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PARTIAL PHASE DIAGRAMS FOR THE WATER–CADMIUM NITRATE, WATER–SILVER NITRATE AND WATER–CADMIUM NITRATE–SILVER NITRATE SYSTEMS

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ABSTRACT

Sub-ambient differential scanning calorimetry has been used to determine partial binary phase diagrams for the water–silver nitrate and water–cadmium nitrate systems. Both systems are shown to be eutectic with eutectic temperatures of 263 ± 0.5 K and 256.5 ± 0.5 K for the water–silver nitrate and water–cadmium nitrate systems, respectively. The eutectic compositions are at approximately 40.5 wt.% nitrate for each system. The freezing of ternary solutions containing a fixed silver nitrate/cadmium nitrate ratio but increasing concentrations of total nitrates are explained in terms of a partial ternary system containing two binary eutectic systems and a ternary eutectic reaction. The ternary eutectic temperature is shown to be 254 ± 0.5 K.

INTRODUCTION

The freeze-drying of various inorganic salt–water solutions has been used over recent years in the field of metallurgy and materials science for the production of a wide range of materials[1]. Aqueous solutions of iron sulphate have been processed for the preparation of small particles of Fe_2O_3 in the size range 200–1000 Å[2]. Mixed solutions of copper and thorium sulphates have been used for the manufacture of Cu–ThO_2 composite powder[3] for the production of dispersion-strengthened copper and solutions based on ammonium paratungstate have been treated for subsequent conversion to metallic tungsten[4–6] or tungsten alloys by conventional processing routes.

The basic principles of the freeze-drying of any solution are similar to those of conventional vacuum distillation with the essential difference that the solution is

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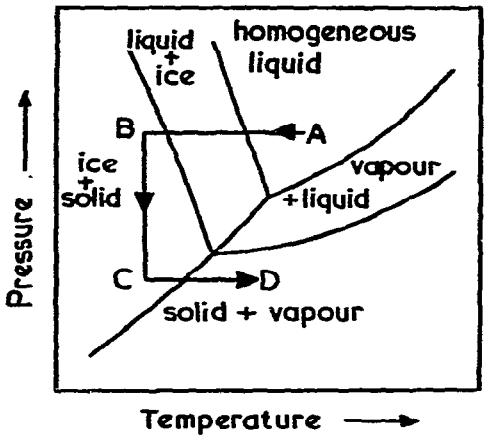

Fig. 1. Schematic pressure/temperature diagram showing stages in the operation of the freeze-drying process.

first frozen before being subjected to a low absolute pressure. The operation of the process may be explained with reference to Fig. 1. Once the solution is frozen (point A to point B) the pressure in the system can be lowered (point B to point C) such that the temperature may be increased (point C to point D) to sublime the water from the frozen solid without causing melting (i.e. the quadruple point on the pressure–temperature phase diagram for the solution has been by-passed). It is apparent that it is vital to know the temperatures required to produce the solid phases in the initial stage of the process in order to operate the freeze-drying technique successfully. One application of the technique that has recently been investigated by the present authors is the production of cadmium oxide–silver electrical contact material from freeze-dried cadmium nitrate and silver nitrate. Consequently, the partial binary phase diagrams, cadmium nitrate–water and silver nitrate–water, and the ternary diagram at the ratio silver nitrate–12.8 wt.% cadmium nitrate–water, for various total nitrate concentrations of 10, 33 and 49 wt.% have been determined using differential scanning calorimetry. The fixed ratio of cadmium nitrate to silver nitrate was selected as this would produce a cadmium oxide–silver composite of commercial proportions. The range of total nitrate contents was investigated to allow the effects of overall concentration on the morphologies of the freeze-dried products to be studied. The partial binary diagrams were determined from dilute concentrations up to approximately 50 wt.% nitrate in water.

EXPERIMENTAL PROCEDURE

"Analar" analytical grade silver nitrate and cadmium nitrate tetrahydrate of purity 99.9% were used as the nitrates for the preparation of the binary and ternary solutions studied.

