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Short Communication

Study of salt hydrates by gas–solid chromatography

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ABSTRACT

    Gas–solid chromatographic experiments were conducted with salt hydrate systems [particularly those of copper(II) sulphate] in order to study the chromatographic consequences of phase transition in the solid. The results reflect the equilibrium phase diagrams of the hydrates involved, but can be strongly affected by non-attainment of equilibrium under the chromatographic conditions. It is suggested that chromatographic methods could be of value in the determination of phase diagrams, and as an alternative to thermogravimetric analysis.

INTRODUCTION

    Hitherto, experiments in gas–solid chromatography have been virtually limited to systems in which no phase change occurs in the solid: indeed, for the most part such studies have been concerned only with adsorption at solid surfaces. However, it is possible to pack a chromatographic column with a solid which undergoes a complete compositional and thus a phase change throughout its bulk. If equilibrium is then achieved within the chromatographic time scale, two kinds of useful and informative experiments may be performed. In the first, which provides an alternative to thermogravimetric analysis (TGA), the temperature of the column is raised continuously and the evolved gases are monitored by a chromatographic detector: we shall call this method thermal evolved-gas analysis (TEGA). Similar experiments with copper(II) sulphate hydrates were mentioned by Wendlandt [1], although he seems to have made no attempt to measure the exact amounts of water vapour evolved and to have assumed that the dehydration took place simply from 5 to 3 to 1 to 0 H_2O. In the second, carried out isothermally, it should be possible (again under equilibrium conditions) for the chromatogram simply to reflect and thus determine the phase diagram. Each step height would then give an equilibrium pressure and the dehydration step areas would measure the compositional changes. In order to investigate these techniques, we have made a particular study of hydrated copper(II) sulphate. Fig. 1 shows the isothermal chromatogram expected, and its relation to the phase diagram.
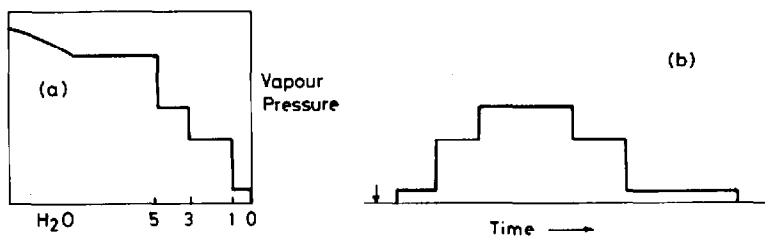
Fig. 1. (a) Phase diagram and (b) the chromatogram expected following an injection of the appropriate amount of water on to a column of anhydrous $CuSO_4$ with dry carrier gas under conditions which are both isothermal and at equilibrium. In the chromatogram, the water vapour pressure rises to the 0:1 phase diagram value after the dead time of the column. Any water vapour pressure larger than this value will be reduced in order to produce hydrated $CuSO_4$. The second chromatographic step starts when all the anhydrous $CuSO_4$ has disappeared, and corresponds to the 1:3 phase diagram value; it continues until all the $CuSO_4 \cdot H_2O$ has disappeared. The highest chromatographic step in (b) corresponds to the 3:5 equilibrium value. Thereafter the column dehydrates under continued flow of dry carrier gas.

In practice, the results obtained show up the effects of non-attainment of equilibria under the conditions of the chromatographic experiments.

EXPERIMENTAL

The chromatographic work was carried out with a Pye Model 104 gas chromatograph (Pye Unicam, Cambridge, UK), but using a thermal conductivity detector (Gow-Mac, Madison, NJ, USA) with matched tungsten filaments to measure the water released. It was necessary to calibrate this detector carefully with known water vapour concentrations, and to house it separately from the column. Oxygen-free nitrogen was used as the carrier gas. The temperature measurements refer generally to those of the oven rather than the sample in the chromatographic column. There is, of course, some lag in the temperature of the sample behind that of the oven. To determine this a second thermocouple was placed inside the column and compared with the thermocouple in the oven. The differences in temperature are illustrated in Fig. 2,
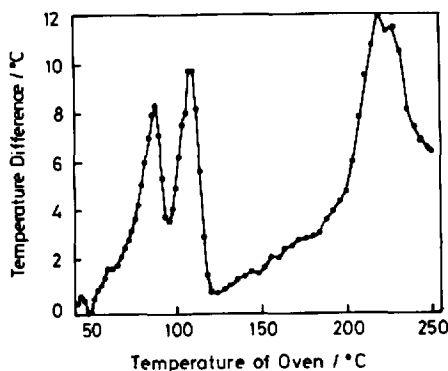

