

**763.** *A Study of Ammonium, Lithium, Silver, and Pyridinium Nitrates in Saturated Solution in Pyridine and, together with Potassium Nitrate, in Pyridine–Water Mixtures, by Means of Infrared Absorption Spectroscopy.*

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The infrared absorption spectra of ammonium, lithium, silver, and pyridinium nitrates in saturated solution in pyridine and in various pyridine–water mixtures have been examined, together with potassium thiocyanate in pyridine only. Two species of nitrate ion have been distinguished in some of these solutions and their presence is explained in terms of solvated cation structures. Spectral measurements for potassium thiocyanate in pyridine solution showed that there were only very weak associations, if any, between cation and solvent. It is shown that for solutions  $\leq 2$  mole of water per mole of pyridine there is virtually no bulk water present and that the latter is necessary for the dissolution of potassium nitrate in aqueous pyridine. Extraction of potassium nitrate from its saturated aqueous solution can only be achieved if there is sufficient water present to hydrate the pyridine completely.

#### EXPERIMENTAL

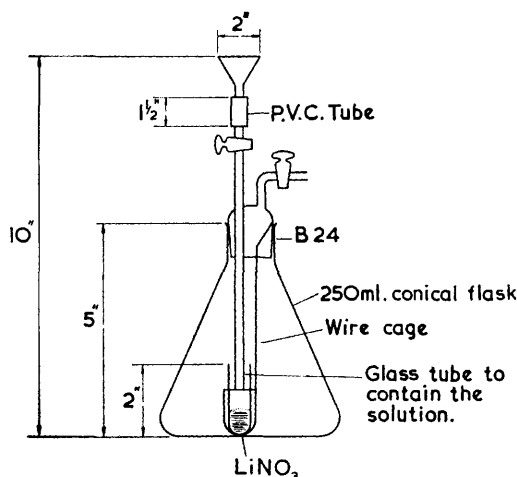
Spectra were recorded from a variable thickness cell fitted with barium fluoride windows. A Unicam S.P. 100 infrared spectrophotometer was used to scan the frequency range 800–4000  $\text{cm}^{-1}$  with sodium chloride and silica prisms. The instrument was calibrated over this frequency range with water vapour, carbon dioxide, and polystyrene. In some cases compensation for solvent absorption was effected with a second variable thickness cell fitted with potassium bromide windows, but then some erratic variation of the background occurred.

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AnalaR pyridine was distilled before use and a middle fraction taken and stored in a brown glass bottle. A range of pyridine-water mixtures was prepared immediately before use 0.03, 0.08, 0.17, 0.25, 0.30, 0.35, 0.44, 1.0, 1.5, 2.0 moles of water per mole of pyridine, respectively. Solutions of deuterium oxide (99.7%) were prepared containing 0.40 and 0.90 moles per mole of pyridine, respectively.

The solubilities of ammonium and fused lithium nitrates in pyridine were found to be 15.7 and 12.2 g. per 100 ml. pyridine, respectively. These approximate values were obtained by preparing saturated solutions at room temperature, evaporating the pyridine, and determining the nitrates Leithe's method<sup>1</sup> using potassium dichromate. The solubility of potassium thiocyanate in pyridine was 1.9 g. per 100 ml. determined by evaporation of the pyridine, dissolution of the residue in water, addition of excess of standard silver nitrate, and back titration with standard ammonium thiocyanate in presence of ferric ions.

To a saturated solution of a mixture of 2.00 g. of AnalaR potassium nitrate and 1.92 g. of AnalaR ammonium bromide in 1 ml. of water, was added 10 ml. of pyridine. After thorough mixing the mixture was filtered, a portion was removed to fill the infrared cell, and the solvent was evaporated from the remainder. Determination of the nitrate, as described



above, showed that the filtrate contained approximately 0.40 g. of ammonium nitrate and by difference from the weight of residue after removal of the solvent, 0.26 g. of ammonium bromide. The portion used to fill the cell accounted for 0.1 g. of mixed salts.

