Intercalation of Pyridine and Quinoline into α-Zirconium Phosphate

YOSHITSUGU HASEGAWA,* TAKESHI AKIMOTO, and
DAISUKE KOJIMA
Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184, Japan.

Abstract. The uptake of pyridine and quinoline into α-zirconium phosphate has been investigated by the batch method. The effect of solvent on the reactions was also studied. Pyridine was taken up from ethanol, chloroform, carbon tetrachloride, ethanol–water, and acetone–water solutions, but not from pure acetone at 25 °C. Water accelerated the uptake of pyridine. These facts indicate that a water molecule was involved in the uptake reaction of pyridine. Quinoline was taken up easily in an ethanol–water solution at 25 °C, and in an ethanol solution at the boiling point. Two reactions – ion exchange and intercalation – occur on taking up the quinoline. An IR spectrum of the quinoline form is reported.

Key words: α-Zirconium phosphate, pyridine, quinoline, intercalation, ion-exchange.

1. Introduction

α-Zirconium phosphate is one of the most extensively investigated layered compounds. It behaves not only as an inorganic ion-exchanger, but also as a host for intercalation reactions [1]. Many organic compounds have been investigated as a guest. Intercalation behavior depends on the size and polarity of the guests. Primary alkylamines have been studied as intercalants and the relationship between the alkyl chain length and the interlayer distances of the products has been discussed [2, 3]. However, few amines having a cyclic structure have been investigated. Previously, it was found that cyclohexylamine could be accommodated in the interlayer region of α-zirconium phosphate, and the cyclohexylamine was replaced easily with Ni(II) ion in solution [4]. These facts indicate that the cyclohexylamine was present as a cyclohexylammonium ion in the solid. The uptake of pyridine has been investigated in an aqueous medium [5].

During the course of our intercalation study of an aza-compound, we found that acridine and benzo[*f*]quinoline were intercalated into α-zirconium phosphate in an alcoholic medium [6]. Recently, Kanzaki and Abe reported the effect of solvent on the intercalation of *n*-alkylamines into γ-zirconium phosphate [7].

---

* Author for correspondence.

In this work the effect of solvent on the uptake of pyridine into α-zirconium phosphate was investigated. The intercalation behavior of quinoline was also studied.

2. Experimental

2.1. PREPARATION OF α-ZIRCONIUM PHOSPHATE

α-Zirconium phosphate was prepared by the modified direct precipitation method according to the literature [8]. Identification was made by means of X-ray diffractometry, thermal analysis, and the loss on ignition. The α-zirconium phosphate used had a median size (D_{50}) of 3 μm. (The particle size distribution was measured with a Shimadzu centrifugal particle size analyzer SACP-3.)

2.2. UPTAKE REACTION

The reaction was carried out batchwise. The concentration of the guest was usually varied over the range of 0.01 to 0.1 mol/L, the volume of solution was 10 mL and the weighed amount of α-zirconium phosphate was 100 mg.

a. *Uptake of Pyridine*

Ethanol, acetone, chloroform and carbon tetrachloride solutions of pyridine were used initally. The reaction was then carried out in a mixture of an organic solvent–water (9 : 1 v/v). A weighed amount of α-zirconium phosphate was added to the solution of pyridine. Then the mixture was shaken continuously at 25 °C for a specified period of time.

b. *Uptake of Quinoline*

Neat ethanol or a mixture of ethanol–water (3 : 7 v/v) were used as solvent. The reaction temperature was 25 °C or the boiling point of the solution.

2.3. ANALYTICAL PROCEDURE

2.3.1. a. *Determination of Pyridine or Quinoline*

After the uptake reaction, the solid phase was separated by centrifugation, then an aliquot of the supernatant was titrated with standardized hydrochloric acid using a pH meter. The titration curve was differentiated and the end-point was calculated to determine pyridine or quinoline in a solution phase.

Structural change in the solid phase was measured by X-ray diffractometry using Ni-filtered CuK$_\alpha$ radiation (λ = 1.542 Å) (Geigerflex Rad 2B, Rigaku Denki Co. Ltd.). When ethanol was employed as a solvent, the X-ray diffractogram of the solid was recorded with Mylar film preventing possible structural change due

TABLE I. Uptake of pyridine into α-zirconium phospate in some solvents.

