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THE DETECTION OF QUADRUPLE POINTS IN METAL SALT HYDRATE SYSTEMS BY ELECTRICAL CONDUCTIVITY MEASUREMENTS*

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ABSTRACT

The application of electrical conductivity measurements to the detection of liquid water and/or the quadruple point in metal salt hydrate systems is discussed. The apparatus used for the electrical conductivity measurements is described. The application of the technique is discussed for the $CuSO_4 \cdot 5H_2O$, $BaCl_2 \cdot 2H_2O$, and $BaBr_2 \cdot 2H_2O$ systems.

INTRODUCTION

In a rather comprehensive investigation, Borchardt and Daniels[1] studied the dehydration reactions of a number of metal salt hydrates. They found that in the copper sulfate 5-hydrate system, the first endothermic peak was due to the formation of copper sulfate 3-hydrate and liquid water. The second endothermic peak was caused by the vaporization of the liquid water from the saturated solution. These two processes can be represented by the equations:

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

$$H_2O(l) \rightarrow H_2O(g) \quad \text{(from saturated solution)}$$

These results were vastly different from the previous interpretation of the dehydration curve by Taylor and Klug[2] who postulated the existence of the hydrate, $CuSO_4 \cdot 4H_2O$, to explain the presence of the first endothermic peak.

Of interest in this investigation is the detection of the processes leading to the first endothermic peak in various metal salt hydrate systems. The first peak in the $CuSO_4 \cdot 5H_2O$ system was due to the presence of a quadruple point in the system, *i.e.* the temperature at which the four phases, $CuSO_4 \cdot 5H_2O$, $CuSO_4 \cdot 3H_2O$, H_2O (l) and H_2O (g), can co-exist. The required conditions[1] for the appearance of a liquid phase in a metal salt hydrate system are: (*1*) the system contains a quadruple point; (*2*) the quadruple point occurs at a water vapor pressure which is less than atmospheric pressure; (*3*) the rate of dissociation of the hydrate must be rapid; and (*4*) the water vapor which is evolved must be confined to the immediate vicinity of the sample.

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Since the formation of a saturated solution containing the salt hydrate or lower hydrates significantly increases the electrical conductivity of the initial compound, this technique was used to detect the presence of a liquid phase in the metal salt hydrate systems and hence, the presence of a quadruple point.

EXPERIMENTAL

Electrical conductivity apparatus

A schematic diagram of the apparatus is illustrated in Fig. 1.

The apparatus consisted of an E–H Research Laboratories Model 240 recording micro-microammeter, a Moseley Model 135 X–Y recorder, a 3–25 regulated d.c. power supply, a sample holder and probe, and a simple brass block furnace whose temperature rise was programmed with a T and T Controls linear temperature programmer. Basically, the apparatus recorded the current flow through the sample on the Y-axis of the recorder as a function of furnace temperature which was recorded on the X-axis. The EMF of the probe circuit was controlled by the variable voltage power supply. Normally, a probe voltage of about 5.00 V was employed. Generally, the current ranges employed were from $1 \times 10^{-2} \mu A$ to $1 \times 10^{-3} \mu A$.

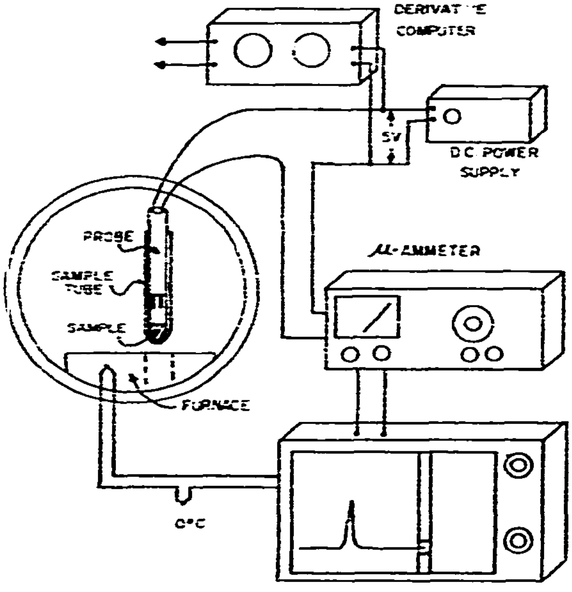

Fig. 1. Schematic diagram of electrical conductivity apparatus.