Since pyridine solutions of the nitrates are hygroscopic, care was taken to avoid absorption of water vapour. A saturated solution of fused lithium nitrate in pyridine was prepared in a special apparatus (Figure). Anhydrous lithium nitrate was loaded into the apparatus in a dry-box containing phosphoric oxide as desiccant. The apparatus was removed from the dry-box to add pyridine, the flow of which could be controlled by the air outlet tap. Transfer operations of the solution from this apparatus to the cell were effected as rapidly as possible. The nitrate-pyridine-water solutions (Table 2) were prepared by the rapid addition of 10 ml. aliquot portions of the saturated solutions in pyridine to the appropriate volume of water immediately before spectroscopic measurement. The barium fluoride cells were dismantled and thoroughly washed and dried after each measurement.

## RESULTS AND DISCUSSION

*Pyridine.*—The vibrational spectrum of pyridine has close similarities to that of benzene, the differences being consistent with the reduction of symmetry from  $D_{6h}$  to  $C_{2v}$  which occurs when a CH group in benzene is replaced by a nitrogen atom. In Table 1, the modes of vibration are for benzene and will not have the same significance for pyridine, but they assist in the discussion.

<sup>1</sup> Leithe, *Analyt. Chem.*, 1948, **20**, 1082.

TABLE I.

Frequency No.	Approx. mode of vibration (for benzene)	Pyridine (liquid) (cm. <sup>-1</sup> )	Pyridine plus water or deuterium oxide (ca. 1 mole/mole) (cm. <sup>-1</sup> )	Pyridinium ion (cm. <sup>-1</sup> )	Symmetry species
1	C-C	992s-vs	1001s-vs	1010	A <sub>1</sub>
2	C-H	3056*	3056(s)	—	A <sub>1</sub>
3	CH	1216s	1216s	1326	B <sub>1</sub>
4	C-C-C⊥	675	—	738	B <sub>2</sub>
5	CH⊥	~942w, b	942w	980	B <sub>2</sub>
6a, b	C-C-C	605, 652	—	—	A <sub>1</sub> B <sub>1</sub>
7a, b	C-H	3056	3056(s)	3236, 3045	A <sub>1</sub> B <sub>1</sub>
8a, b	C-C	1583vs, 1572	1593vs, 1572s, inf.	1638, 1608	A <sub>1</sub> B <sub>1</sub>
9a, b	CH	1216	1222s †	1194, 1235	A <sub>1</sub> B <sub>1</sub>
10a, b	CH⊥	886, R749	—	ia. 855	A <sub>2</sub> B <sub>2</sub>
11	CH	703	—	671	B <sub>2</sub>
12	C	1030	1030s-vs	?IR 1050R	A <sub>1</sub>
13	C-H	3056	3056(s)	3060	A <sub>1</sub>
14	C-C	1375	—	?	B <sub>1</sub>
15	CH	1146s	1146s	1161	B <sub>1</sub>
16a, b	C⊥	374, 405	—	ia.	A <sub>2</sub> B <sub>2</sub>
17a, b	CH⊥	981	—	i.a.	A <sub>2</sub> B <sub>2</sub>
18a, b	CH	1070, 1070s	1070s	1030	A <sub>1</sub> B <sub>1</sub>
19a, b	C-C	1481s, 1439s-vs	1485vs, 1442s	1484	A <sub>1</sub> B <sub>1</sub>
20a, b	C-H	3025vs, 3080s	3020vs, 3075s	—	A <sub>1</sub> B <sub>1</sub>

\* The 3056 cm.<sup>-1</sup> frequency appears at 3043 cm.<sup>-1</sup> in 0.9M-D<sub>2</sub>O-m-pyridine. † D<sub>2</sub>O superimposed on 1220 cm.<sup>-1</sup> peak.