	$\overline{Ipy}/\overline{I\alpha}$ [1]	
Solvent	Pure	With H_2O
Ethanol	15/100	98/2
Acetone	0/100	98/2
Chloroform	20/100	100/0[2]
Carbon tetrachloride	100/6	100/0[2]

[1]$\overline{IPy}$ and $\overline{I\alpha}$ represent the intensity of the peak due to the interlayer distance of the pyridine form and of α-zirconium phosphate.
[2]In these solvents the solution is composed of two phases, and a large amount of α-zirconium phosphate is suspended in the aqueous phase. Hence, the intensity ratio does not necessarily show the effects of water.

to evaporation of ethanol, and after air drying. As the two diffractograms were the same, the X-ray diffractogram was measured using the air-dried sample.

The infrared (IR) spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer as KBr discs.

3. Results and Discussion

3.1. UPTAKE OF PYRIDINE

To determine the equilibration time, the reaction was carried out in four kinds of solutions containing 10 meq of pyridine per g α-zirconium phosphate (hereafter abbreviated to meq/g). The change in the concentration of pyridine and an X-ray diffractogram were measured at a given period of time.

Table I shows the uptake of pyridine in various solvents containing 10 meq/g. Pure carbon tetrachloride is a good solvent and acetone a poor one. The change in the concentration of pyridine was confirmed by titration. The ratio of pyridine to exchangable protons in zirconium phosphate was equal to 16.5% in pure ethanol solution. No change in the concentration of pyridine and in the X-ray diffraction pattern were observed in pure acetone solution. This indicates that pyridine was not taken up from the acetone solution, or that it was difficult to diffuse into the α-zirconium phosphate crystallite.

These facts show that the uptake of pyridine is affected by solvents, especially by the presence of water, and that it takes about one day to attain equilibrium in an aqueous solution.

To clarify the effect of water, the ratio of water to pyridine was varied from 1 : 80 to 1 : 250. The amount of pyridine was fixed at 7 meq/g. The reaction proceeded
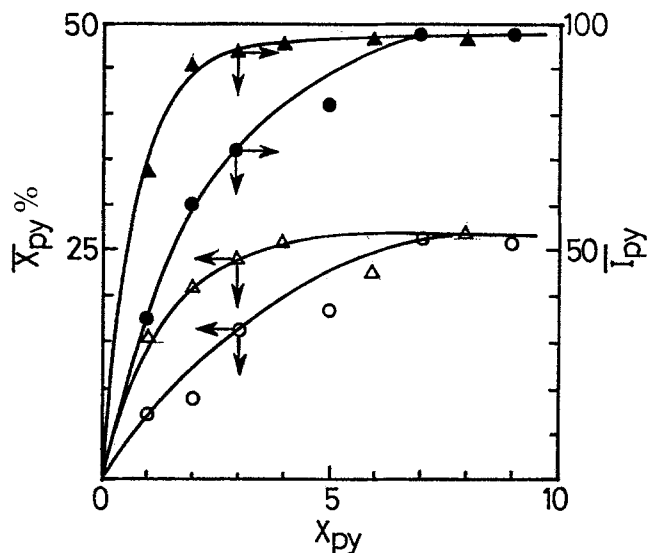
Fig. 1.   Uptake of pyridine: ○ ● in the aqueous ethanol solution. △ ▲ in aqueous acetone solution. $\overline{Xpy}$ is the mole percentage of pyridine in the solid phase determined by titration. $\overline{Ipy}$ is the approximate percentage of the pyridine form in the solid phase determined by X-ray diffractometry (see the text). Xpy is the mmol of pyridine added to α-zirconium phosphate.

much the same and uniformly in both mixtures, namely ethanol–water and acetone–water.

α-Zirconium phosphate and its salt form have a layered structure [9, 10]. Since the interlayer distances of these compounds depend on the size of an existing cation or molecules between the layers, it affords a good tool for observing the change in the interlayer distance in order to trace the uptake process. The interlayer distance can be seen in the lowest angle region of an X-ray powder diffractogram. Assuming that the intensity of the peak in an X-ray pattern is proportional to the amount of each phase, the ratio of phases can be approximately estimated.