A Du Pont 990 thermal analyser, which possessed a sub-ambient differential scanning calorimeter facility, was used for the phase diagram determinations. Various

solutions of differing compositions were studied. Cadmium nitrate at weight percentages of 1.0, 2.5, 5.0, 7.0, 9.0, 17.0, 25.0, 29.0, 32.5, 36.0, 39.0, 40.0, 41.0, 42.0, 42.5, 44.5, 50.0 and 52.5 was investigated, whilst silver nitrate solutions at 1.5, 3.0, 7.5, 8.5, 25.0, 32.0, 33.0, 36.0, 39.0, 40.5 and 44.0 wt.% constituted the part of the binary silver nitrate–water system studied. As outlined in the Introduction ternary solutions of ratio silver nitrate–12.8 wt.% cadmium nitrate were investigated at total nitrate concentrations of 10, 33 and 49 wt.%.

From each solution 10 μl were delivered from an epimer into an empty aluminium specimen pan. The constantan disc which covered the specimen chamber of the DSC head was removed and the aluminium specimen pan placed in position. An empty specimen pan was placed in the reference side of the calorimeter. The constantan disc was replaced and the whole chamber was covered by a special dewar flask into which liquid nitrogen was poured in order to freeze the solution. The estimated rate of cooling was approximately 2–3 K sec^{-1}. The calorimeter was subsequently allowed to scan from 233 K to room temperature 295 K at sensitivities of 2.092 or 8.368 mJ sec^{-1} with a heating rate of 2 K min^{-1}.

RESULTS AND DISCUSSION

Cadmium nitrate–water

The DSC traces for the heating of the solid aqueous solutions containing less than or equal to 40 wt.% cadmium nitrate between 233 and 295 K showed essentially two peaks. The solutions containing between 40 and 50 wt.% gave rise to one peak only on the DSC traces. However, the solution containing 52.5 wt.% produced two peaks on the DSC trace. Typical curves of four of the solutions are shown in Fig. 2. The temperatures of initiation of the lowest temperature peaks are taken to be the temperatures at which the first liquid phase is formed whilst the peak maximum temperatures of the second peaks are taken to be the temperatures at which a fully liquid solution has been produced. These temperatures are represented graphically as a function of solution concentration in Fig. 3 to yield the partial phase diagram of the cadmium nitrate–water system at a pressure of 1 bar. The line AEB is the liquidus curve of the diagram and shows a depression in freezing point as concentration is increased to the eutectic level of approximately 40.5 wt.%. Point E is the eutectic point at a temperature of 256.5 $\pm$ 0.5 K. Line EB represents the increasing freezing point of the hypereutectic solutions. It is apparent that the first peak on the DSC traces for solutions containing up to 40 wt.% cadmium nitrate corresponded to fusion of the eutectic mixture. The second peak on the traces of these solutions was the fusion of the last primary ice crystals of the frozen material. The single peak obtained for the 40 wt.% solution shows this composition to be close to the eutectic value. Two peaks were expected for solutions greater than 40 wt.%. These peaks would represent the fusion of the eutectic mixture and the dissolution of the primary cadmium nitrate crystals, respectively. However, for compositions in the region of the eutectic value, broad single peaks were obtained. Two separate peaks were only