The frequency numbering is that of Wilson;<sup>3</sup> the descriptions of the vibrations are from Herzberg<sup>4</sup> and the data for the pyridinium ion is taken from Cook.<sup>5</sup> Those pyridine frequencies which have no indication of intensity are taken from the work of Corrsin *et al.*<sup>2</sup>

ia. = Infrared-inactive.

In the region examined, most of the absorptions observed by Corrsin *et al.*<sup>2</sup> were recorded, with the exception of 8b which was not resolved from 8a.

*Pyridine-water.*—The spectra of pyridine-water mixtures have been investigated by a number of workers and reviewed by Sidorov.<sup>6</sup> Saumagne and Josien<sup>7</sup> concluded that water and pyridine diluted with carbon tetrachloride was largely made up of C<sub>5</sub>H<sub>5</sub>N ··· HOH units. Sidorov<sup>6</sup> from a further examination concluded that the above species and also C<sub>5</sub>H<sub>5</sub>N ··· HOH ··· NC<sub>5</sub>H<sub>5</sub> were present, together with associated water.\* The present work indicates that the O-H stretching absorption bands are complex, but that attempts to assign slight inflexions on the principal asymmetrical envelope, would be unwise.

Solutions of deuterium oxide in pyridine reveal that quite moderate intensity absorption occurs at 1633 and 1644 cm.<sup>-1</sup>. For solutions of water in pyridine, these maxima sit on the side of the ν<sub>2</sub> water absorption which occurs near 1658 cm.<sup>-1</sup>. In consequence, the 1644 cm.<sup>-1</sup> band gives the appearance of a relatively more intense ν<sub>2</sub> water absorption, which was considered by Sidorov<sup>6</sup> to be due to associated water. In Sidorov's<sup>6</sup> experiments, this absorption would not be compensated by the pyridine in the reference beam, because pyridine does not absorb at 1644 cm.<sup>-1</sup>. The presence of associated water is, therefore, doubtful.

Comparison of the frequencies of pyridine between 800 and 4000 cm.<sup>-1</sup> with those of the more concentrated aqueous pyridine solutions did not confirm Sidorov's<sup>6</sup> observation that almost all frequencies were shifted to higher values, though marked shifts do occur

\* The term "associated water" is used instead of "water" which in solution can refer to molecular water (H<sub>2</sub>O) depending on the nature of the solvent.

<sup>2</sup> Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, **21**, 1170.

<sup>3</sup> Wilson, Jr., *Phys. Rev.*, 1934, **45**, 706.

<sup>4</sup> Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co. Inc., N.Y.

<sup>5</sup> Cook, *Canad. J. Chem.*, 1961, **39**, 2009.

<sup>6</sup> Sidorov, *Optics and Spectroscopy*, 1960, **7**, 24.

<sup>7</sup> Saumagne and Josien, *Bull. Soc. chim. France*, 1958, 813.

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for the following bands: (1) 992  $\longrightarrow$  1003  $\text{cm.}^{-1}$ , (12) 1030  $\longrightarrow$  1036  $\text{cm.}^{-1}$ , and (8a) 1583  $\longrightarrow$  1593  $\text{cm.}^{-1}$  for the fundamentals and (1 + 6a) 1597  $\longrightarrow$  1613  $\text{cm.}^{-1}$  and (6a + 12, 1 + 6b) 1633  $\text{cm.}^{-1}$   $\longrightarrow$  1634, 1644  $\text{cm.}^{-1}$ . Of these, (1), (6a), (6b), (8a), and (12) are fundamentals, which in benzene arise from C-C stretching and bending vibrations. It is noteworthy that the two combination bands which fall together at 1633  $\text{cm.}^{-1}$  in pyridine appear to be at 1634 and 1644  $\text{cm.}^{-1}$  in pyridine plus deuterium oxide or water. These values agree with those calculated by Corrsin *et al.*<sup>2</sup> The 1572  $\text{cm.}^{-1}$  band present in pyridine, but not resolved in these experiments, became just visible in the spectrum of 0.90 mole of deuterium oxide per mole of pyridine, as a strong inflexion on the (1 + 6a) band at 1611  $\text{cm.}^{-1}$ . For 2 moles of water per mole of pyridine, this band is at 1613  $\text{cm.}^{-1}$ . The constant frequency 1572  $\text{cm.}^{-1}$  was noted by Chiorboli<sup>8</sup> for the Raman spectra of solutions of pyridine in water, alcohols, phenols, and acids.