Figure 1 shows the molar ratio of pyridine in the solid phase as a function of the initial amount of pyridine in the solution. The percentage of the phase having an interlayer distance of 10.9 Å is also shown. The ratio was estimated as follows;

$$\% \ \overline{IPy} = 100 \times \overline{IPy} / (\overline{IPy} + \overline{I\alpha}),$$

where $\overline{IPy}$ and $\overline{I\alpha}$ are the intensities of the first reflection maxima of two immiscible phases. Pyridine was taken up more easily in acetone–water solution than in ethanol–water solution. The total amount of pyridine taken up was equal to about 25% of the exchangeable protons in α-zirconium phosphate, and was independent of the solvent.

Figures 2 and 3 show the X-ray powder diffraction patterns of solid phases during the uptake reaction in both the aqueous ethanol and acetone solutions. The
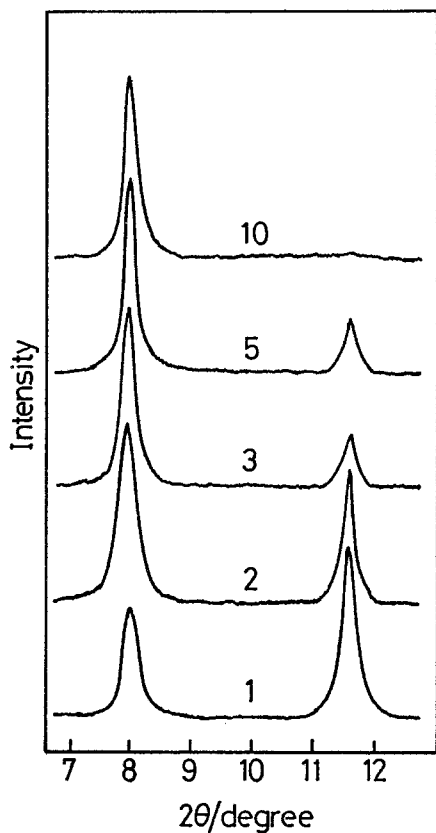
Fig. 2. Structural change during uptake of pyridine in the aqueous ethanol solution. Numerals in the figure correspond to Xpy in Fig. 1.

diffractograms show a new peak at 10.9 Å in two systems, and that the uptake reaction proceeds in one stage. This agrees with results reported by Yamanaka *et al.* [5]. Two phases – α-zirconium phosphate and a new phase – coexist up to 10 meq/g addition. A small amount of α-zirconium phosphate was present at the final stage of the reaction.

Figure 4 shows the structural change of the solid in pure ethanol solution containing 10 meq/g pyridine at 25 °C (A) and under repeated reflux (B). These curves indicate that the uptake of pyridine proceeds easily in pure ethanol solution, especially under reflux.

Assuming that the intensity of the peak in an X-ray diffraction pattern is proportional to the amount of each phase present, the ratio of phases can be approximately estimated. The composition of the solid is shown in Figure 1 as a function of the initial concentration of pyridine in the solution.

In a pure solvent only an intercalation reaction takes place (Equation 1), because pyridinium cations are not present. Two reactions, ion exchange (Equation 2) and
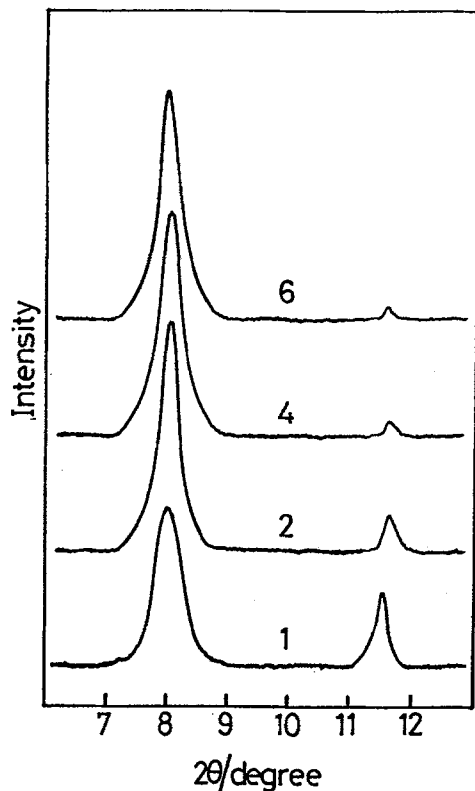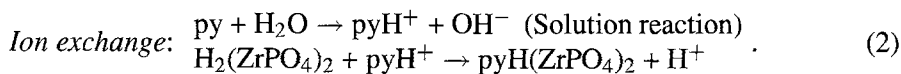
Fig. 3.   Structural change during uptake of pyridine in the aqueous acetone solution. Numerals in the figure correspond to Xpy in Fig. 1.

intercalation (Equation 1), are possible in an aqueous solvent. Pyridine is expected to behave as a pyridinium ion in an ion-exchange, and as a proton-acceptor in an intercalation reaction.