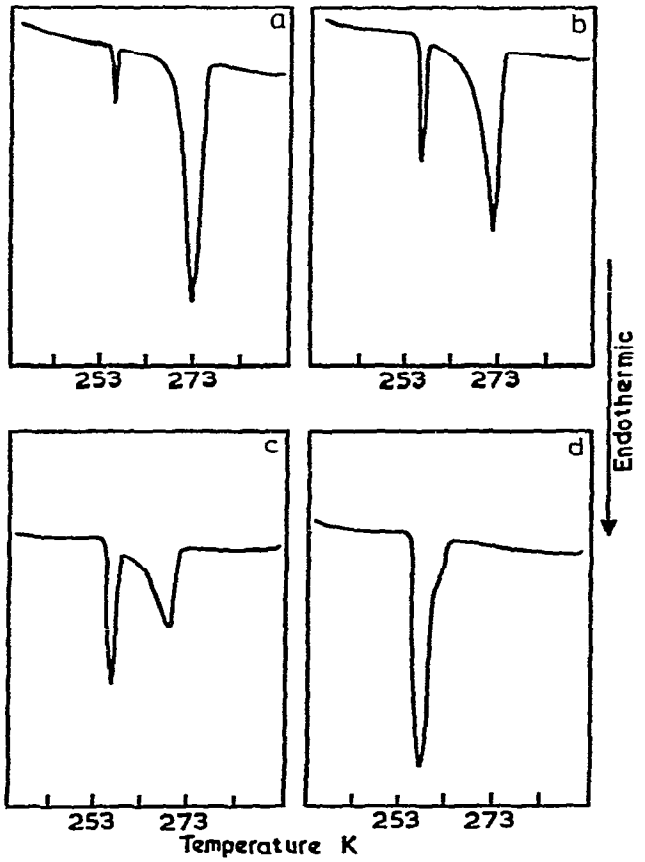

Fig. 2. Representative DSC curves for cadmium nitrate–water solutions. (a) 2.5 wt.% cadmium nitrate; (b) 7.0 wt.% cadmium nitrate; (c) 25 wt.% cadmium nitrate; (d) 41 wt.% cadmium nitrate.

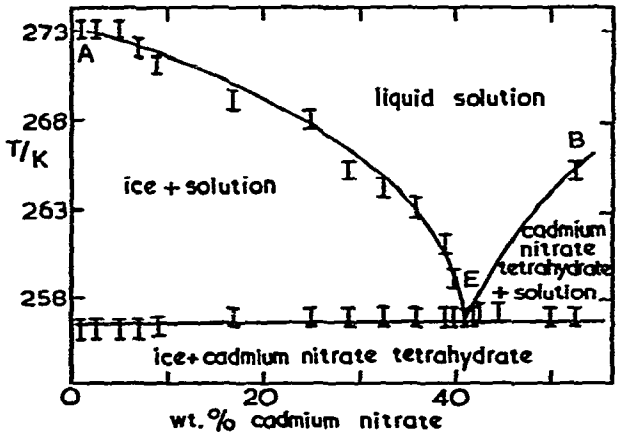

Fig. 3. Partial phase diagram for binary water–cadmium nitrate system.

determined at 52.5 wt.% cadmium nitrate. The broad peaks indicate the departures from true thermal equilibrium that occurred in the cooling of the hypereutectic solutions and demonstrate the difficulties associated with the nucleation and growth of the primary cadmium nitrate crystals on cooling the solutions in the DSC. No

evidence was detected for the existence of a region of solid solubility in the partial phase diagram in the composition range studied. Hence, the diagram may be considered as a simple eutectic system with a eutectic temperature of 256.5 ± 0.5 K and a eutectic composition of approximately 40.5 wt.% cadmium nitrate. Any solid

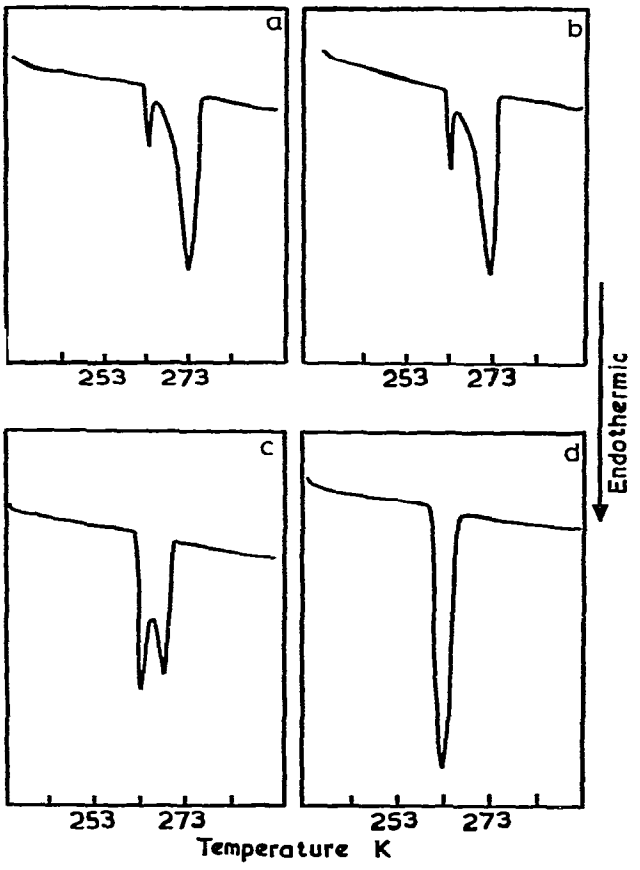

Fig. 4. Representative DSC curves for silver nitrate–water solutions. (a) 1.5 wt.% silver nitrate; (b) 3.0 wt.% silver nitrate; (c) 25 wt.% silver nitrate; (d) 44 wt.% silver nitrate.