The sample chamber consisted of a Pyrex tube, 5 mm in outside diameter by 50 mm in length. To facilitate removal of the probe from the apparatus, the wires were attached to it by two gold-plated detachable connectors.

The furnace consisted of a machined brass block, 35 mm in diameter by 80 mm in length. It was heated by a 210-W (120 V) heater cartridge, positioned in the center of the block. The temperature of the block was detected by two Chromel–Alumel thermocouples: one to control the rate of temperature rise *via* the temperature programmer, the other the block temperature and whose EMF output was recorded on the X-axis of the recorder.

The first derivative of the voltage change (proportional to the current change) could be recorded, if desired, by use of a Cahn Time Derivative Computer connected to the voltage divider circuit. The output of the derivative computer was recorded on another X–Y recorder, using the same temperature-base.

Procedure

A typical procedure for the measurement of the electrical conductivity of a metal salt hydrate consisted of the following: from 50 to 100 mg of the finely powdered sample was placed into the sample chamber, tamping it firmly into a layer of 3–4 mm thickness in the sealed end of the tube. The probe was placed into the sample tube so that the two platinum wires penetrated the sample. The sample tube and probe were then connected to the apparatus and placed into an opening in the brass block furnace. The furnace heating cycle was begun and the output of the recording ammeter recorded, as a function of temperature, on the X–Y recorder. A furnace temperature rise of $2.5°C \cdot min^{-1}$ was normally employed. No control of the sample chamber atmosphere was necessary because due to its geometry, the atmosphere surrounding the sample was essentially a "self-generated" one containing water vapor[3].

DTA studies

The same brass block furnace and temperature programmer were employed. Two identical sample chambers were used, each containing a Chromel–Alumel thermocouple, but one containing the sample and the other aluminum oxide. The EMF output of the differential thermocouples was amplified by a Leeds and Northrup d.c. microvolt amplifier, and recorded on the X-axis of the X–Y recorder. Sample sizes ranged in weight from 20 to 50 mg while the furnace heating rates were identical to those used for the EC measurements. Dehydration conditions in the sample chamber were identical to those used in the EC measurements, *i.e.* a "self-generated" atmosphere of water vapor.

Metal salt hydrate samples

The compounds used, $CuSO_4 \cdot 5H_2O$, $BaCl_2 \cdot 2H_2O$, and $BaBr_2 \cdot 2H_2O$, were all of analytical reagent grade quality. The crystals were ground to a fine powder in a mortar and pestle before use.

RESULTS AND DISCUSSION

DTA–EC studies

The DTA–EC curves for $CuSO_4 \cdot 5H_2O$ and $BaCl_2 \cdot 2H_2O$, respectively, are shown in Figs. 2 and 3.

The DTA curve for $CuSO_4 \cdot 5H_2O$ was similar to that previously described[1] except for the more pronounced resolution of the first endothermic peak. The first peak began at about 91 °C, with a ΔT_{min} (peak minimum temperature) of 101 °C. The ΔT_{min} values for the second and third peaks were 112 and 135 °C, respectively. Formation of liquid water was readily shown by the EC curve in that the current flowing through the sample began to increase at about 95 °C and obtained a maximum, EC_{max}, at 103 °C. Rapid vaporization of the liquid water from the saturated salt solution was readily apparent by the steep slope of the descending portion of the curve. No EC peak was observed for the $CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O$ transition.

