

The alkali halide disk technique in infra-red spectrometry

Anomalous behaviour of some samples dispersed in alkali halide disks

A. TOLK

Analytical Chemical Laboratory
State University, Utrecht, The Netherlands

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Abstract—Some difficulties encountered in the application of the alkali halide disk technique in infra-red spectrometry are discussed. Complications due to interaction of the sample with the alkali halide have been studied experimentally. It was found that the anomalous behaviour of benzoic acid, succinic acid, adipic acid and succinimide in KBr and KCl disks must be ascribed to adsorption of the molecules of the sample on the surface of the alkali halide particles. The anomalous behaviour of α -naphthylacetamide, however, is caused by polymorphism of this substance, whereas the unusual spectrum of succinimide in KI disks is due to the formation of an addition product. The anomalies caused by adsorption can be eliminated by storage of the disks in a moist atmosphere; this "ageing process" is primarily caused by recrystallization of the alkali halide under the influence of water from the surrounding atmosphere.

Introduction

THE infra-red spectra of solid samples can be obtained by the alkali halide disk technique whereby a mixture of finely divided sample and alkali halide is converted into a disk under pressure [1–3]. When the technique was introduced it was received with considerable enthusiasm; even in quantitative analysis good results were claimed to be obtainable. The disk technique soon encountered some difficulties, however: spectra could not always be reproduced to the desired degree for quantitative or even qualitative purposes and sometimes considerable differences were observed when spectra of samples dispersed in alkali halide disks and mullied in Nujol, respectively, were compared. A review of the difficulties encountered has recently been given by DU YCKAERTS [4].* We shall draw attention here in particular to the anomalous phenomena observed by FARMER [6, 7] and BAKER [8].

FARMER [6, 7] stated that the spectra of solid organic acids and phenols suspended in alkali halide disks differed from the spectra of the same samples mullied in Nujol. Sample and alkali halide were ground and mixed in an electromagnetic vibrator; the powder was pressed in a mould using a thrust of 8 tons. For a further study of the phenomena FARMER used benzoic acid. KI being used as a carrier benzoic acid showed the spectrum of the normal crystalline dimer. If KBr, KCl or NaCl was used as a carrier the infra-red absorption bands of the dimer at 7.02 and

* See also [5].

- [1] M. M. STIMSON and M. J. O'DONNELL, *J. Am. Chem. Soc.* **74**, 1805 (1952).
- [2] U. SCHIEDT and H. REINWEIN, *Z. Naturforsch.* **7b**, 270 (1952).
- [3] U. SCHIEDT, *Z. Naturforsch.* **8b**, 66 (1953).
- [4] G. DU YCKAERTS, *Analyst* **84**, 201 (1959).
- [5] A. TOLK, Thesis, University Utrecht (1959).
- [6] V. C. FARMER, *Chem. & Ind. London* 586 (1955).
- [7] V. C. FARMER, *Spectrochim. Acta* **8**, 374 (1957).
- [8] A. W. BAKER, *J. Phys. Chem.* **61**, 450 (1957).

7.73 μ were weakened relative to the rest of the spectrum; this weakening of the dimer bands was increased if a longer grinding time was used. If the ground mixture of the acid with NaCl was heated for 2 hr at 80°C before pressing, the bands of the dimer were completely absent from the spectrum of the disks and new bands at longer wavelengths became visible.

According to FARMER the new bands in the spectrum are to be ascribed to monomeric benzoic molecules adsorbed on the surface of the alkali halide particles. The crystalline dimer is readily volatile and, on heating the ground mixture of benzoic acid and NaCl in a thin layer at 80°C before pressing, the excess of the normal dimeric form of the acid is evaporated leaving the monomeric form alone adsorbed on the NaCl surface. Examination of other carboxylic acids and of phenols under conditions similar to those used with benzoic acid revealed spectral changes which could again be ascribed to adsorbed molecules.

In contradiction to FARMER the variations between mull and disk spectra of organic compounds are ascribed by BAKER [8] to polymorphic or amorphous forms of the sample in the alkali halide disk. The adsorption effects in alkali halide disks should be limited to a small percentage of the total sample because even in the most finely ground mixture the included sample has particle sizes which contain large aggregates of molecules.

BAKER described experiments with hexamethylenetetramine, benzil, succinimide α -naphthalene acetamide and 2-aminobenzoic acid in support of his view. Unfortunately he did not implicate the substances used by FARMER in his investigation.