Intercalation: $H_2(ZrPO_4)_2 + py \rightarrow pyH_2(ZrPO_4)_2[\equiv(pyH^+)(HZrPO_4)_2^-](1)$

Ion exchange: $py + H_2O \rightarrow pyH^+ + OH^-$ (Solution reaction)
$H_2(ZrPO_4)_2 + pyH^+ \rightarrow pyH(ZrPO_4)_2 + H^+$.   (2)

The effect of solvents on the uptake of pyridine is obvious. Two factors are considered: solvation and structural change in α-zirconium phosphate due to the solvent used. Formation of a complex through solvation to pyridine and/or a decrease in the interlayer distance hinder the uptake reaction. By contrast, the ionization (hydrolysis) of pyridine, and the expansion of the interlayer distance make it easy for pyridine to be taken up by α-zirconium phosphate.

   (Pure solvent): ethanol is a protic solvent, and able to solvate to pyridine through a hydrogen bond and a dipolar interaction. Also, ethanol can intercalate into α-
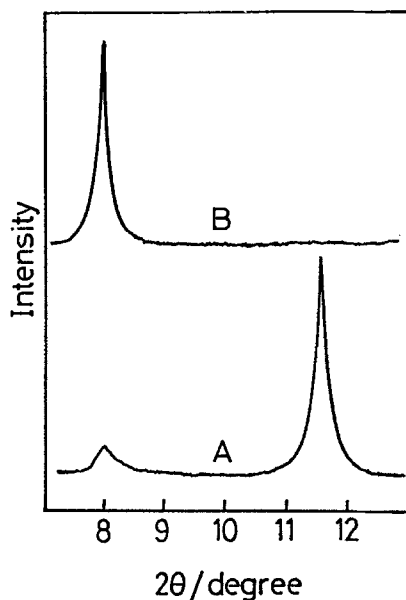
Fig. 4.   Uptake of pyridine in pure ethanol solution. A; at 25 °C. B; under reflux.

zirconium phosphate, and expand the interlayer distance to 14.1 Å [11]. The former has an adverse effect, and the latter is favorable to the uptake.

Other solvents are aprotic. In these solvents pyridine will be weakly solvated. Carbon tetrachloride has a low dielectric constant and no dipole moment. This means that formation of a complex scarcely takes place in carbon tetrachloride. As this solvent does not dissolve water practically (solubility of water in CCl_4 about 0.08%), it is not probable to extract the hydration water of α-zirconium phosphate and to cause a decrease in the interlayer distance. These factors work to favor the uptake of pyridine.

Acetone is a dipolar solvent. As acetone dissolves water freely, partial dehydration of α-zirconium phosphate, and a decrease of the interlayer distance are probable. Also a specific solvation is suggested. It is difficult for pyridine to diffuse into α-zirconium phosphate due to these factors. Since chloroform will solvate less to pyridine, and dissolve less water than acetone, pyridine would intercalate easily into α-zirconium phosphate in this solution.

(Aqueous solutions): it is obvious that water was strongly involved in the uptake reaction. The water prevents the water of hydration being extracted into the solution phase from a structural point of view. Water forms a hydrogen bond with pyridine, and will give pyridine a cationic nature, because water has a larger auto-dissociation constant than ethanol. The resultant cationic species will react easily with exchangable protons in α-zirconium phosphate.
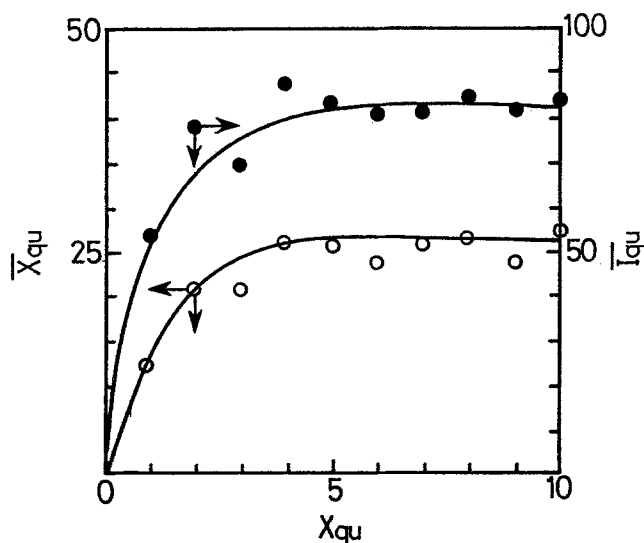
Fig. 5.   Uptake of quinoline in aqueous ethanol solution. $\overline{Xqu}$ is the mole percentage of quinoline in the solid phase determined by titration. $\overline{Iqu}$ is the approximate percentage of the 13.0 Å phase in the solid phase determined by X-ray diffractometry (see the text). Xqu is the mmol of quinoline added to α-zirconium phosphate.