Table I shows that the spectrum of a pyridine-water mixture, typical of those examined, lies intermediate between the spectra of pyridine and pyridinium cation. A solution of 2.2 moles of water per mole of pyridine gives a water deformation frequency at 1661s-vs,  $\text{cm.}^{-1}$  a single strong band at 1593  $\text{cm.}^{-1}$ , and bands at 1643s-vs, 1634s-vs, 1613s,  $\sim$ 1228w-m inf., 1216s, 1150s, 1071s, 1033s-vs, and 1001s-vs  $\text{cm.}^{-1}$ , respectively.

*Ammonium Nitrate-Pyridine.*—The pyridine bands in the spectrum of a saturated solution of ammonium nitrate in pyridine are similar to those obtained from a solution of *ca.* 0.4 mole water or deuterium oxide per mole of pyridine. Notable differences are the greater relative intensity of the 1231  $\text{cm.}^{-1}$  inflexion, and the 1592  $\text{cm.}^{-1}$  band. The pyridine C-H stretching absorptions obscure those due to N-H stretching of the ammonium ion except for that at 3190  $\text{cm.}^{-1}$ . Strong absorption at 1464  $\text{cm.}^{-1}$  is assigned to  $\nu_4$  deformation of the ammonium ion. One or two other components resulting from a partial or total loss of triple degeneracy of this frequency, could be superimposed on the 1440 and 1482  $\text{cm.}^{-1}$  pyridine absorptions. The nature of the fundamental vibrations of the nitrate ion in electrostatic fields of various symmetry have been described previously.<sup>9</sup> Bands at 830, 1320, and 1386  $\text{cm.}^{-1}$  for ammonium nitrate in pyridine (Tables 2 and 3) are assigned to  $\nu_2$  and the two components resulting from loss of degeneracy of  $\nu_3$ , respectively.

TABLE 2.

Mole water per mole pyridine	Mole water per mole $\text{NH}_4\text{NO}_3$	$\text{NH}_4\text{NO}_3$ $\text{cm.}^{-1}$	$\text{NH}_4\text{NO}_3$ $\text{cm.}^{-1}$	$\Delta\nu$	$\text{LiNO}_3$ $\text{cm.}^{-1}$	$\text{LiNO}_3$ $\text{cm.}^{-1}$	$\Delta\nu$	Mole water per mole $\text{LiNO}_3$	Mole water per mole pyridine	Mole water added
0.00	0.00	1320	1386	66	1420	1329	91	0.00	0.00	0.00
0.18	0.96	1327	$\sim$ 1382	55	1417	1338	79	1.07	0.17	0.019
0.27	1.42	1328	„	54	1412	1338	74	1.57	0.26	0.028
0.38	1.98	1332	„	50	1409	1340	69	2.2	0.36	0.039
0.53	2.84	1335	„	47						
0.70	3.68	1338	„	44	1394	1342	52	4.07	0.66	0.072
0.86	4.54	1339	„	43						
1.04	5.10	1339	„	43	1397	1340	57	5.65	0.92	0.10
1.07	5.67	1340	„	42	1390( $\sim$ 1413s, inf.)	1342	48	6.27	1.02	0.111
					1387 (1416s)	1341	46	7.5	1.22	0.133
					1380 (1416s)	1350?	30	8.5	1.39	0.151
					1360? (1417s)	1340	20	9.43	1.53	0.167
$\infty$	—	1340	{ $\nu_1$ 1380 1049	40	1450	{ $\nu_1$ 1340 1055	—	—	$\infty$	$\infty$