Independent of FARMER we also observed the anomalous spectrum of benzoic acid dispersed in alkali halide disks. Besides this we observed that this spectrum was converted into the normal spectrum of benzoic acid when the disks were exposed to the atmosphere during a few days [9]. As this "ageing process" might give a clue to the origin of the anomalous spectra of benzoic acid and other substances we started a closer examination of the phenomena.

Materials and methods

The investigated substances were benzoic acid, succinic acid, adipic acid, succinimide and α -naphthylacetamide. The alkali halides used were KCl, KBr and KI reagent grade, manufactured by Merck.

Sampling techniques

A. *Mixing of sample and alkali halide*

(1) Vibrating technique: 0.2–2.0 mg of the sample and 200–1000 mg alkali halide were mixed together with two ball-bearings (2 mm diameter) and ground during 20 min in a solenoid vibratory grinder manufactured by Weber, Stuttgart-Uhlbach.

(2) Dry-freezing technique: 0.2–2.0 mg of the sample and 200–1000 mg alkali halide were dissolved in about 5 ml of distilled water and poured into a Pyrex test tube (internal diameter 14 mm). The test tube rotating in vertical position with a

[9] A. TOLK and H. J. VAN DER MOLEN, *Chem. Weekblad* **53**, 656 (1957).

speed of about 2000 rev/min was surrounded by a carbon dioxide-acetone mixture to freeze the solution quickly. After removal of the carbon dioxide-acetone mixture the ice in the tube was evaporated completely in high vacuum at room temperature in about 3 hr; the vacuum was maintained with an ordinary oil vacuum pump.

The "effective surface" of pure KCl powder dry frozen in this way was determined using the B.E.T.-method with nitrogen. The surface proved to be 4.3 ± 0.3 m² per g KCl.*

B. Pressing of the disks

The finely divided mixture of sample and alkali halide was brought into a die with splittable cone (internal diameter 13 mm) designed by Schiedt and manufactured by Weber, Stuttgart-Uhlbach. The die was evacuated for 5 min by a vacuum pump and then a pressure of 13 tons was applied for 20 min, followed by a pressure of 3 tons during 10 min. After this the outer atmosphere was admitted and the die disassembled. The disk mounted in a microholder was placed in the sample beam of the spectrophotometer. No reference disk was used in the reference beam.

The spectrophotometer used was a Perkin-Elmer model 21 with linear wavelength scale and equipped with a NaCl prism in the wavelength range of 2-15 μ and a KBr prism in the range of 10-22 μ .

Investigation of the validity of the adsorption hypothesis of Farmer

In this study the behaviour of benzoic acid, succinic acid, adipic acid, α -naphthylacetamide and succinimide are included.

A. Benzoic acid

The anomalous behaviour of benzoic acid can be illustrated with the spectra, Fig. 1(a-c). Fig. 1(a) is the spectrum of a Nujol mull of the acid between two NaCl windows. Fig. 1(b) is the spectrum of a disk pressed from a dry-frozen mixture of benzoic acid (0.8 mg) and KCl (1000 mg) and Fig. 1(c) is the spectrum of the same disk after storage in air during four days. Spectra (a) and (c) correspond to benzoic acid in the normal dimeric form. Spectrum (b) on the contrary corresponds to benzoic acid in the anomalous form: a number of absorption peaks characteristic of the normal dimeric form are absent, for instance the peaks at 7.02 and 7.73 μ mentioned above, whereas new peaks have appeared, for instance at 8.10 and 15.40 μ .† For a further study of the phenomena, disks containing increasing amounts of benzoic acid relative to the amount of KCl were examined. If the adsorption hypothesis of FARMER is true a saturation value may be expected for the amount of anomalous product per gramme of the alkali halide carrier. The experiments were carried out with concentrations of the acid in the range of 0.4-8.0 mg per g KCl.

As the dry-freezing technique resulted in a more pronounced anomalous behaviour of benzoic acid and furnished results that were more reproducible than those obtained with the vibration technique, the former was used for the mixing process. The mixtures were pressed as described above and the spectra of the disks

* This measurement was carried out by Dr. A. B. C. VAN DOORN and Dr. F. N. HOOGE of the Rijks Verdedigings Organisatie/T.N.O. in Delft.

† The wavelengths of these new peaks change a little with the alkali halide used.