Fig. 2. Differences in temperature between column and oven during the temperature-programmed dehydration of $CuSO_4 \cdot 5H_2O$.

which thus corresponds to a differential thermal analysis (DTA), the three peaks arising from the three dehydration steps. Normal TGA and DTA experiments were made with a Stanton Redcroft (London, UK) simultaneous thermal analyser.

Salts of AnalaR grade were obtained from BDH (Poole, UK).

RESULTS AND DISCUSSION

In the TEGA studies, the chromatographic column was packed with, *e.g.*, 0.0299 g of $CuSO_4 \cdot 5H_2O$ (AnalaR grade). This was held in place by two plugs of silanized glass-wool. The oven was heated at 1°C/min from 30 to 105°C and then at 5°C/min to 270°C. A typical result is shown in Fig. 3. If the heating rate is increased to 2°C/min the first two peaks for $CuSO_4$ are incompletely resolved. Fig. 4 gives the related TGA and DTA curves.

In the TGA experiments, the weight losses were found to be in the ratios 2.02:1.97:1.01, corresponding closely to the 5 to 3, 3 to 1 and 1 to 0 dehydration steps expected. However, in the TEGA experiments, the water vapour released in the three stages corresponded to ratios of 2.27:1.68:1.06, as is shown in Table I. It is of interest that ratios of 2.5:1.5:1.0 and 2.12:1.84:1.00 have been reported by Mu and Perlmutter [2] and by Reisman and Karlak [3], respectively, for analyses conducted in connection with DTA studies.

We believe that the TEGA results are caused by a first-stage dehydration (under the dry carrier gas), which goes beyond the $CuSO_4 \cdot 3H_2O$ expected, to give a "trihydrate" phase in which some of the $CuSO_4$ has been dehydrated to the monohydrate, and on the surface to the anhydrous material which then blocks any further dehydration until a higher temperature is reached. The particular slowness of the trihydrate decompostion has been commented upon by Langfelderova *et al.* [4] in kinetic studies of the dehydration process. The difference between the TEGA and the TGA results can be explained by the rapid removal of water vapour in the former instance. It was found that proper equilibrium could be established in the chromatography system in one of two ways. In the first, the gas flow is stopped for a period of time. In the second, the temperature is first raised and then lowered back to the original temperature.
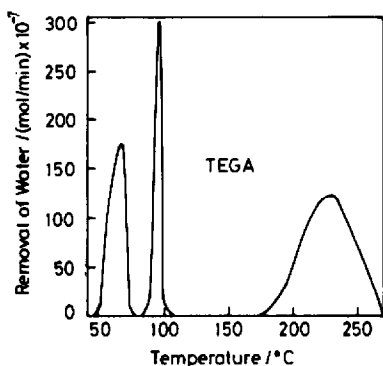

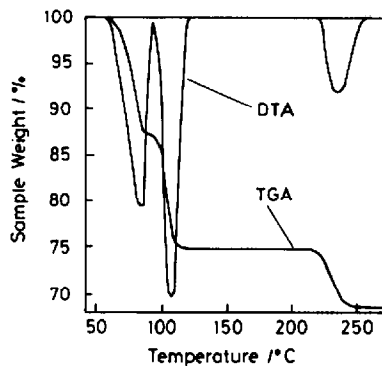Fig. 3. TEGA study of the dehydration of $CuSO_4 \cdot 5H_2O$.

Fig. 4. TGA and DTA curves for the dehydration of $CuSO_4 \cdot 5H_2O$.