It can be concluded that: (1) the uptake of pyridine into α-zirconium phosphate was affected by the solvent used; (2) carbon tetrachloride was a good solvent, and (3) water caused and/or accelerated the uptake.

3.2. UPTAKE OF QUINOLINE

Quinoline is soluble in ethanol, but not in water, to give a 0.1 mol/L solution at 25 °C. The intercalation of pyridine suggests that the reaction will proceed more easily in an aqueous solution than in a pure ethanol one. Hence, the intercalation of quinoline was carried out in ethanol and aqueous ethanol solutions.

1. Uptake in an Aqueous Ethanol Solution

A reaction time of 3 days was adopted. Figure 5 shows the molar ratio of the quinoline in the solid phase as a function of the initial amount of quinoline in the solution. The figure also shows the ratio determined by X-ray diffractometry. The ratio was estimated in the same manner as that in Figure 1. A quarter of the exchangeable protons in α-zirconium phosphate were replaced by quinolinium ions. The interlayer distance of α-zirconium phosphate expanded to 13.0 Å. However, the X-ray powder patterns of the solids showed an imperfect conversion.

Figure 6 shows the X-ray powder diffraction patterns of the solid phase during the uptake reaction in the aqueous ethanol solution. The diffractograms showed
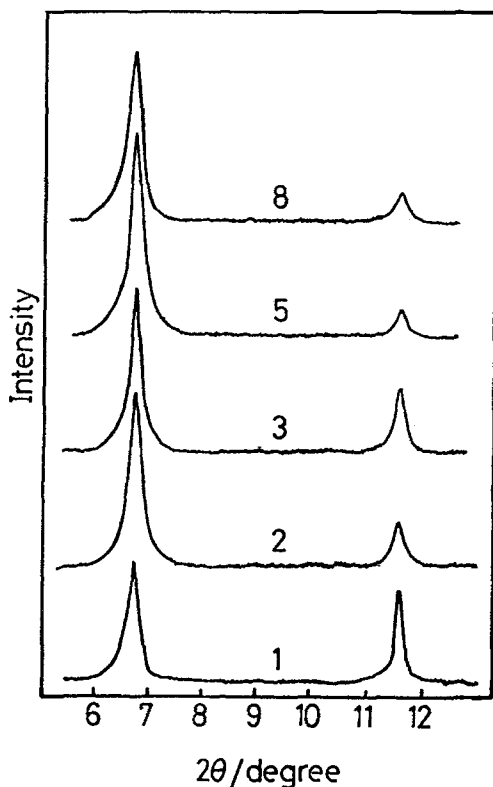
Fig. 6.   Structural change during uptake of quinoline in the aqueous ethanol solution. Numerals in the figure correspond to $\overline{Xqu}$ in Fig. 5.

a new peak at 13.0 Å, and that the uptake reaction proceeded in one stage. Two phases, α-zirconium phosphate and a new phase, coexisted up to 8 meq/g addition. A small amount of α-zirconium phosphate was present at the final stage of the reaction.

It will take a long period of time to reach equilibrium at 25 °C, and the formation of quinolinium ions will be less . The reaction was carried out at the boiling point of the solution. The X-ray powder pattern showed that water hindered diffusion of quinoline towards the interlayer region of α-zirconium phosphate.

