DETECTION OF THE QUADRUPLE POINT IN THE CuSO$_4$·5H$_2$O AND BaCl$_2$·2H$_2$O SYSTEMS: EFFECT OF EXPERIMENTAL PARAMETERS

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ABSTRACT

The effects of sample mass, particle size, and furnace heating rate were studied for the detection of the quadruple point in the CuSO$_4$·5H$_2$O system using the simultaneous differential thermal analysis–electrical conductivity (DTA–EC) technique. As the sample mass decreased, both the DTA and EC peak amplitudes decreased. Increasing the furnace heating rate caused an increase in the peak splitting for the first DTA peak. In the case of particle size, an optimum size of about 80 mesh was found to give a maximum in the EC curve peak. The simultaneous DTA–EC curves for BaCl$_2$·2H$_2$O are also given.

INTRODUCTION

Borchardt and Daniels[1] first observed the quadruple point in the dehydration of CuSO$_4$·5H$_2$O and BaCl$_2$·2H$_2$O, as well as other metal salt hydrates. A quadruple point is present in these systems when the initial hydrate, the next lower hydrate, water (liquid) and water (gaseous) exist in equilibrium at a fixed pressure and temperature. Detection of the quadruple point has been investigated by numerous thermal techniques, including DTA[1], X-ray[1] and electrical conductivity[2]. Wendlandt[2] found that the electrical conductivity (EC) technique was particularly useful for this purpose and detected the quadruple points in BaBr$_2$·2H$_2$O, cobalt(II) salt hydrates, the [Co(NH$_3$)$_5$H$_2$O]X$_3$ complexes, and other systems. For measurements of the quadruple point at elevated pressures, a high pressure EC apparatus has also been described[3].

The purpose of this investigation is to study the effect of various experimental parameters, such as sample mass, particle size, and furnace heating rate on the detection of the quadruple points in the CuSO$_4$·5H$_2$O and BaCl$_2$·2H$_2$O systems. The apparatus employed permitted concurrent DTA and EC curves to be recorded on each sample.

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EXPERIMENTAL

The $CuSO_4 \cdot 5H_2O$ and $BaCl_2 \cdot 2H_2O$ used in this investigation were Baker Analyzed Reagent grade chemicals. The DTA–EC apparatus has been described previously[4].

RESULTS AND DISCUSSION

The effect of furnace heating rate on the DTA and EC curves of $CuSO_4 \cdot 5H_2O$, in an open crucible-type of sample holder, is illustrated by the curves in Fig. 1. At a heating rate of $5°C/min$, the DTA curve consisted of two distinct peaks and was similar to the curves which have been previously reported by numerous investigators. These two peaks represent the two-step dehydration of $CuSO_4 \cdot 5H_2O$ to $CuSO_4 \cdot H_2O$ by the following reactions:

$$CuSO_4 \cdot 5H_2O \ (s) \ \rightarrow \ CuSO_4 \cdot 3H_2O \ (s) + 2H_2O \ (g)$$

$$CuSO_4 \cdot 3H_2O \ (s) \ \rightarrow \ CuSO_4 \cdot H_2O \ (s) + 2H_2O \ (g)$$

Electrical conductivity measurements obtained simultaneously with the DTA curves showed no response which indicates that the liquid phase was not present in large enough quantities to form a conducting solution. When the heating rate was increased to $40°C/min$, the DTA curve peaks were considerably distorted with pcor resolution

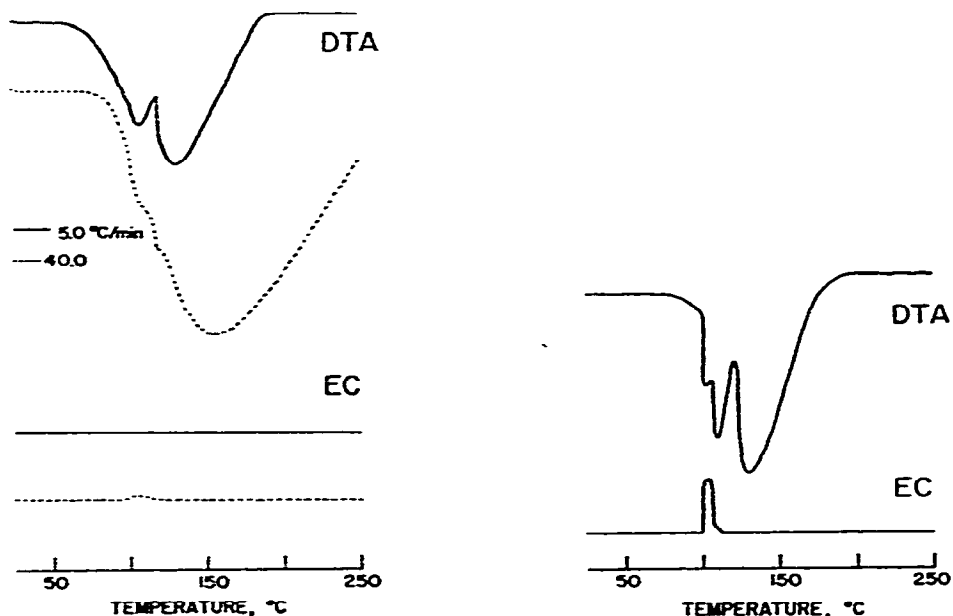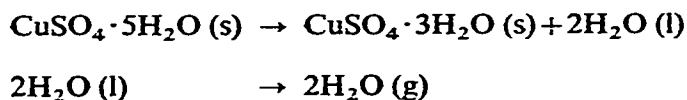
Fig. 1 (left). Effect of heating rate on the DTA and EC curves of $CuSO_4 \cdot 5H_2O$ in an open crucible-type sample holder.