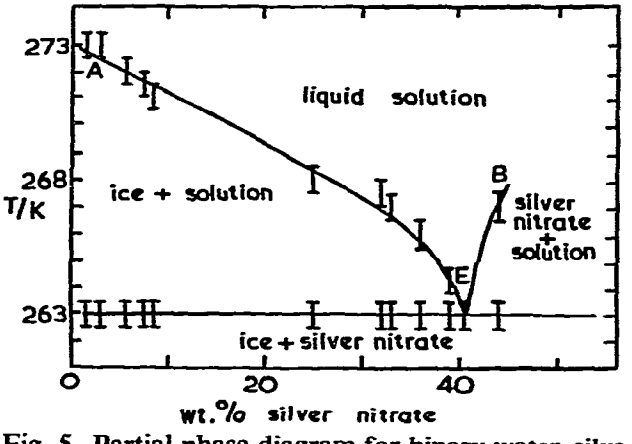

Fig. 5. Partial phase diagram for binary water–silver nitrate system.

solubility in this part of the diagram must occur at compositions of less than 1 wt.% cadmium nitrate in water.

Silver nitrate–water

The DSC traces for solutions containing less than or equal to 39 wt.% silver nitrate showed two peaks, whilst those for higher concentrations showed only one peak of varying degrees of broadness. Representative curves of four solutions are shown in Fig. 4. Treatment of the experimental data in the manner used for the cadmium nitrate–water solutions yields the partial phase diagram for the water–silver nitrate system at 1 bar pressure given in Fig. 5. The first peak on the DSC curves for hypoeutectic compositions corresponded to fusion of the eutectic mixture whilst the second peak was caused by the fusion of the last primary ice crystals (i.e. the liquidus curve of the diagram). Consequently, in Fig. 5, line AEB represents the liquidus of the system and shows a decrease in the freezing point of the solutions as the silver nitrate concentration is increased up to the eutectic composition of approximately 40.5 wt.%. The eutectic temperature of the partial system is 263 ± 0.5 K. The

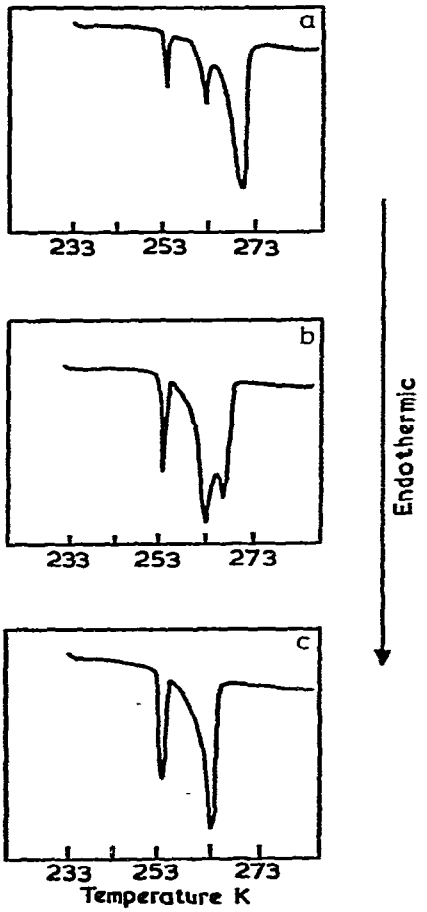

Fig. 6. Representative DSC curves for silver nitrate–cadmium nitrate–water solutions at varying total nitrate concentrations. (a) 10 wt.% total nitrates; (b) 33 wt.% total nitrates; (c) 49 wt.% total nitrates.