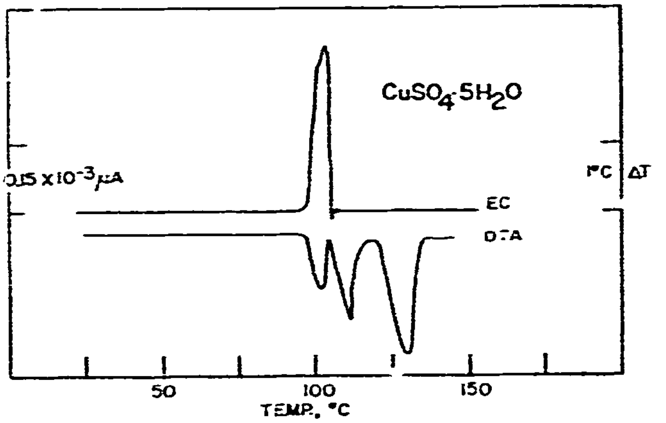

Fig. 2. DTA and EC curves of $CuSO_4 \cdot 5H_2O$. Heating rate of 2.5 °C^{-1}.

For the $BaCl_2 \cdot 2H_2O$ system, the DTA curve contained two endothermic peaks, in agreement with previous studies[1]. The first endothermic peak, which is of primary interest here, began at about 90 °C with a ΔT_{min} of 112 °C. The presence of a liquid phase was indicated by the appearance of a peak in the EC curve. The peak began at about 98 °C, with an EC_{max} value of 108 °C. The presence of the liquid phase in this system was not observed by Borchardt and Daniels[1]. They stated that the relatively small difference between the vapor pressure of the salt hydrate at the quadruple point and atmospheric pressure required close adherence to equilibrium conditions if the formation of a liquid was to be observed. This condition, they stated, obviously was not met. On closer inspection of their DTA curve, however, a slight shoulder peak is observed in the curve. Perhaps if they had used a slower heating rate, a more pronounced peak would have been observed. This shoulder peak is observed also in the DTA curve in Fig. 3 although the slower heating rate (2.5 °C·min^{-1}) did not reveal another peak in this region of the curve.

Electrical conductivity studies

Effect of heating. — As with any other dynamic thermoanalytical technique[4], the electrical conductivity curve of a sample is influenced by the furnace heating rate. The EC curve of $BaCl_2 \cdot 2H_2O$ at various heating rates are shown in Fig. 4. As the heating rate decreased from 20 to 1.25 °C·min^{-1}, the slope of the peak changed rather drastically. At the high heating rates, the peak was much smaller and broader; on decreasing the heating rate, the peaks became sharper and of greater height. The area of the peaks varied also but much of this was due to the inability to pack the sample in a uniform, consistent manner. The effect of heating rate on the shape of the peaks is related to conditions (*3*) and (*4*) previously discussed. At rather high heating rates, the system is too far from equilibrium and condition (*3*) cannot be met. Low heating rates would allow more time for the water vapor to diffuse away from the sample but with the enclosed sample chamber, the diffusion process is hindered.

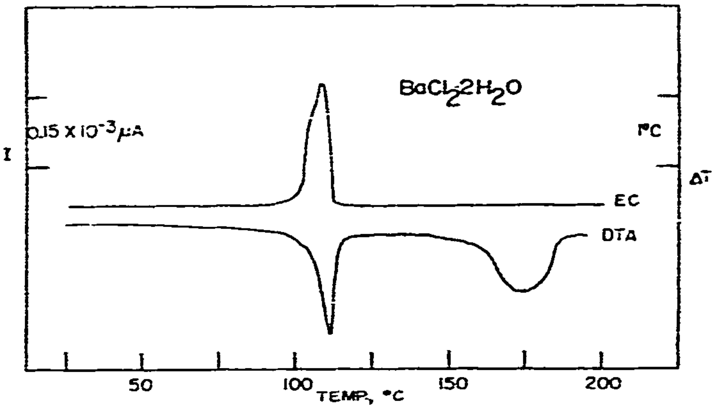

Fig. 3. DTA and EC curves of $BaCl_2 \cdot 2H_2O$. Heating rate of $2.5\,^\circ C \cdot min^{-1}$.

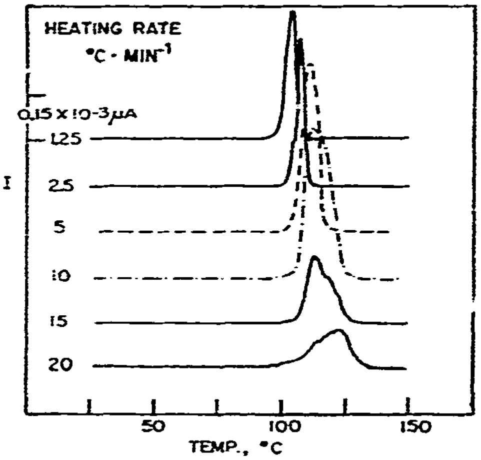

Fig. 4. Effect of heating rate on the EC peaks of $BaCl_2 \cdot 2H_2O$.

