

707. *An Infrared Absorption Study of the State of Adsorbed Water Molecules and the Effect of Sodium Ions on Potassium Bromide Pressed Discs, and on Dipotassium Hydrogen Phosphate Dispersed in Potassium Bromide Pressed Discs.*

By W. K. THOMPSON.

An infrared (i.r.) study has been made of water molecules adsorbed on potassium bromide pressed discs and on dipotassium hydrogen phosphate dispersed in potassium bromide pressed discs. The intensity of water absorption-bands is not proportional to the amount of water present in discs prepared from finely ground potassium bromide, unless the discs are optically clear. The results are best interpreted in terms of two types of water molecules—an adsorbed layer, at the most only a few molecules thick, and clustered molecules. Failure to form ice on cooling and the effect of changes in the structure of the discs on the state of adsorbed water are discussed. Under certain conditions dipotassium hydrogen phosphate is shown to react with sodium ions in potassium bromide discs in the presence of water molecules to give successively anhydrous disodium hydrogen phosphate and disodium hydrogen phosphate dihydrate.

THE potassium bromide pressed-disc technique for the examination of samples by i.r. spectroscopy has been widely used but relatively few studies have been made on the behaviour of water normally present in such discs. Workers in this field have studied the action of water on potassium bromide containing various dispersed substances,<sup>1-2</sup> but have assumed that the intensity of the i.r. absorption of water is proportional to the concentration of water in the discs. The frequencies of the water absorptions on different alkali-metal halides have been studied by Price *et al.*<sup>3</sup>

The phase system, dipotassium hydrogen phosphate–water, has been examined by Ravich,<sup>4</sup> and no hydrate lower than the trihydrate has been reported.

#### EXPERIMENTAL

Unless otherwise stated, all transfer operations and disc preparations were carried out with strict precautions to exclude water vapour. AnalaR grades of potassium bromide\* and dipotassium hydrogen phosphate were used, both being finely ground in an agate mortar, and heated to 320 and 110°, respectively, before use. Discs were prepared by estimating the volume of powder required for a weight of about 0.1–0.2 mg. dipotassium hydrogen phosphate and 500 mg. potassium bromide and grinding the powder in an agate-vibrator ball-mill. After 7 min. the powder was freed from the sides of the mortar with a spatula and ground for a further 7 min. The amplitude of vibration of the mill blade was 7 mm. Phosphorus pentoxide was used as a desiccant in the dry-box with a slight positive pressure of dry nitrogen free of carbon dioxide. Discs were pressed in a 15-mm. diam. die (Research & Industrial Instruments Ltd.) at *ca.* 40° and 3150 kg. cm.<sup>-2</sup> (20 ton inch<sup>-2</sup>).

Humidity chambers were constructed from 20-oz. wide-neck bottles containing a range of sulphuric acid–water mixtures. The discs were supported in glass phials 1.9-cm. diam. and 5.3 cm. in length, which were themselves supported by wire secured to the rubber bottle-stoppers. These humidity chambers were kept at a temperature of 24–26° in a water-bath with thermostat. The sulphuric acid–water compositions required to give atmosphere of known percent relative humidities were obtained from the data given by Spencer-Gregory and

\* Chemical analysis showed this material to contain 0.12% w/w Na<sup>+</sup>.

<sup>1</sup> Van der Maas and Tolck, *Spectrochim. Acta*, 1962, **18**, 235.

<sup>2</sup> (a) Farmer and Russell, *Spectrochim. Acta*, 1962, **18**, 461; (b) Farmer, *Chem. and Ind.*, 1959, 1306.

<sup>3</sup> Price, Sherman, and Wilkinson, *Proc. Roy. Soc.*, 1958, *A*, **247**, 467.

<sup>4</sup> Ravich, *Bull. Acad. Sci. U.R.S.S. Classe sci. math. nat. Ser. chim.*, 1938, No. 1, 137–146.

Rourke.<sup>5</sup> The strength of the sulphuric acid solutions was checked by titration with standard sodium hydroxide solution.

When discs were heated they were placed on a copper plate in a stream of dry nitrogen. To the underside of the plate was pressed an iron-constantan thermocouple which had been calibrated over the range 22–100° where it gave a rectilinear response. Temperatures >100° were read by extrapolation.