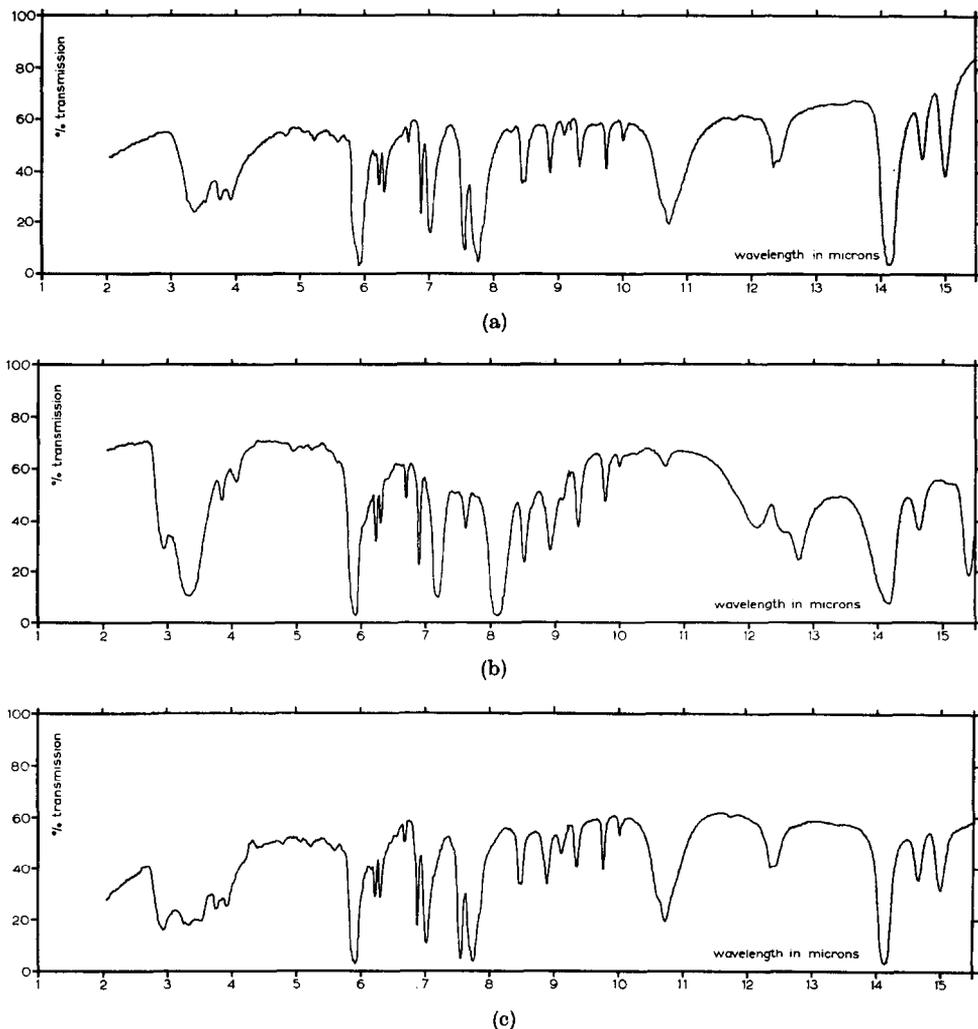


Fig. 1.

- (a) Spectrum of benzoic acid milled in Nujol.
 (b) Spectrum of a disk pressed from a dry frozen water solution of 1000 mg KCl and 0.8 mg benzoic acid.
 (c) Spectrum of the disk used for spectrum (b) after storage in a moist atmosphere for 4 days.

were determined instantly after pressing. The disks with a low benzoic acid/KCl ratio contained the acid in the anomalous form only, as the spectra showed. At higher concentrations the normal form showed up additionally.

Fig. 2 illustrates the amount of anomalous acid per gramme KCl found in the disks as a function of the weighed-in quantities of benzoic acid. The amounts of the anomalous product were determined with the absorption peak at 8.10μ using the horizontal through the transmission maximum at 6.78μ in each spectrum as a base line. The extinction coefficient of the 8.10μ peak was determined with the

disks containing less than 1 mg of the acid per g KCl, as these disks contained the acid in the anomalous form only.

The horizontal part in the curve on Fig. 2 shows that a saturation value of the anomalous acid exists indeed; a mean value of 2.68 mg/g KCl was found. Using the effective surface of the KCl of $4.3 \pm 0.3 \text{ m}^2$ per g mentioned above the KCl surface is calculated to be $32.5 \pm 2.5 \text{ \AA}^2$ per molecule anomalous acid.