Fig. 2 (right). DTA and EC curves of $CuSO_4 \cdot 5H_2O$ in a covered sample holder.

of the peaks. Electrical conductivity measurements produced a small conductivity peak under high amplification which indicates that the liquid phase was present in larger quantities than at the lower heating rate.

Since the shape of the DTA and EC curves is greatly influenced by the rate of diffusion of water vapor from the sample surface, data were obtained for conditions in which the diffusion was severely restricted. This was achieved by covering the sample crucible with a tight fitting Teflon cover. The DTA and EC curves for $CuSO_4 \cdot 5H_2O$ which were obtained under these conditions are presented in Fig. 2. The DTA curve consists of three endothermic peaks due to the splitting of the first dehydration peak previously observed in the open crucible. An EC curve peak, which coincides with the first DTA peak, was also obtained with the closed crucible. Both of the curve peaks increased to a maximum value in phase with each other with the EC peak beginning to decrease as the second DTA peak began to form. When the second peak, which is narrow rather than the characteristic rounded shape of a dehydration peak, reached a maximum, the EC signal had completely disappeared. These two peaks are explained by the reactions:

$$CuSO_4 \cdot 5H_2O \text{ (s)} \rightarrow CuSO_4 \cdot 3H_2O \text{ (s)} + 2H_2O \text{ (l)}$$

$$2H_2O \text{ (l)} \rightarrow 2H_2O \text{ (g)}$$

The Teflon cover created a self-generated atmosphere within the crucible which led to the formation of a saturated solution and hence, the EC response. Evaporation of the water from the saturated solution produced the narrow endothermic peak in the DTA curve and led to a decrease of the EC peak. The sample conditions produced in the course of this experiment are responsible for the DTA peak temperatures of 102.5, 110 and 130°C, which are slightly higher than peak temperatures previously reported[5].

The curves obtained in Fig. 2 show that restriction of the diffusion of water from the sample, in this case by covering the sample crucible with a Teflon cap, leads to the formation of a quadruple point. Therefore, the degree of restriction of diffusion of water from the sample influences the results obtained in a DTA or EC experiment and may be significant when using capillary tube or long diffusion path sample holders.

The effect of sample mass on the DTA and EC curves of $CuSO_4 \cdot 5H_2O$ in a closed crucible is shown in Fig. 3. As the mass of the sample decreased, the amplitude of both the DTA and EC curves decreased, with the EC curve peak disappearing completely when a sample mass of less than 10 mg was employed. Since the diffusion of water vapor from the crucible was restricted by the Teflon cover, the absence of an EC peak was interpreted as due to the sample being too small to generate enough water vapor to saturate the atmosphere in the holder, which is a prerequisite for the formation of a quadruple point. The small sample size also removed the splitting of the first DTA peak arising from the evolution of liquid water.

Increasing the sample mass increases the amplitude of the DTA and EC curve peaks as well as increases the peak temperature range, with the liquid phase persisting