TABLE I

WATER LOSS IN SUCCESSIVE STEPS IN TEGA OF $CuSO_4 \cdot 5H_2O$

	Dehydration step		
	1	2	3
Ratio of areas	2.26	1.63	1.11
	2.25	1.72	1.03
	2.27	1.72	1.04
	2.28	1.66	1.07
Average ratio	2.27	1.68	1.06

For $BeSO_4 \cdot 4H_2O$, three dehydration steps were found in TEGA, corresponding to weight ratios of water of 2.0:0.9:1.1. TGA indicates that 2 mol of water are removed at 100°C and a further 2 mol between 150 and 300°C. Some evidence for the latter involving two separate losses of 1 mol of water is provided by DTA. All three techniques give one peak for $LiSO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$. A double-humped trace for $CaSO_4 \cdot 2H_2O$ is more clearly shown by DTA than by TEGA.

Fig. 5 is an example of the behaviour found when dry nitrogen is passed isothermally (60°C) through a column of $CuSO_4 \cdot 5H_2O$ (in this instance 3.939 g). The regions of pentahydrate, "trihydrate", monohydrate and anhydrous $CuSO_4$ can be clearly distinguished by their colours, namely dark blue, pale blue, very pale blue and white. These changes are also shown in Fig. 5. After *ca.* 14 h, dehydration to the "trihydrate" appears to be complete, but instead of dropping to a value corresponding to the 3:1 equilibrium pressure, the water vapour pressure now leaving the column falls to zero. This is in agreement with our earlier postulate of surface blocking by dehydration to some anhydrous $CuSO_4$. In the particular experiment illustrated in Fig. 5, nucleation of the 3 to 1 dehydration then started accidentally at about a quarter of
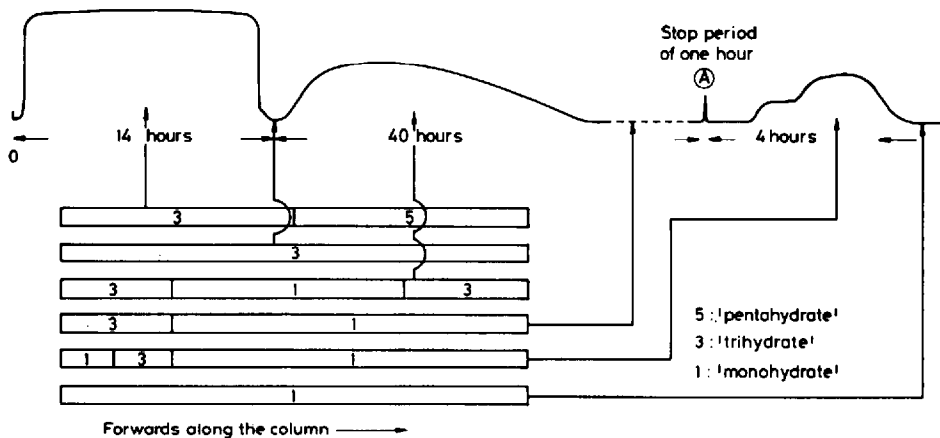

Fig. 5. "Isothermal" chromatographic dehydration of $CuSO_4 \cdot 5H_2O$. For details, see text.

the way along the column, and further water then left the column over a period of *ca.* 40 h, corresponding to the dehydration of the last three quarters of the column to "monohydrate" (*i.e.*, presumably also blocked with a surface layer of anhydrous material). At the point marked A in Fig. 5 the gas flow was stopped for a period of 1 h, so enabling equilibrium to be re-established. After this the remaining water could be removed as shown, the first step corresponding to the 1 to 0 dehydration vapour pressure at the column outlet. It was also found that the dehydration of the "trihydrate" could be restarted by using moist carrier gas with a water vapour content lower than the 3 to 1 dehydration equilibrium pressure.

CONCLUSIONS

We believe that the methods developed in this work have much wider application. Dehydration was chosen as the behaviour of salt hydrates is already well known, but from a chromatographic point of view water is particularly difficult because of the detector problems which it causes. As our experience with $CuSO_4$ shows, care must always be taken to allow for the possibility of non-equilibrium processes occurring in the special circumstances of the chromatographic experiment.

REFERENCES

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3 A. Reisman and J. J. Karlak, *J. Am. Chem. Soc.*, 80 (1958) 6500.
4 H. Langfelderova, M. Linkesova and E. Jona, *J. Thermal. Anal.*, 19 (1980) 117.