Compared with a surface of 22 \AA^2 for the mean cut of fatty acid molecules found with the Langmuir trough, this value looks quite reasonable. The pressing factor

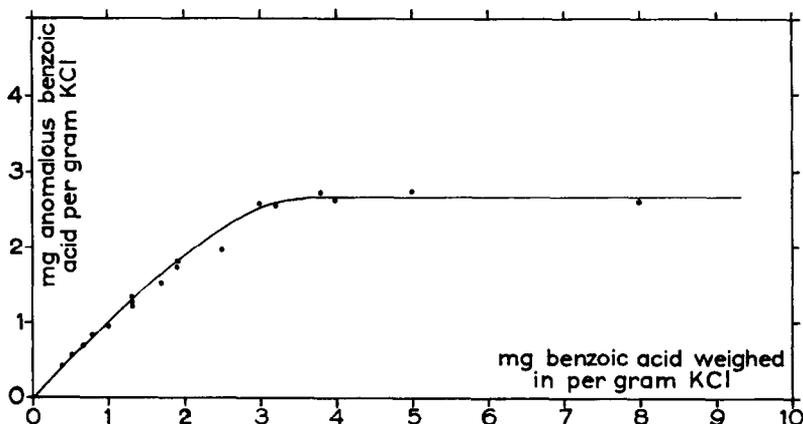


Fig. 2. Amount of anomalous benzoic acid as a function of benzoic acid weighed in per g KCl.

proved to be of minor importance for these phenomena: Nujol mulls of dry-frozen mixtures of 0.40 mg benzoic acid and 300 mg KCl showed the anomalous spectrum as well. It proved to be possible to make the benzoic acid adhere to finely divided KCl via the gas phase at room temperature and also at 110°C . The disks pressed from these samples showed the spectrum of the anomalous product (phenanthrene treated in the same way did *not* adhere to KCl).

Summarizing, we are led to the conclusion that the anomalous behaviour of benzoic acid in alkali halide disks has to be ascribed to acid molecules deformed by adsorption on the surface of the alkali halide crystals, in accordance with the adsorption hypothesis of FARMER. The critical factor appears to be the method of mixing of sample and carrier.

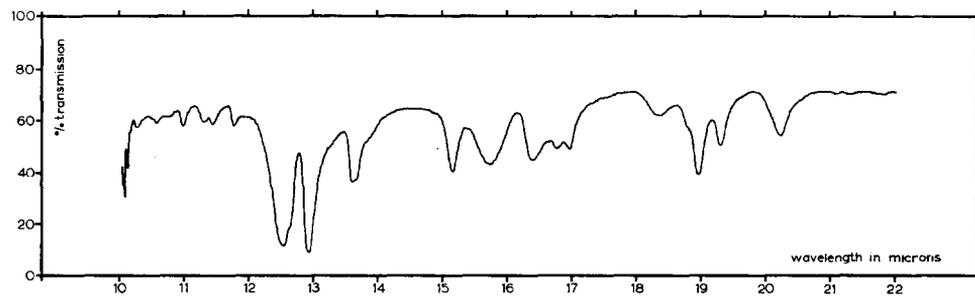
B. Succinic acid and adipic acid

These acids proved to behave in the same way as benzoic acid. The most characteristic peak of the anomalous form in KCl disks is in both cases situated at 8.12μ .^{*} The saturation value of the anomalous form of succinic acid in disks pressed from mixtures of the acid and KCl dry frozen from water solutions proved to be 2.04 mg per g KCl. This corresponds to an effective KCl surface of $41.5 \pm 3 \text{ \AA}^2$ per molecule of adsorbed acid. The saturation value of adipic acid in the anomalous form proved to be 2.01 mg per g KCl. This corresponds to an effective KCl surface of $52 \pm 4 \text{ \AA}^2$ per molecule of the adsorbed acid.

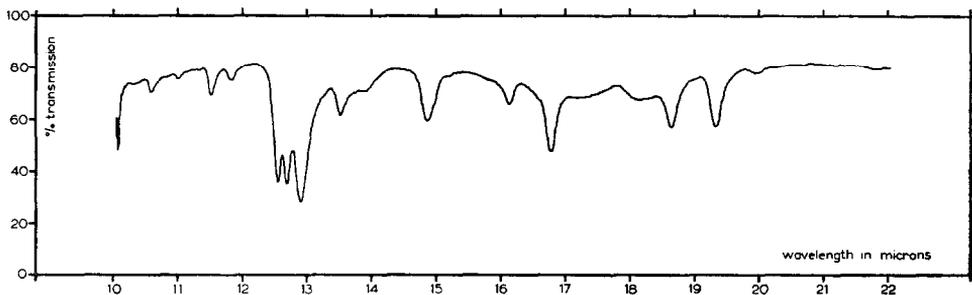
* The wavelengths of these new peaks change a little with the alkali halide used.