Spectra of aqueous solutions were recorded between pressed discs of silver iodide sealed with adhesive tape.

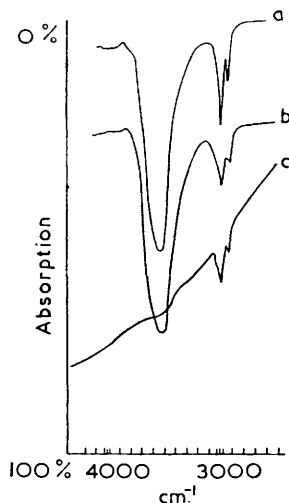
Disodium hydrogen phosphate dihydrate was obtained by storing the finely-ground dodecahydrate over phosphorus pentoxide for 3 days, when a correct analysis was obtained. Disodium hydrogen phosphate dodecahydrate was obtained by stirring a saturated solution of the AnalaR material for 17 hr. at 25°.

X-Ray analysis showed that the dihydrate previously present had been removed.

Crystallisation of the dodecahydrate at 25 and at 35° yielded crystals showing identical X-ray powder patterns equivalent to the  $\alpha$ -form described by Corbridge,<sup>6a</sup> but not the  $\beta$ -form.

## RESULTS AND DISCUSSION

*Influence of Relative Humidity on Appearance of Discs and Infrared Spectra.*—The Figure shows a typical result obtained by exposing nominally anhydrous discs of potassium bromide (AnalaR grade) to atmospheres of varying relative humidity. A series of curves lying between these extremes of intensity was obtained for a series of relative



(a) Freshly prepared disc, clear and transparent, assigned to atmosphere of 1.3% relative humidity. (b) After 33 days' storage, in atmosphere of 1.3% relative humidity, clear and transparent. (c) Turned white and opaque after further 30 days storage in atmosphere of 20% relative humidity.

Ordinate not deliberately moved.

Absorption near 3000 cm<sup>-1</sup> is due to a trace of hydrocarbon impurity.

humidity values. Detailed intensity measurements were hampered by the increasing background absorption or scatter, but clearly the intensity of the 3450 and 1640 cm<sup>-1</sup> absorptions decrease as the relative humidity of the atmosphere, with which they were in equilibrium, was increased.

*Discs with Low Water Content.*—Discs prepared in the normal way behaved as follows: (a) in 0–10% relative humidity storage atmosphere, no loss of optical clarity for periods in excess of 3 months, though a slightly milky appearance may be noticed in some discs; (b) in 10–16% relative humidity atmosphere, the appearance of the discs after, for example, 7 days, varied from clear to opalescent. However, equilibrium was not established much before 22 days, when the 13.5% relative humidity atmosphere gave a white almost opaque disc; (c) in 20% and greater R.H. atmospheres the discs exhibited very severe to total scattering of radiation between 5000 and 2000 cm<sup>-1</sup> (2.0–5.0  $\mu$ ) and water absorptions

<sup>5</sup> Spencer-Gregory and Rourke, "Hygrometry," Crosby, Lockwood & Son, Ltd., London.

<sup>6</sup> (a) Corbridge and Tromans, *Analyt. Chem.*, 1958, **30**, 1101; (b) Corbridge and Lowe, *J.*, 1954, **493**.

of such reduced intensity that, even when the background in the 1500—1700  $\text{cm}^{-1}$  region was about 70% transmission, the band near 1640  $\text{cm}^{-1}$  was barely perceptible.

*Discs with high Water Content.*—Discs prepared without evacuation were stable under conditions (a), above, for more than three months; under conditions (b) they turned white and opaque after only three days' exposure at the upper limit.

Similar results were obtained with optically-pure potassium bromide from ground-up fractured windows. Attempts to determine the water content of discs by weighing on a microbalance failed, but investigations with a silica spring-balance could be profitable.

Explanation of these effects must clearly attempt to correlate macroscopic crystallographic changes occurring in the solid phase with significant alteration in the properties of the trace quantities of water associated with the halide grains.