to higher temperatures. The liquid phase was present into the beginning of the third DTA peak with the 110 mg sample, as indicated by the EC curve. Thus, the 1.5 g samples used by Taylor and Klug[6] and the 0.2 g sample employed by Borchart and Daniels[1] were advantageous to the formation of a liquid phase and hence a quadruple point.
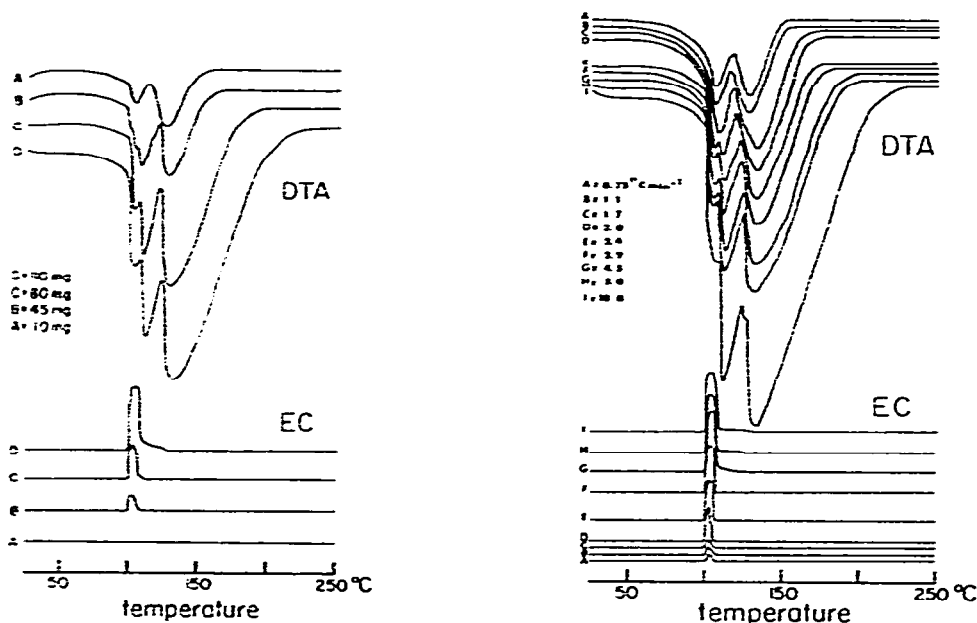

Fig. 3 (left). Effect of sample mass on the DTA and EC curves of 100 mesh size $CuSO_4 \cdot 5H_2O$ in a covered crucible-type sample holder at a heating rate of $5°C/min$.

Fig. 4 (right). Effect of heating rate on the DTA and EC curves of 80 mg samples of 100 mesh size $CuSO_4 \cdot 5H_2O$ in a covered crucible-type sample holder.

The effect of the heating rate on the DTA and EC curves of $CuSO_4 \cdot 5H_2O$ in a closed-type sample crucible is shown in Fig. 4. As the heating rate increased, the magnitude of the splitting of the first dehydration peak increased in the DTA curve. The EC curve peak also increased in amplitude with increasing heating rate which indicates the formation of a more substantial liquid phase within the system. At heating rates of $1.7°C/min$ or less, the liquid phase was present in quantities too small to be detected by DTA although a small EC curve peak was obtained.

The amplitude of the EC peaks, as a function of the heating rate, is shown in Fig. 5. When the heating rate drops below about $4°C/min$, the EC peak decreases sharply. This effect occurs because the sample holder is covered but not sealed so that the water vapor diffuses away from the vicinity of the sample at a finite rate. If the heating rate is not fast enough to produce vapor at a rate greater than the rate of diffusion from the crucible, the formation of a liquid phase is retarded, as indicated by the small EC peak observed.
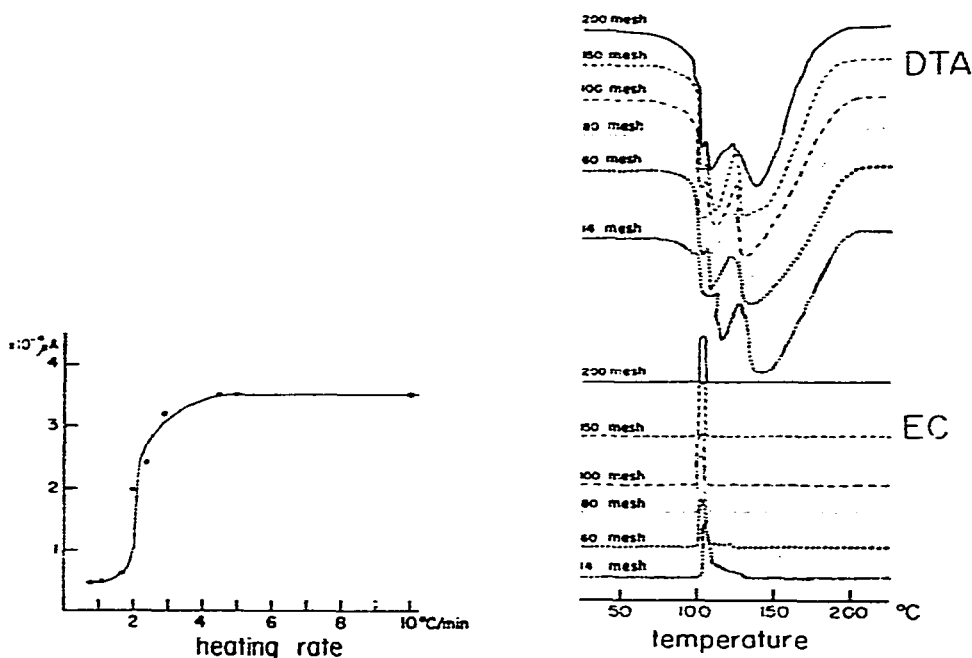
Fig. 5 (left). Effect of heating rate on the EC peak amplitude of 80 mg samples of 100 mesh size $CuSO_4 \cdot 5H_2O$ in a covered crucible-type sample holder.