C. α -Naphthylacetamide

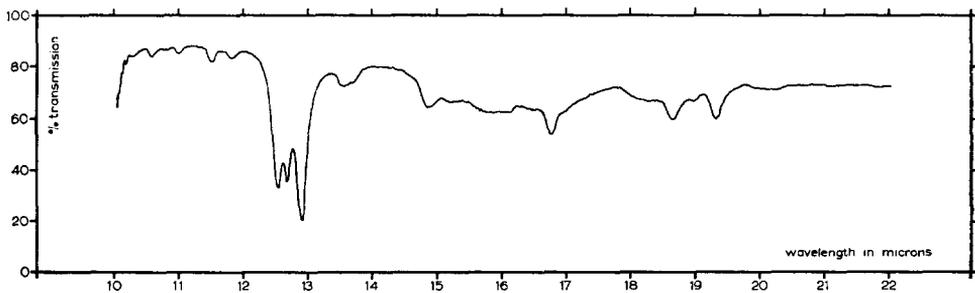
The anomalous behaviour of α -naphthylacetamide can be illustrated with the spectra Fig. 3(a-c) in the wavelength range of 10–22 μ giving greater spectral differences than the normal range of 2–15 μ . Fig. 3(a) is the spectrum of a Nujol mull of the amide between two KBr windows. Fig. 3(b) is the spectrum of a Nujol mull of the amide being recrystallized from acetone. This is the spectrum of the anomalous product. Fig. 3(c), showing a combination of the spectra (a)



(a)



(b)



(c)

Fig. 3

- (a) Spectrum of normal α -naphthylacetamide mull in Nujol.
 (b) Spectrum of anomalous α -naphthylacetamide (obtained by recrystallization from acetone) mull in Nujol.
 (c) Spectrum of a disk pressed from a dry-frozen water solution of 300 mg KCl and 1.2 mg α -naphthylacetamide.

and (b), is the spectrum of a disk pressed from a mixture of 1.20 mg α -naphthylacetamide and 300 mg KCl dry-frozen from a water solution. α -Naphthylacetamide and KCl mixed in the solenoid vibrator and pressed to a disk showed a spectrum of the same kind as spectrum (c).

We could transfer the "anomalous" form of the amide into the normal crystalline form by recrystallization from a saturated solution of the product in water or

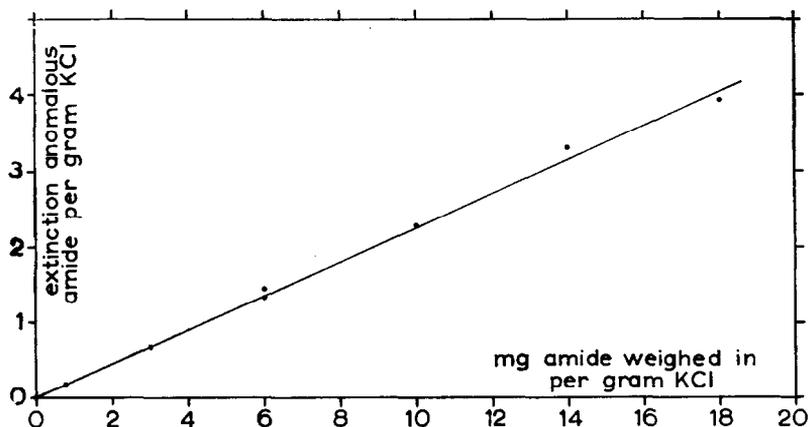


Fig. 4. Extinction of anomalous α -naphthylacetamide as a function of the total amount of α -naphthylacetamide weighed in per g KCl.

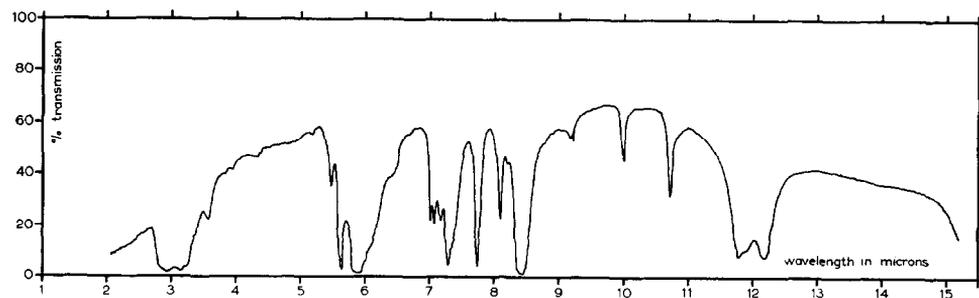
acetone. The presence of seeding crystals of the normal product in the solution proved to be essential here.