*Nature of the Halide Crystal-Water Interaction.*—Pressed alkali-halide discs have been examined by Price, Sherman and Wilkinson<sup>3</sup> and shown to be mosaics of minute crystals about  $1\mu$  in diameter. In such structures there will be capillaries of much smaller dimensions and under normal conditions of preparation considerable elastic strain may be expected to be created within the discs. Water, even in trace amounts, has a profound influence on the physical properties in such systems as shown in recent work by Cabané<sup>7</sup> on pressed alkali halides, a decrease in density and optical clarity being produced on contact with water vapour. Such moisture-controlled expansion may be explained both by the well-known influence of water on the plasticity of single crystals of alkali halides (Joffé effect<sup>8</sup>) and strain-release due to movement of micro-crystals when grain boundaries are weakened and enlarged through attack of water vapour. Such expansion of grain boundaries has been clearly observed in the present work by optical reflectance microscopy on polished specimens of discs subjected to the humidification treatment previously described. At higher water contents large-scale recrystallisation occurs within the discs.

The evidence regarding a variation of the 3450  $\text{cm}^{-1}$  band intensity and the optical properties of these discs with the humidity of the atmosphere surrounding them, is thus consistent with localised structural changes caused by water adsorption at grain boundaries at low humidities (<10% R.H.) followed by large-scale recrystallisation prompted by water of a more mobile type at higher humidities (>10% R.H.). The large drop in intensity under the latter conditions may then be attributed to a decrease in internal surface area as preferential growth of large crystals proceeds, and the previously extended boundary water-films contract to give randomly distributed multimolecular clusters. While these would produce sharply increased localised infrared absorption, the decreased absorbing area presented to the beam would lead to a net decrease in absorption of the beam as a whole. This clustering mechanism assumes a more powerful interaction between water molecules than between water molecules and halide ions. Hall and Tompkins,<sup>9</sup> working on the heats of adsorption of water vapour on salts near  $-25^\circ$ , including potassium chloride, thought clustering of water molecules occurred before monolayer formation was completed. The large difference between the librational frequency of water molecules in water and in chloride, bromide, and iodide solutions is attributed by Swain and Bader<sup>10</sup> to a looser binding between water molecules and these ions, than between water molecules themselves.

Referring again to the experiments on discs prepared with and without evacuation and, therefore, containing less or more residual moisture, respectively, confirms that the process of optical densification can proceed at water levels below those where recrystallisation and coalescence through moisture, by the above mechanism, takes place.

Finely powdered pure potassium bromide left for 17 hours in a sealed tube gave rise to discs showing good optical properties and very weak water absorptions.

<sup>7</sup> Cabané, *Compt. rend.*, 1962, **59**, 1123.

<sup>8</sup> Joffé, Kirpitschewa, and Lewitsky, *Z. Physik*, 1924, **22**, 286; 1925, **31**, 576.

<sup>9</sup> Hall and Tompkins, *Trans. Faraday Soc.*, 1962, **58**, 1734; *J. Phys. Chem.*, 1962, **66**, 2260.

<sup>10</sup> Swain and Bader, *Tetrahedron*, 1960, **10**, 182.

*Effect of Heat on the Optical Properties of Discs.*—A clear disc was placed partially on a brass block at *ca.* 100°. A small white area formed at the hot spot and slowly spread across the whole disc. It was possible to follow the change in the i.r. spectrum before and after the strain-releasing expansion had traversed the diameter of the disc. The spectra were identical to those in Fig. (a) and (c), respectively. When the disc was re-ground and pressed, a spectrum identical to Fig. (b) was obtained. A disc made white with water vapour will not be regenerated in this way. Discs heated in a stream of dry nitrogen become opaque at 127°, those heated in a sealed tube change at 40° strongly indicating that the mechanism already described is applicable. On local heating some water is vapourised and travels to cooler regions where it triggers off the expansion process.

Cabané<sup>7</sup> has shown that on warming pressed discs of alkali, rapid recrystallisation occurs, the volume of the sample increases, the grains become enlarged, and there is a decrease in optical clarity proportional to the amount of water present. Optical microscopy clearly shows an increase in the breadth of the grain boundaries and in the size of the grains during the humidity experiments.