The EC peak maximum is also affected by the heating rate. At $20\,^\circ C \cdot min^{-1}$, the EC_{max} was about 122 °C, while at $1.25\,^\circ C \cdot min^{-1}$, it had decreased to 103 °C. Although the peak maximum temperature changed with heating rate, the temperature at which the peak began changed little. They all began in the temperature range from 97 to 100 °C.

$CuSO_4 \cdot 5H_2O$ system. — The EC curve of $CuSO_4 \cdot 5H_2O$ is given in Fig. 5. The peak began at about 97 °C, with an EC_{max} of about 105 °C. This peak has been interpreted in the previous discussion.

$BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$ systems. — The EC curves for these two compounds are given in Fig. 6. The peak in the $BaCl_2 \cdot 2H_2O$ curve began at about 98 °C with EC_{max} at 108 °C. For $BaBr_2 \cdot 2H_2O$, the EC peak began at about 100 °C with an EC_{max} at 110 °C. The $BaCl_2 \cdot 2H_2O$ peak has been interpreted in the previous discussion. For $BaBr_2 \cdot 2H_2O$, the origin of the peak is similar; the reactions present during the EC peak are:

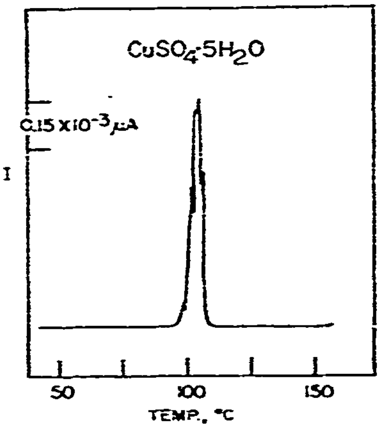

Fig. 5. The EC curve of $CuSO_4 \cdot 5H_2O$.

$$BaBr_2 \cdot 2H_2O(s) \rightarrow BaBr_2 \cdot H_2O(s) + H_2O(l)$$

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

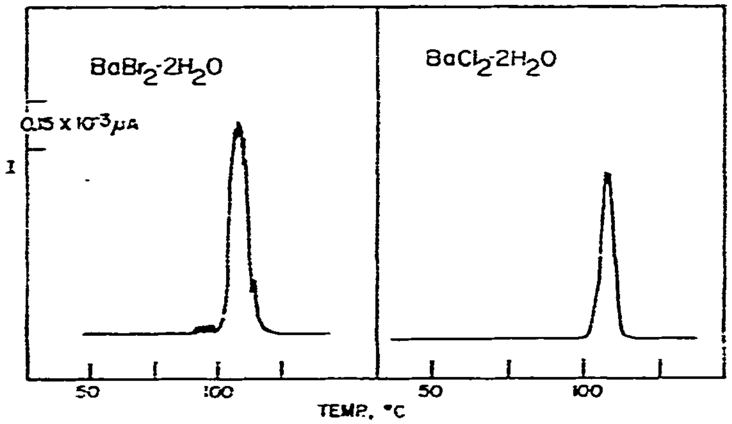

Fig. 6. EC curves of $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$.

A DTA curve was also obtained for this compound (not shown here). The curve contained only two peaks, not three as previously described by Borchardt and Daniels[1]. Its dehydration behavior was similar to that of $BaCl_2 \cdot 2H_2O$.

CONCLUSIONS

From the above results, it is seen that electrical conductivity measurements can definitely be used to detect the presence of liquid water in the dehydration of metal salt hydrates and also quadruple points. The technique is simple and convenient to use. It should prove to be a useful technique to aid in the interpretation of data obtained by other thermoanalytical techniques. Other metal salt hydrate systems are currently under investigation in this laboratory.

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