Storage of a disk containing the anomalous form did not show any effect, however. α -Naphthylacetamide in the normal form heated in the air for 2 hr at temperatures below 135°C , mullied in Nujol, showed the normal spectrum. The normal product heated above 135°C for 2 hr showed (in Nujol mull) the anomalous spectrum only. Thus α -naphthylacetamide shows enantiotropism phenomena with a transition point at about 135°C . Below this temperature the normal form is the stable product and above this point the anomalous form is the stable one. At room temperature the conversion of the anomalous into the normal form goes very slowly, if at all. In contrast with the acids mentioned above the anomalous form of α -naphthylacetamide can be isolated. This adds evidence in favour of the polymorphism hypothesis of BAKER in this case. To be quite sure disks containing increasing amounts of α -naphthylacetamide relative to the amount of KCl used were examined. If the polymorphism hypothesis is right there is no reason for a saturation value of the anomalous form per g KCl used.

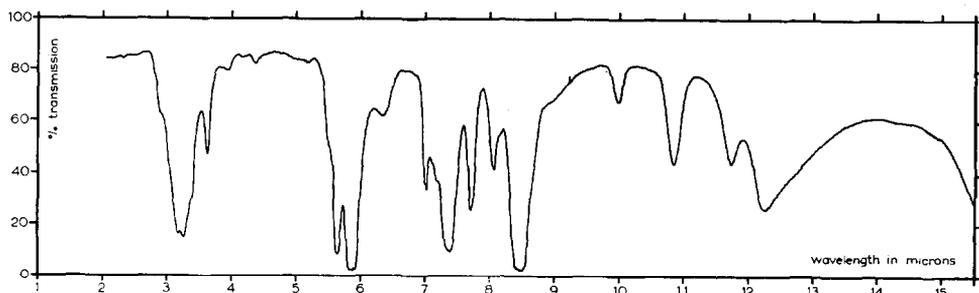
The results of our experiments are summarized in Fig. 4, giving the extinction of the $14.86\ \mu$ peak of the anomalous form as a function of the weighed-in quantities of the amide per g KCl. The horizontal through the transmission maximum at $14.00\ \mu$ in each spectrum was used as a base line.

The dry-freezing method was used again as a mixing technique. Unfortunately we were not able to produce disks with the amide in the anomalous form only and this is the reason why only the extinction of the anomalous form and not its

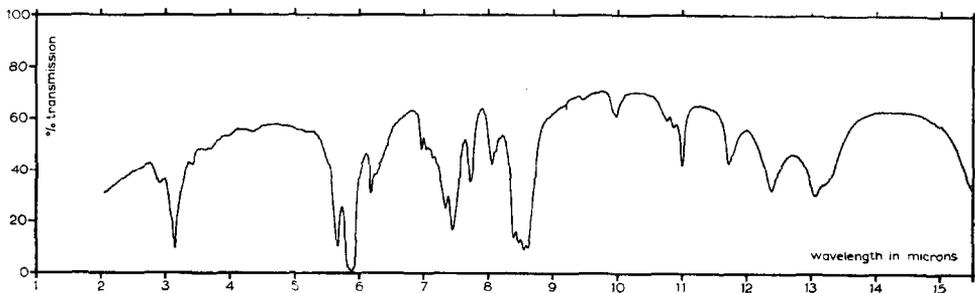
amount has been given. Though the investigated concentration region is rather large, Fig. 4 gives no indication of any saturation value of the anomalous form of α -naphthylacetamide.



(a)



(b)



(c)

Fig. 5.

- (a) Spectrum of a disk with 500 mg KCl and 1.00 mg normal succinimide.
 (b) Spectrum of a disk pressed from a dry-frozen water solution of 500 mg KCl and 1.00 mg succinimide.
 (c) Spectrum of a disk pressed from a dry-frozen water solution of 421 mg KI and 1.06 mg succinimide.

From these results we may conclude that the anomalous behaviour of α -naphthylacetamide has to be ascribed to polymorphism phenomena, in accordance with BAKER's hypothesis. Here again the critical factor appears to be the way of mixing of sample and carrier.

D. Succinimide

The anomalous behaviour of succinimide can be illustrated with the spectra Fig. 5(a-c). Fig. 5(a) represents the spectrum of a disk with 1.00 mg of normal succinimide in 500 mg KCl. Fig. 5(b) shows the spectrum of a disk prepared from a dry-frozen water solution of 1.00 mg succinimide and 500 mg KCl. The disk used for spectrum (b) gave the spectrum (a) after storage in a moist atmosphere. Fig. 5(c) is the spectrum of a disk prepared from a dry-frozen water solution of 1.06 mg succinimide and 421 mg KI.* Storage of this disk did not show any effect.

