open circles and the solid line (taken from Ref. 2), respectively. Note that the plot is given relative to $I_R(100)$.

their intensity change with temperature. This may also support the consideration about the increase in polaron states in the solid solution.

In Table 1, the difference in $I_R(T)$ between the present system and the parent compound seems to become larger as the temperature increases. This may be because polar states are also promoted by the mixing of the axial configurations of piperazine; the axial configurations increase as x decreases, as described above, and probably increase as temperature increases.² Hence, $I_R(T)$ in the present system with $x = 0.80$ can be reasonably explained in terms of the polaron model, supporting the conclusion reported previously for band B.^{1,2}

REFERENCES

- I. Kanesaka, K. Kuwano and T. Ishioka, *J. Raman Spectrosc.* **24**, 889 (1993).
- I. Kanesaka, K. Kuwano and T. Ishioka, *J. Raman Spectrosc.* **26**, 238 (1995).
- D. M. Alexander and J. A. Krumhansl, *Phys. Rev. B* **33**, 7172 (1986).
- A. C. Scott, I. J. Bigio and C. T. Johnston, *Phys. Rev. B* **39**, 12883 (1989).
- C. T. Johnston and B. I. Swanson, *Chem. Phys. Lett.* **114**, 547 (1985).
- J. L. Sauvajol, R. Almairac, J. Moret, M. Barthes and J. L. Ribet, *J. Raman Spectrosc.* **20**, 517 (1989).
- G. Careri, U. Buontempo, F. Carta, E. Gratton and A. C. Scott, *Phys. Rev. Lett.* **51**, 304 (1983).
- G. Careri, U. Buontempo, F. Galluzzi, A. C. Scott, E. Gratton and E. Shyamsunder, *Phys. Rev. B* **30**, 4689 (1984).
- D. Schwarzenbach, *J. Chem. Phys.* **48**, 4134 (1968).
- H. S. Kim and G. A. Jeffrey, *J. Chem. Phys.* **53**, 3610 (1970).
- I. Kanesaka, K. Kuwano, S. Yonezawa and T. Ishioka, *J. Raman Spectrosc.* **27**, 395 (1996).
- I. Kanesaka and S. Kamide, *J. Raman Spectrosc.* **27**, 401 (1996).
- I. Kanesaka and Y. Fujii, *Spectrochim. Acta, Part A* **52**, 741 (1996).