The frequency  $\nu_1$  which should now be infrared-active, is presumably superimposed on the 1036  $\text{cm.}^{-1}$  pyridine absorption. A band of weak to moderate intensity at 1750  $\text{cm.}^{-1}$  could be assigned to  $\nu_4$  of the ammonium ion made infrared-active by perturbation of the ion, but the presence of absorption in this region in the spectra of metal nitrates in pyridine solution leads to the assignment ( $\nu_1 + \nu_4$ ) of the nitrate ion, for this frequency.

<sup>8</sup> Chiorboli, *Ann. Chim. (Italy)*, 1957, **47**, 443.

<sup>9</sup> Thompson, *J.*, 1963, 998.

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*Ammonium Nitrate-Pyridine-Water.*—Addition of water to ammonium nitrate in pyridine solution results in a gradual shift in the nitrate ion frequencies from those characteristic of the pyridine solution to those characteristic of a saturated aqueous solution. This change is shown in Table 2 in which it is seen that for 1.07 mole of water per mole of pyridine the  $\nu_3\nu_3'$  absorptions are at 1340 and 1382  $\text{cm}^{-1}$  which are precisely the values obtained for moderately strong aqueous solutions. The difference in frequency  $\Delta\nu$  between the two components of  $\nu_3$ , is seen to change continuously from 66 to 42  $\text{cm}^{-1}$ . A plot of  $\Delta\nu$   $\text{cm}^{-1}$  against moles of water per mole of ammonium nitrate in pyridine yields a smooth curve which passes through the origin and is almost rectilinear between 3.7 and 5.7 moles of water per mole of ammonium nitrate. These spectra will be referred to again after discussing the silver nitrate-pyridine system.

*Lithium Nitrate-Pyridine.*—In lithium nitrate solution in pyridine, the nitrate ion absorbs at two frequencies in the  $\nu_3$  region (1300–1450  $\text{cm}^{-1}$ ; Table 2), which with the single  $\nu_2$  829  $\text{cm}^{-1}$  absorption indicates that the symmetry of the field around the cavity in which the nitrate ion is situated is either  $C_{2v}$  or  $C_s$ . Under these conditions  $\nu_1$  should be infrared-active and is probably responsible for the higher background absorption on the high frequency side of the pyridine band near 1036  $\text{cm}^{-1}$  relative to aqueous pyridine.

*Lithium Nitrate-Pyridine-Water.*—Addition of successive amounts of water to the solution of lithium nitrate in pyridine results in a lowering of the 1420  $\text{cm}^{-1}$  frequency and a raising of the 1329  $\text{cm}^{-1}$  band such that the former rapidly approaches the latter. At higher water concentrations, a band emerges from the high frequency side of the higher frequency band to form a third absorption peak near 1416  $\text{cm}^{-1}$ . Simultaneously, a band appears near  $\nu_2$  at 816  $\text{cm}^{-1}$  indicating the presence of a second species of nitrate ion, because  $\nu_2$  is a non-degenerate vibration.

At higher water concentrations, there are three absorptions in the  $\nu_3$  region which can be explained on the assumption that one belongs to a nitrate ion of  $D_{3h}$  or  $C_{3v}$  symmetry ( $\nu_4$  and  $\nu_3$  degeneracy retained) and the other two belong to a nitrate ion of symmetry  $C_{2v}$  or  $C_s$  ( $\nu_4$  and  $\nu_3$  degeneracy lost). It is not possible to assign these bands to symmetric or antisymmetric modes of vibration without Raman polarization data. To explain the existence of two species of nitrate ion, we must consider the environment of the lithium ion. Strong interaction of the nitrate ion and the proton acceptor molecule pyridine is unlikely.