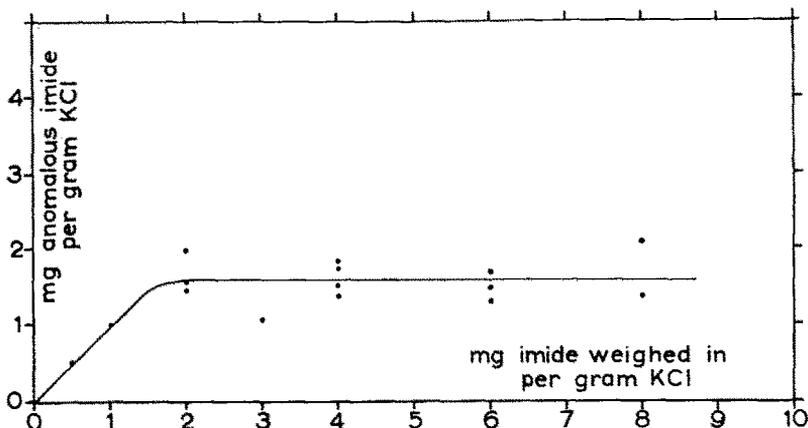


Fig. 6. Amount of anomalous succinimide as a function of the total amount of succinimide weighed in per g KCl.

According to BAKER the three different spectra mentioned here should be ascribed to three different polymorphic modifications of succinimide.

We studied first the behaviour of succinimide in KCl disks (the behaviour in KBr is nearly the same). Disks were prepared again with increasing amounts of the sample relative to the amount of KCl used. Sample and carrier were mixed by dry freezing from a water solution. The results of these experiments are shown in Fig. 6 where the amount of the anomalous product is given as a function of the weighed-in quantity of succinimide per g KCl. Here the anomalous absorption peak at 10.85μ is used with the horizontal through the transmission maximum at 10.25μ in each spectrum as a base line.

The reproducibility of the experiments is not very satisfactory; yet here is a strong indication that the amount of anomalous product is limited to 1 or 2 mg per g KCl. Contrary to BAKER we therefore are inclined to ascribe the anomalous spectrum of succinimide in KCl to an adsorbed form.

The behaviour of succinimide in KI proved to be quite different from the behaviour in KCl and KBr (and CsI). The conversion into this new form was always complete, both with the vibration method used as a mixing method and the dry-freezing method, if the molecular ratio KI/succinimide was $\frac{1}{2}$ or more. We could not change the spectrum in a KI disk in any way. Here also the pressing factor proved to be of minor importance: mixtures of succinimide and KI mullied in

* The peaks at 11.00 , 13.05 and 13.25μ are absent in the spectrum published by BAKER.

Nujol also gave the anomalous spectrum only. Supposing that this anomalous spectrum was the spectrum of an addition product of succinimide with KI we determined the amount of the anomalous product with increasing KI/succinimide ratio. KBr was used as a carrier for those mixtures. The procedure was as follows:

Various amounts of succinimide and KI were mixed very thoroughly in the solenoid vibrator. Weighed-in amounts of these mixtures were mixed with about

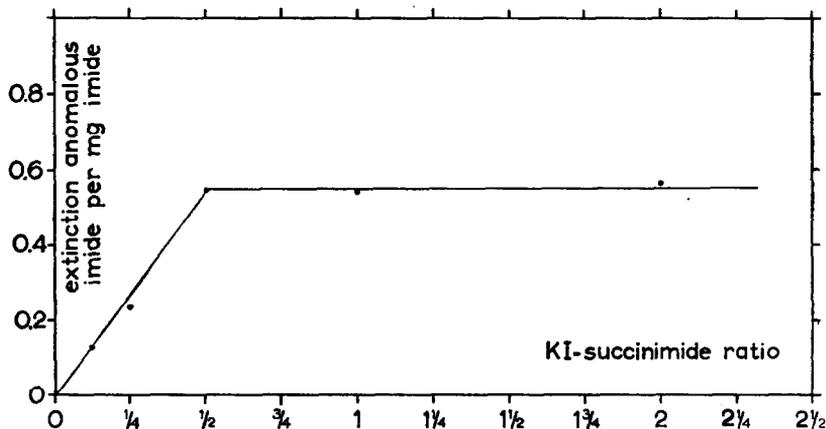


Fig. 7. Extinction of the anomalous band at 11.00μ in dependence of the KI-succinimide ratio.

400 mg KBr in the vibrator and pressed into disks. These disks showed the anomalous spectrum. The extinctions were determined for the 11.00μ peak of the anomalous product using the horizontal through the transmission maximum at 11.40μ as a base line.