Fig. 6 (right). Effect of particle size on 80 mg samples of $CuSO_4 \cdot 5H_2O$ in a covered sample holder at a heating rate of 5 °C/min.

The effect of sample particle size on the DTA and EC curves was investigated with the results presented in Fig. 6. All of the DTA curves have the same general shape and the magnitude of the EC response did not change significantly with respect to particle size. However, with large particle sizes, there is some distortion of the DTA and EC peaks which indicates that the process leading to the formation of a liquid phase becomes more complex. With large particle sizes (>14 mesh) the EC curve
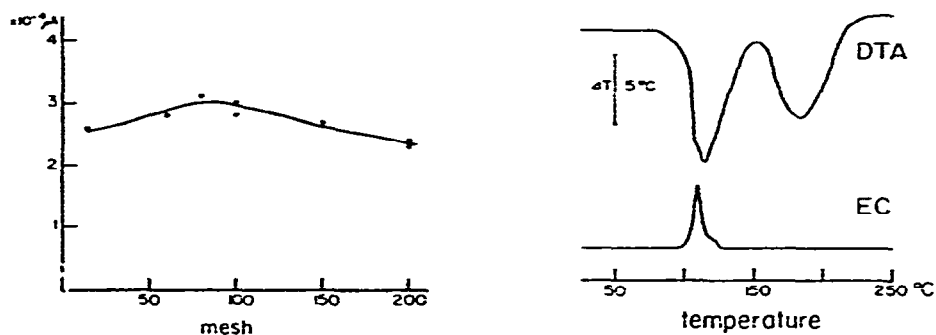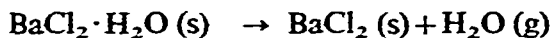

Fig. 7 (left). Effect of particle size on the EC peak amplitude of 80 mg samples of $CuSO_4 \cdot 5H_2O$ in a covered crucible-type sample holder at a heating rate of 5°C/min.

Fig. 8 (right). Simultaneous DTA and EC curves of $BaCl_2 \cdot 2H_2O$.

peaks indicate that a saturated solution exists in high concentration during the interval of the first DTA peak and extends, although in lower concentration, into the region of the second and third peaks. This effect is thought to be due to the formation of a liquid phase on the surfaces of small crystals where the large surface area allows the water to evaporate rapidly at a lower temperature and hence produces a narrow EC peak. A large sample particle size permits the liquid phase to form inside as well as on the surface of the crystals which creates many microscopic inclusions of saturated solution within the crystal. This encased water will evaporate at higher temperatures causing a "tailing" effect, as shown by the EC curve for the 14 mesh particle size.

The EC peak amplitude is shown as a function of particle size in Fig. 7. As the particle size decreases from the optimum value of about 80 mesh, the EC peak decreases due to the physical shrinkage of the sample. This effect was observed visually during the course of the experiment. As the particle size increased from 80 mesh, the EC peak again decreased. This effect is probably due to the formation of the liquid phase inside the crystal, which decreases the conductivity since there is less conducting solution present.

The DTA–EC curves of $BaCl_2 \cdot 2H_2O$ are shown in Fig. 8. The shoulder on the first endothermic peak is due to the formation of a liquid phase in the sample. However, it is not as well defined in this curve as was previously found using a high resolution DTA instrument[7]. Dehydration reactions for $BaCl_2 \cdot 2H_2O$ are:

$$BaCl_2 \cdot 2H_2O \ (s) \ \rightarrow \ BaCl_2 \cdot H_2O \ (s) + H_2O \ (l)$$

$$H_2O \ (l) \qquad \qquad \rightarrow \ H_2O \ (g)$$

$$BaCl_2 \cdot H_2O \ (s) \ \rightarrow \ BaCl_2 \ (s) + H_2O \ (g)$$

As expected, the EC curve peak appears in the same temperature range as the shoulder peak, indicating the formation of a saturated, conducting solution. No EC peak is observed during the second DTA peak.

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