approximate form of the hypereutectic liquidus shown in Fig. 5 was obtained by taking the temperature of the initiation of the broad peak determined for the 44 wt.% solution as the eutectic temperature (263 K) and the temperature of the maximum of the peak (267 K) as the hypereutectic liquidus temperature. It is apparent that, as for the binary cadmium nitrate–water solutions, the nucleation and growth of primary nitrate crystals during the cooling of marginally hypereutectic compositions in the water–silver nitrate system is kinetically fairly slow and this is reflected in the broad peak, as opposed to the predicted two peaks, on the DSC trace for the 44 wt.% solution. No experimental evidence was obtained for the existence of a region of solid solubility in the range of solutions investigated. Hence, the partial phase diagram may be considered as a simple eutectic system. Any region of solid solubility of silver nitrate in water must be at compositions less than the 1.5 wt.% silver nitrate which was taken as the minimum concentration of possible commercial importance for the freeze-drying process.

Silver nitrate–cadmium nitrate–water

The DSC curves obtained for the three ternary solutions of interest in the preparation of the cadmium oxide–silver contact material are given in Fig. 6. The 10 wt.% total nitrate solution can be seen to show three peaks at temperatures of 254, 262 and 270 K, whilst that containing 33 wt.% total nitrate showed a single peak at 254 K and a broad doublet peak with maxima at 263 and 266 K. The solution containing 49 wt.% total nitrates produced a DSC trace containing only two peaks at 254 and 263 K.

The experimental observations for the three solutions may be explained with

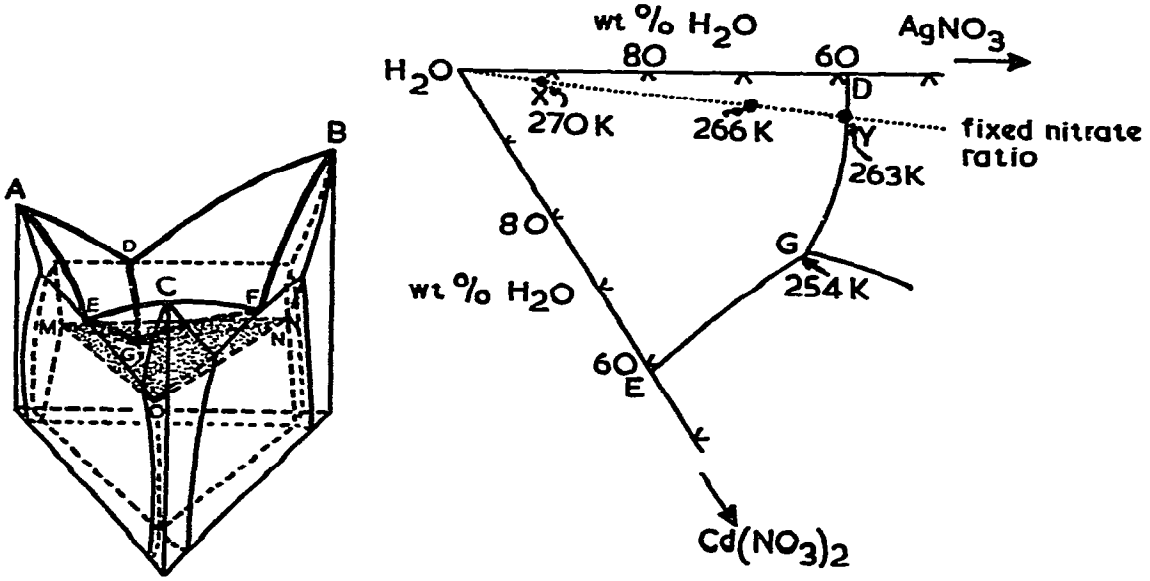

Fig. 7. Space model of system showing a ternary eutectic reaction (after West[7]).