The results of these experiments are summarized in Fig. 7 giving the extinction of the anomalous product per mg imide as a function of the KI/succinimide mole ratio. The curve in Fig. 7 shows a sharp break at the mole ratio of $\frac{1}{2}$. This suggests the presence of an addition product with the formula $(C_4H_5O_2N)_{2n} \cdot (KI)_n$. The melting point of this product proved to be $138^\circ C$ (m.p. succinimide is $126^\circ C$). The melt contained succinimide only; KI was present as a solid. As far as we are aware the addition product described here is not mentioned in literature. The addition product already known $(C_4H_5O_2N)_4 \cdot KI \cdot I_2$ proved to give a quite different spectrum.

Summarizing we conclude that adsorption processes play an important role in the anomalous behaviour of succinimide dispersed in KCl (KBr) disks, whereas the anomalous behaviour in KI disks has to be ascribed to the formation of an addition product contrary to the conception of BAKER.

The ageing process

Studying the anomalous behaviour of benzoic acid in alkali halide disks we observed that the acid was converted completely into the normal form after storage of the disks in a moist atmosphere during a few days. A further study of the phenomena gave the following results:

(a) The deciding factor for the ageing process is the relative humidity of the surrounding atmosphere. The conversion of anomalous benzoic acid in KCl disks is complete after three days at room temperature in atmospheres with a relative humidity of 30 per cent or more. In atmospheres with a relative humidity of 15 per cent or less the acid is not converted at all. With KBr used as a carrier the conversion occurs at still lower relative humidities: anomalous benzoic acid in KBr disks stored in an atmosphere of 15 per cent relative humidity during 3 days is converted for the greater part into the normal form. For these conversions the temperature of the surrounding atmosphere proves to be of minor importance.

(b) During the ageing process water from the surrounding atmosphere enters into the disk: the absorption band of water at 2.94μ is intensified during the ageing process (and decreases again afterwards); the take-up of water is about 0.1 mg in a disk of 200 mg.

(c) The water taken up diffuses through the whole disk: KCl disks of the anomalous acid stored in a D_2O atmosphere of 47 per cent relative humidity at room temperature showed after 3 days the spectrum of the normal C_6H_5COOD -dimer only. In a D_2O atmosphere of 15 per cent relative humidity, there had not taken place any change at all.

(d) The alkali halide recrystallizes during the ageing process: in an X-ray diffraction diagram of a KCl disk with benzoic acid in the anomalous form the KCl lines are diffuse and a little shifted whereas the KCl lines in the same disk after the ageing process are sharp and at the right places.*

From these results we may draw the conclusion that the ageing process is primarily caused by the recrystallization of the alkali halide in the disks into (larger) crystalline particles. During the recrystallization the adsorption capacity for benzoic acid, etc., of the alkali halide diminishes to (nearly) zero. Succinic acid, adipic acid and succinimide in KCl and KBr disks behave in the same way as benzoic acid. α -Naphthylacetamide in KCl and KBr disks and succinimide in KI disks behave quite differently; the recrystallization of the alkali halide during the ageing process obviously does not have any effect on the modification of these samples.

Discussion and conclusions

Reviewing the experimental evidence available so far, it must be concluded that one should be very careful in the interpretation of the infra-red spectra of solids, dispersed in alkali halide disks. A good many circumstances may give rise to anomalous spectra—in particular, polymorphism of the investigated substances and interaction between these substances and the alkali halides, varying from adsorption† to real chemical compound formation.

There is no reason, however, to reject the alkali halide disk technique as being

* These X-ray measurements were performed by Prof. Dr. A. F. PEERDEMAN and J. B. HULSCHER of the Laboratory for Crystal Chemistry in Utrecht.

† According to BUUR JENSEN [10, 11] the adsorption hypothesis is wrong; the anomalies should be caused by the sample present in supersaturated solutions in the physically bound water in the disk due to the high pressure applied during the manufacture of the disk. According to us the hypothesis of BUUR JENSEN is not applicable in the cases mentioned above.

[10] J. BUUR JENSEN, *Dansk Tidsskr. Farm.* **32**, 205 (1958).

[11] J. BUUR JENSEN, *Dansk Tidsskr. Farm.* **33**, 33 (1959).

unreliable on the grounds of the phenomena described above. In quite a number of cases none of the complications pointed out above will occur; in other cases it is possible to eliminate them, for instance: anomalies caused by adsorption of a number of organic substances on finely divided alkali halides can be depressed by exposing the disks to a moist atmosphere.

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