*Structure of the Solvated Cation.*—Dissolution of a salt by a solvent of high dielectric constant does not necessitate appreciable association of the solvent with the solute, but in cases where solvent-solute associations are strong, this can assist solubility. The lithium cation has high polarizing power and, therefore, it is not surprising that the spectrum of lithium nitrate in pyridine possesses many of the characteristics of the pyridine-water system, and, with respect to the pyridine vibrations, corresponds to approximately 0.3 mole of water per mole of pyridine. The spectrum strongly supports a solution structure in which the lithium cations are solvated by pyridine molecules.

We have seen that when water is added to pyridine, a new molecular species  $\text{C}_5\text{H}_5\text{N}\cdots\text{HOH}$  is formed. The intensity of absorption in the 3670  $\text{cm}^{-1}$  region, for non-associated water molecules, is relatively low, so that the equilibrium:



lies well to the right. There are then two principal species of solvent molecule, pyridine and pyridine-water complex, both potentially capable of solvating solute cations. The two  $\nu_2$  frequencies (Table 3) exhibited by a solution of lithium nitrate in aqueous pyridine can be explained now in terms of two species of nitrate ion. These correspond to nitrate ions paired with lithium ions which are solvated with pyridine molecules (I) and pyridine-water complex (II), respectively. The Raman spectra of concentrated aqueous solutions of alkali-metal nitrates, for example 7M-sodium nitrate, showed two bands in the  $\nu_3$  region

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which Mathieu and Lounsbury<sup>10</sup> attributed to a cessation of degeneracy because of the close approach of cations and anions. The polarizing power of the cation is experienced by the nitrate ion when the cation hydration shell is broken down.

Table 3 shows the number and values of frequencies assigned to the  $\nu_2$  vibration of the

TABLE 3.

NH <sub>4</sub> NO <sub>3</sub>			LiNO <sub>3</sub>			C <sub>5</sub> H <sub>5</sub> NH·NO <sub>3</sub>			AgNO <sub>3</sub>		
A	B	C	A	B	C	A	B	C	A	B	C
830	830	833	828	816	833	823	827	833	828	—	816
—	—	—	—	829	—	—	831	—	831	830	—

A = Saturated solution in anhydrous pyridine. B = Aqueous pyridine solution. C = Aqueous solution.

For pyridinium and silver nitrates, the solubility in pyridine was not determined and hence the ratio of mole water to mole pyridine was not known.

For silver nitrate, 2 ml. water were added to 10 ml. saturated solution in pyridine.

nitrate ion in the solvents described. It is seen that pyridinium nitrate in solution in aqueous pyridine behaves in a similar manner to lithium nitrate, though the  $\nu_2$  frequencies are much closer together in the former.

The same explanation for the appearance of two  $\nu_2$  frequencies is applicable but in the case of the pyridinium cation ( $M = H^+$ ) the bands would be better re-drawn to show a



hydrated pyridinium cation, not a hydronium ion solvated with pyridine. The ratio of moles of water per mole of pyridine reaches unity before the second species of nitrate ion appears, which is judged by the emergence of the 1416 cm.<sup>-1</sup> absorption. This indicates that those pyridine molecules which are not involved directly in solvation are hydrated preferentially to those which are in the solvate shell. When the hydration of the unattached pyridine molecules is complete, conversion of solvated cation (I) to solvated cation (II) can proceed.

*Silver Nitrate-Pyridine.*—A saturated solution in pyridine of the well-known silver nitrate-pyridine complex<sup>11</sup> shows two  $\nu_2$  nitrate frequencies at 828 and 831 cm.<sup>-1</sup> and two broad overlapping bands in the  $\nu_3$  region with maxima at about 1340 and 1376 cm.<sup>-1</sup>. The appearance of the pyridine spectrum is similar to that of a solution of 0.2 mole of water per mole of pyridine. The appearance of two bands of similar intensity in the  $\nu_2$  region can be explained if in addition to the two pyridine molecules strongly co-ordinated to the silver ion, there are pyridine molecules weakly bound in a solvate shell. In pyridine solution, then, there could be solvated and non-solvated silver-pyridine complex cations. These two cations would be shielded to different degrees and would exhibit different polarizing effects on the nitrate ion.