Fig. 8. Projected liquidus view of ice–silver nitrate–cadmium nitrate partial ternary eutectic system.

reference to Figs. 7 and 8. Figure 7 (after West[7]) shows a space model of a system that contains a ternary eutectic reaction and is based on three binary systems that each contain a simple eutectic reaction and a small amount of solid solubility. Consequently, any of the materials A, B or C on this diagram could represent the water corner of the water–silver nitrate–cadmium nitrate system. This is so because in the preceding sections it has been shown that the water-rich portions of each of the binary nitrate–water systems are simple eutectics, although it may be that a more complicated system exists at hypereutectic compositions in the cadmium nitrate system because of the known existence of at least two hydrated forms of cadmium nitrate, ($Cd(NO_3)_2 \cdot 2H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$). If corner A of Fig. 7 is considered to be the water corner of the ternary nitrate system of interest, it is clear that on cooling solutions containing various total nitrate contents of fixed ratio of 87.2 wt.% silver nitrate and 12.8 wt.% cadmium nitrate, a ternary liquidus surface and a ternary eutectic plane have to be traversed. The liquidus surface extends from the pure water/ice point down towards the ternary eutectic plane and is bounded on its sides by the liquidus lines for the binary systems (AD and AE) and by the binary eutectic valleys (DG and EG) that lead from the binary eutectic points to the ternary eutectic point (G). The ternary eutectic plane is given in Fig. 7 by the shaded area MNO. Beneath this plane there lies the three-phase region, which in the present system consists of ice, silver nitrate and cadmium nitrate. The projected view of the partial system based on the water corner is shown in Fig. 8. The solidification of the solution containing 10 wt.% total nitrates may be considered in relation to this diagram. This solution is designated point X on the diagram. The solution is far outside any possible region of solid solution in the system (as indicated by the studies of the binary solutions). Consequently, the solution may be considered to lie in the three-phase region of the diagram. As the solution (X) is cooled ice is produced (with a negligible silver nitrate content) on reaching the temperature corresponding to the liquidus surface. The solution is then concentrated with respect to the fixed nitrate ratio and so the composition changes according to the line H_2O–X–Y in Fig. 8. Eventually, as the temperature is decreased the concentration is increased to the point Y which lies on the binary eutectic valley that connects the binary eutectic in the water–silver nitrate system to the ternary eutectic point. Once the binary eutectic valley is reached the solidifying liquid produces the binary eutectic mixture ice plus silver nitrate. Consequently, as the temperature is further decreased, the remaining liquid becomes enriched in cadmium nitrate and so the composition of the liquid changes according to the binary eutectic valley as more eutectic ice plus silver nitrate is produced. Eventually the temperature and composition of the ternary eutectic point are reached and the ternary mixture ice, silver nitrate and cadmium nitrate is produced on further cooling.

If the reverse of the cooling process is considered as the heating that occurs in the DSC, then for the 10 wt.% total nitrates solution thermal events may be expected to occur at the ternary eutectic temperature, at the point Y where the binary eutectic valley is left behind and finally at the point where the liquidus surface is

crossed at point X. Consequently, from the DSC trace shown for the 10 wt.% total nitrate solution in Fig. 6 it can be seen that the ternary eutectic temperature is 254 K, the temperature at point Y on the binary eutectic valley is 262 K and the point X on the liquidus surface is at a temperature of 270 K. For the more concentrated solution containing 33 wt.% total nitrate, the ternary eutectic temperature is again found to be 254 K, the binary eutectic valley at point Y is confirmed at a temperature of 263 K, however, the point on the liquidus surface at this concentration is at 266 K, some 4 K lower than that of the 10 wt.% total nitrate solution. The DSC trace obtained for the solution containing 49 wt.% total nitrates indicates that this composition actually lies on, or very close to, the binary eutectic valley. Consequently, only two thermal events are observed at the ternary eutectic point (254 K) and point Y at 263 K on the binary eutectic valley.

CONCLUSIONS

(1) The partial system water–silver nitrate is shown to be eutectic with negligible solid solubility. The eutectic temperature is 263 $\pm$ 0.5 K and the eutectic composition is 40.5 wt.% silver nitrate.

(2) The partial system water–cadmium nitrate is shown to be eutectic with negligible solid solubility. The eutectic temperature is 256.5 $\pm$ 0.5 K at a composition of 40.5 wt.% cadmium nitrate.

(3) The ternary system water–silver nitrate–cadmium nitrate is shown to have a ternary eutectic plane at a temperature of 254 $\pm$ 0.5 K. The freezing of three ternary solutions of fixed silver nitrate–cadmium nitrate ratio is explained in terms of a partial ternary system containing two binary eutectic systems and a ternary eutectic reaction.

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