*Physical State of the Adsorbed Water.*—Optical and AnalaR grades of potassium bromide were examined as discs between 400 and 5000  $\text{cm}^{-1}$  at room temperature and when cooled with liquid oxygen in a conventional cooled disc-holder. The absorption maxima near 1640 and 3450  $\text{cm}^{-1}$  did not shift in frequency, but the latter increased slightly in intensity. Pure potassium-bromide powder was then exposed for 1 hour to saturated water vapour at room temperature, ground and pressed. The resultant disc completely scattered white light, but transmitted radiation from 400 to 2000  $\text{cm}^{-1}$ . Between 2000 and 4000  $\text{cm}^{-1}$  transmission fell rapidly, but the curve contained an inflexion corresponding to the water absorption near 3450  $\text{cm}^{-1}$ . The disc was cooled as before, and the spectrum was identical to that obtained at room temperature except for a slight increase in the overall transmission. AnalaR potassium bromide treated similarly exhibited spectral features identical to those of  $\text{NaBr}\cdot 2\text{H}_2\text{O}$ , with bands at 1620, 1640, and 3450  $\text{cm}^{-1}$ , but no frequency shifts occurred.

The most intense absorption band of ice is at 3250  $\text{cm}^{-1}$ , and so the water in the discs is not capable of assuming the ice structure. This may be explained in either of two ways: (a) the adsorbed monolayer<sup>3</sup> does not allow the tetrahedral value required by ice;<sup>11</sup> (b) from the theory of a flickering cluster for water and a flickering droplet for ice (Frank and Wen<sup>12</sup> and Frank<sup>11</sup>) a statistical minimum size is inherent for the structural units of water and of ice. This minimum size may not be attained in the capillaries considered. It has been shown by Frohnsdorff and Kington<sup>13</sup> that for a zeolite, the cages of which were known to hold 21 water molecules, the OH stretching frequencies only approached those of bulk water when the structure neared saturation. Thus, in this case the layer is ten water molecules thick from the substrate.

*Behaviour of Discs containing Dipotassium Hydrogen Phosphate.*—An analogous series of experiments on this system showed that it behaved similarly but had an increased stability toward water vapour. However, changes in the spectrum of the phosphate occurred (see the Table). The new spectrum (column 3 in the Table) is identical to that of disodium hydrogen phosphate.

Finely-powdered potassium bromide (AnalaR) was exposed to saturated water vapour at 26° for 1 hr., then ground with dried dipotassium hydrogen phosphate and pressed. The spectrum obtained from this disc was that of disodium hydrogen phosphate dihydrate. The disc was clear and transparent by contrast with an identical experiment in the absence of phosphate. Farmer<sup>20</sup> observed the effects of  $\text{Na}^+$  ions in discs of potassium bromide containing glucose. Repetition of the high-humidity experiment described above, but with optically pure potassium bromide, yielded only the spectrum

<sup>11</sup> Frank, *Proc. Roy. Soc.*, 1958, *A*, **247**, 481.

<sup>12</sup> Frank and Wen, *Discuss. Faraday Soc.*, 1957, No. 24, 133.

<sup>13</sup> Frohnsdorff and Kington, *Proc. Roy. Soc.*, 1958, *A*, **247**, 469.

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M. & W.*	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O Ground under Nujol, placed on polyethylene film and compensated	Spectrum obtained from K <sub>2</sub> HPO <sub>4</sub> /K <sup>+</sup> Na <sup>+</sup> Br <sup>-</sup> <i>e.g.</i> , 28% R.H.	Aqueous 2·2M-KH <sub>2</sub> PO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub> ·2H <sub>2</sub> O Pressed disc from coarsely ground KBr
1	2	3	4	5
~465w (b)	460w-m	468w	402 ‡	518s
531m (b) †	524s	534s	514 ‡	542m-s
—	554m	549s		569m
				620w-m
				~768w
				827w-m
865s	860s	862s	~890m-s	866m
				~873m, inf } 955s
958w, sh	945s } (b)	954s	948s	1001w-m
985s	978s }			1072vs
1070vs	1073s (b)	1080vs	1088vs	1125s
1125w, sh				1141s
1145vw, sh				
1185w	~1176s (b)	1164vs	1170s	1267m
1265w		1367w		1622w
1630m		1635m		~1642w
				2450w
2220w (b)		2510w (b)		3130s
3280vs (vb)				3390s
		3450m		3440s

inf = inflexion      sh = shoulder      w = weak      m = moderate      s = strong

\* Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253. † Miller, Carlson, Bentley, and Jones, *Spectrochim. Acta*, 1960, **16**, 135. These workers state that the spectrum was poor. ‡ Raman values taken from Simon and Schulze, *Z. anorg. Chem.*, 1939, **242**, 329.

of dipotassium hydrogen phosphate. The series of experiments at different relative humidities showed that the reaction of dipotassium hydrogen phosphate with Na<sup>+</sup> ions and water molecules will only occur to an extent proportional to the vapour pressure of the water in the atmosphere with which the disc is in equilibrium. A disc which had reached equilibrium with an atmosphere of 25% relative humidity, and undergone complete conversion, when re-ground and pressed gave a spectrum corresponding to about 50% dipotassium hydrogen phosphate and 50% anhydrous disodium hydrogen phosphate.

This may be attributed to a mechanically-induced reversal of the reaction. A disc which had been in an atmosphere of 28% relative humidity was similarly treated and the powder left 17 hours in a stoppered capsule before pressing. The disc then gave the spectrum of anhydrous disodium hydrogen phosphate showing that the redistributed water had migrated further into clusters in a manner analogous to that described for the pure potassium-bromide discs. The frequencies for pure anhydrous disodium hydrogen phosphate mulled in Nujol differ from Corbridge's<sup>6b</sup> values.

*Effect of Humidity in the Absence of Na<sup>+</sup>.*—Discs prepared from optically-pure potassium bromide containing finely-dispersed dipotassium hydrogen phosphate equilibrated with atmospheres of 28 and 35% relative humidity gave the spectra of crystalline dipotassium hydrogen phosphate plus its aqueous solution, and of the aqueous solution, respectively. Cooling of a disc that exhibits the spectrum of an aqueous solution of dipotassium hydrogen phosphate does not lead to a change of spectrum to that of crystalline dipotassium hydrogen phosphate or its trihydrate,<sup>14</sup> and ice.<sup>12</sup> Consequently it is believed that the potassium and hydrogen phosphate ions are detached from their crystal structure by water molecules, the number and character of which are unsuited to form a true aqueous solution. This is believed to be the first i.r. spectroscopic study of such a phenomenon. The transport of sodium and potassium ions is presumably effected by rapid exchange of hydrating water molecules. It should be noted here that discs prepared from potassium bromide coarsely

<sup>14</sup> Ryskin and Stavitskaya, *Optics and Spectroscopy*, 1960, **8**, 320.

ground, *i.e.*, before grinding in the vibrator mill, and which presumably have a much smaller internal surface area, show a very much lower sensitivity toward water vapour.

Comparison of columns 1, 2, and 5 in the Table shows that the material used by Miller and Wilkins had lost water and consisted largely of disodium hydrogen phosphate dihydrate. Differences in frequency as between Corbridge<sup>6b</sup> and column 5, for example, may be attributed in part to refractive-index effects, because Corbridge<sup>6b</sup> used the powder. The intensities are relative and in column 2 only a weak spectrum could be obtained by this technique. It is interesting to compare column 3 of the Table with the spectrum of an aqueous solution of potassium dihydrogen phosphate, in column 4. The considerable similarity prompts the thought that the site symmetry with respect to the hydrogen phosphate ions is not higher than  $C_{2v}$  in crystalline anhydrous disodium hydrogen phosphate. It is assumed here that the  $H_2PO_4^-$  ion is isotropically surrounded by water molecules in aqueous solution.

The results show that under the conditions described, migration of ions can occur only in the presence of trace amounts of water, and that the vapour pressure of this water is less than the vapour pressure of water in disodium hydrogen phosphate dihydrate.

The results of Cabané's autoradiographic work<sup>15</sup> favour the migration at grain boundaries of anions rather than cations, by contrast with bulk diffusion.

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FISONS FERTILIZERS LIMITED, DEPARTMENT OF CHEMISTRY, LEVINGTON RESEARCH STATION,  
LEVINGTON, IPSWICH, SUFFOLK.

[Present address: UNILEVER RESEARCH LABORATORY,  
PORT SUNLIGHT, CHESHIRE.]

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<sup>15</sup> Cabané, *Compt. rend.*, 1962, **59**, 1135.

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