When water is added to the silver-pyridine solution, only the high frequency  $\nu_2$  band is observed. This is assigned to the nitrate ion which is paired with the non-solvated silver-pyridine cation. The pyridine molecules, weakly bound in the solvate shell, are released to form hydrogen bonds with the water molecules. The wave numbers separating the two  $\nu_3$  components of the nitrate ion increase on addition of water, a fact which reflects increased polarization of the nitrate ion.

The absence of two species of nitrate ion from ammonium nitrate in aqueous pyridine

<sup>10</sup> Mathieu and Lounsbury, *Discuss. Faraday Soc.*, 1950, **9**, 196.

<sup>11</sup> Bjerrum, *Chem. Rev.*, 1950, **46**, 381.



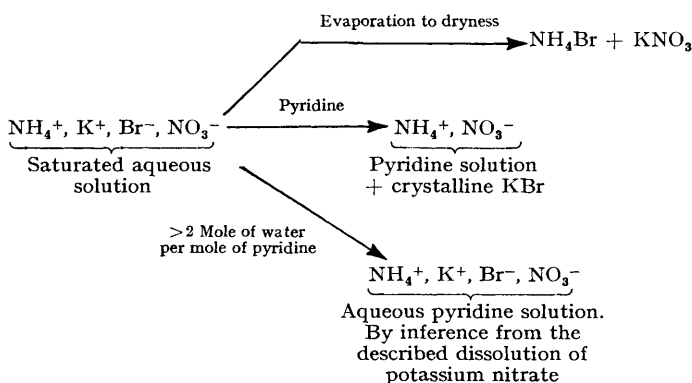
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suggests that the structure of the cation-anion pair is similar both in pyridine and in water solutions. The continuous shift of nitrate-ion frequencies on going from solvent mixtures rich in pyridine to those rich in water could then be explained in terms of the changing polarity of the solvent. A tentative explanation of the similarity of the cation-anion pairs in the two solvents, is that hydrogen bond formation between cation and anion may make a major contribution to the perturbation of the nitrate ion.

When an equimolecular mixture of potassium nitrate and ammonium bromide was treated with a solution of 1 mole of water per mole of pyridine, only a little ammonium bromide dissolved. If the water which was added to the pyridine was, instead, added to the mixed salts, and then treated with pyridine, ammonium and nitrate ions were extracted into the pyridine. The former absorbs at about 1440 and the latter near 1335  $\text{cm}^{-1}$ . The quantity of ammonium nitrate and ammonium bromide present in the pyridine was determined. Crystalline potassium nitrate similarly treated with aqueous pyridine did not dissolve even when the concentration of water was 2 moles per mole of pyridine. Again, when a saturated solution of potassium nitrate was treated with pyridine, dissolution only occurred when there was sufficient water present in the solution to hydrate completely the pyridine molecules, that is, to make a solution  $>1$  mole of water per mole of pyridine.

These results clearly show that water dissolved in pyridine is not capable of behaving like bulk water until a concentration of 2 moles of water per mole of pyridine is reached. This constitutes further evidence for the absence of an equilibrium involving associated water molecules, that is, bulk water in the aqueous pyridine studied.

These results contrast the simultaneous extraction of ammonium and nitrate ions from the mixture with the manner in which the ions pair up on removal of water:



*Potassium Thiocyanate-Pyridine.*—Potassium thiocyanate is soluble in pyridine without changing the pyridine frequencies. In this case, pyridine is obviously not involved in a solvate complex with the potassium ion.

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