2. Intercalation in an Ethanol Solution

Quinoline was taken up into α-zirconium phosphate at 25 °C in an ethanol solution, although the amount of uptake was slight (Figure 7A). Then the reaction was tried at the boiling point of the solution. The diffractograms in Figure 7B show that only the new phase (quinoline form) was present after repeated reactions. This quinoline form was used for the following analyses.
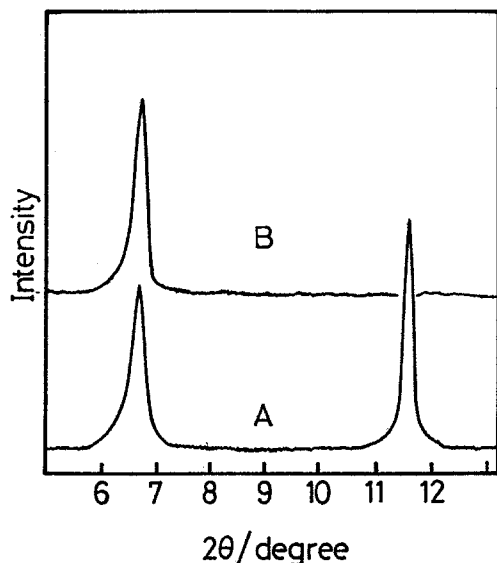
Fig. 7.   Uptake of quinoline from pure ethanol solution. (A); at 25 °C. (B); under repeated reflux.

If quinoline is present between the layers in the same manner as pyridine, the interlayer distance of the quinoline form is estimated to be about 11 Å, which is smaller than that observed.

Scheme 1 shows that the interlayer distance varies depending on the arrangement of quinoline between the layers. If we consider the length of N—C—C—C—H in the quinoline ring, it is approximately 7.5 Å. This is shorter than that calculated for n-propylamine (8.3 Å). According to Alberti and Costantino, the interlayer distance of the mono-n-propylamine form was 13.0 Å, and the *trans,trans* alkyl chain would be inclined by an angle of 55° with respect to the plane. The height of n-propylamine is calculated to be 6.8 Å (=8.3 Å × sin 55°). Assuming that the axis is slanted by 65° to the plane of zirconium phosphate, the estimated height is 6.8 Å for the quinoline form.

IR Analysis.

The IR spectra of the quinoline intercalate were almost identical with the composite spectra of quinoline and α-zirconium phosphate. Changes in the spectra were observed in the 1700–400 cm^{-1} and 900–700 cm^{-1} region. Figure 8a's show the IR spectra of the quinoline intercalate in these regions. The figure also shows the spectra of quinoline and its hydrochloride for comparison. The quinoline intercalate showed new absorption bands at 2010, 1414, 1407, 1384, and 771 cm^{-1}, while some bands disappeared; 1431, 786, and 740 cm^{-1}.

Shindo and Tamura reported that four absorption bands at 1650–1450 cm^{-1} were assigned to C=C and C=N stretching frequencies. Deformation frequencies
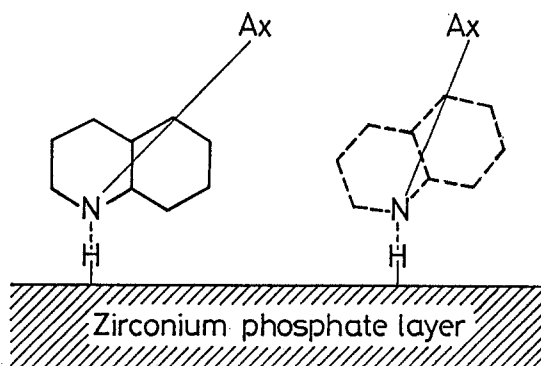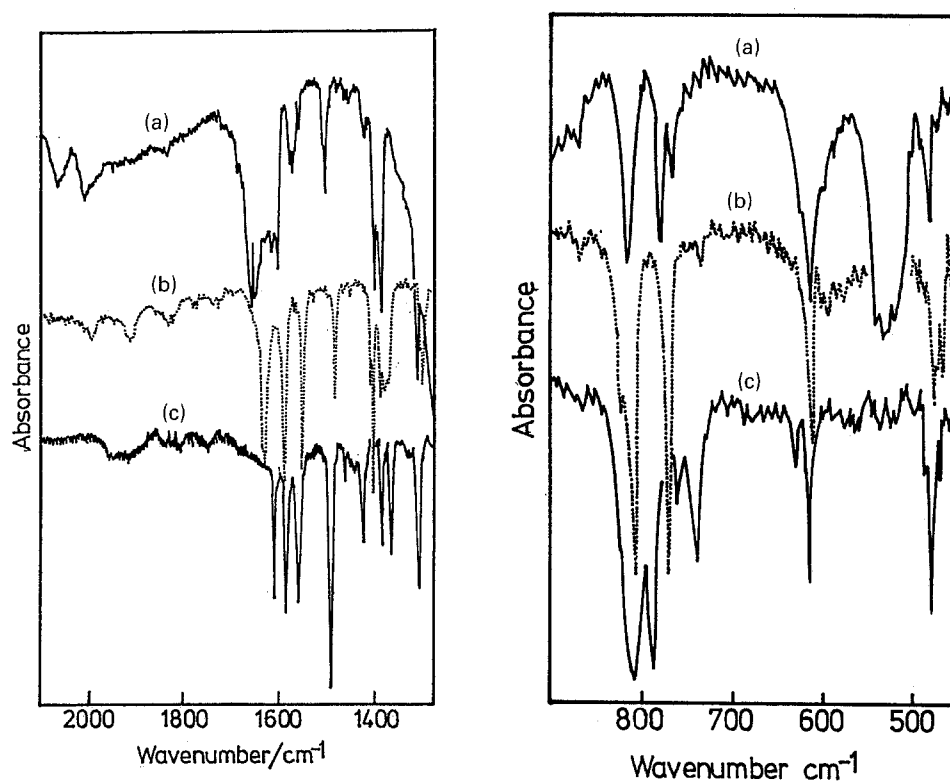
Scheme 1.

Fig. 8. IR spectrum of (a) quinoline Zr(HPO₄)₂ product. (b) quinoline hydrochloride, and (c) quinoline.

of —NH⁺ in protonated heterocyclic nitrogen compounds were observed at 1258 cm⁻¹ on average, and at 1298 cm⁻¹ in quinqidine, while Parry used the change in the spectra of pyridine only at 1700–1400 cm⁻¹ to detect acidic sites on the surface

of a solid. The bands below 1300 cm^{-1} cannot be used to analyze the spectra, because of overlapping with those of the phosphate group.

It can be seen from Figures 8 that a broad absorption band at 2010 and a strong one at 780–770 cm^{-1} was observed for the quinoline intercalate and quinoline hydrochloride. Also, α-zirconium phosphate has two exchangeable protons between the layers. The quinoline can be bonded to the phosphate group as a Brønsted acid.

Acknowledgements

References

1. G. Alberti: *Acc. Chem. Res.* **11**, 163 (1978).
2. G. Alberti and U. Costantino: *Intercalation Chemistry* (Eds. M.S. Whittingham and A.J. Jacobson), Academic Press, New York, Chap. 5, pp. 147–180 (1982).
3. R.M. Tindwa, D.K. Ellis, G-Z. Peng, and A. Clearfield: *J. Chem. Soc., Faraday Trans.* **81**, 545 (1985).
4. Y. Hasegawa, K. Sasaki, and H. Tanaka: *Bull. Chem. Soc. Jpn.* **61**, 413 (1988).
5. S. Yamanaka, Y. Horibe, and M. Tanaka: *J. Inorg. Nucl. Chem.* **38**, 323 (1976).
6. Y. Hasegawa and I. Tomita: *Trends in Inorganic Chemistry* **2**, 171 (1991).
7. Y. Kanzaki and M. Abe: *Bull. Chem. Soc. Jpn.* **5**, 180 (1992).
8. Y. Hasegawa and M. Kuwayama: *Bull. Chem. Soc. Jpn.* **51**, 3485 (1978).
9. A. Clearfield and G.D. Smith: *Inorg Chem.* **8**, 43 (1969).
10. A. Clearfield (Ed.): *Inorganic Ion Exchange Materials*, CRC Press Inc, Boca Raton, Florida, Ch. 1, pp. 20–33 (1982).
11. Y. Hasegawa, S. Konntani, and I. Tomita: *J. Incl. Phenom.* **16**, 329 (1993).
12. H. Shindo and S. Tamura: *Pharm. Bull.* **4**, 292 (1956).
13. D. Cook: *Can. J. Chem.* **42**, 2292 (1964).
14. E.P. Parry: *J. Catal.* **2**, 371 (1963).