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THE THERMAL PROPERTIES OF INORGANIC COMPOUNDS
III. STRONTIUM CHLORIDE 6-HYDRATE

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ABSTRACT

The TG, DTG, DTA, DSC, EC and dilatometric curves of $SrCl_2 \cdot 6H_2O$ are presented. Intermediate hydrates having the composition, $SrCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot H_2O$, were detected while there was evidence for $SrCl_2 \cdot 0.5H_2O$ in the high pressure DSC curves. DSC curves for this compound were obtained at pressures from 0.2 to 50 atm.

INTRODUCTION

The thermal deaquation of strontium chloride 6-hydrate has been the subject of numerous investigations. In the more recent studies, Borchardt and Daniels[1] found extra endothermic peaks in the DTA curve which were due to the formation of a saturated solution containing the 2-hydrate, $SrCl_2 \cdot 2H_2O$, and liquid water. The necessary requirements for the appearance of this liquid phase were: (1) that the hydrate system contains a quadruple point; (2) that this quadruple point occurs at a water vapor pressure which is less than atmospheric pressure; (3) that the rate of dissociation of the hydrate be rapid; and (4) the water vapor pressure which is evolved must be confined to the immediate vicinity of the sample. For $SrCl_2 \cdot 6H_2O$, the quadruple point has been reported[2] to be 61.6°C and 89.7 mm Hg.

The thermal deaquation reactions of $SrCl_2 \cdot 6H_2O$ determined by Borchardt and Daniels[1] and the DTA peak temperatures found were:

$$SrCl_2 \cdot 6H_2O(s) \xrightarrow{66\,^{\circ}C} SrCl_2 \cdot 2H_2O(s) + 4H_2O(l) \quad (1)$$

$$4H_2O(l) \xrightarrow{122\,^{\circ}C} 4H_2O(g) \quad (2)$$

$$SrCl_2 \cdot 2H_2O(s) \xrightarrow{132\,^{\circ}C} SrCl_2 \cdot H_2O(s) + H_2O(g) \quad (3)$$

$$SrCl_2 \cdot H_2O(s) \xrightarrow{183\,^{\circ}C} SrCl_2(s) + H_2O(g) \quad (4)$$

Yamamoto et al.[3] found that either three or four peaks were obtained in the DTA curve depending upon the size of sample employed. For a 25 mg sample, four peaks were observed, while a 0.5 mg sample gave three endothermic peaks. No interpretation was given for the three or four peaks although it was stated that the differences observed were due to differences in the sample surface areas and the water vapor pressures in the immediate vicinity of the sample.

More recently, Buzagh-Gere et al.[4] studied the effect of sample holder geometry in the DTA curves of $SrCl_2 \cdot 6H_2O$ and other alkaline earth salt hydrates, using the derivatograph. In a labyrinth type sample holder[5], five endothermic peaks were observed while in an open crucible type holder, only three peaks were evident. The DTA peak temperature for the $6 \rightarrow 2$ hydrate transition was reported to be 60°C. From the DTG curve, $6 \rightarrow 3$, $1 \rightarrow 0.5$ and $0.5 \rightarrow 0$ hydrate transitions were also reported.

We wish to report here new data on the thermal deaquation of $SrCl_2 \cdot 6H_2O$ obtained by use of the thermal analysis techniques of DTA, DSC, TG, DTG, EC, dilatometry, and low- and high-pressure DSC.

EXPERIMENTAL PART

TG

A DuPont Model 951 thermobalance was employed, using sample sizes of 5–6 mg, heating rates of 5 or 10°C min^{-1}, and a dynamic dry N_2 furnace atmosphere.

DSC

The high pressure DSC curves were obtained on a DuPont high pressure DSC cell. Sample sizes ranged in mass from 8–12 mg and they were heated at 10°C min^{-1}. Dry cylinder N_2 was used as the cell pressurization gas.

DTA

A Mettler TA-2000 DTA apparatus was used to record the DTA curves. The sample (2.49 mg) was encapsulated in an Al sample holder containing a pin-hole vent. The heating rate was 10°C min^{-1}.

EC

The EC measurements were obtained on an apparatus that has previously been described[6]. The heating rate was 5°C min^{-1}.

Dilatometry

The dilatometry curves were obtained on an apparatus that has previously been described[7]. The heating rate was 10°C min^{-1}.

RESULTS AND DISCUSSION

TG and DTG

The TG curves obtained under a dynamic dry N_2 atmosphere, as shown in Fig. 1, indicate the presence of intermediate hydrates containing 2- and 1-moles of water per mole of salt, respectively, and giving anhydrous $SrCl_2$ as the final product.

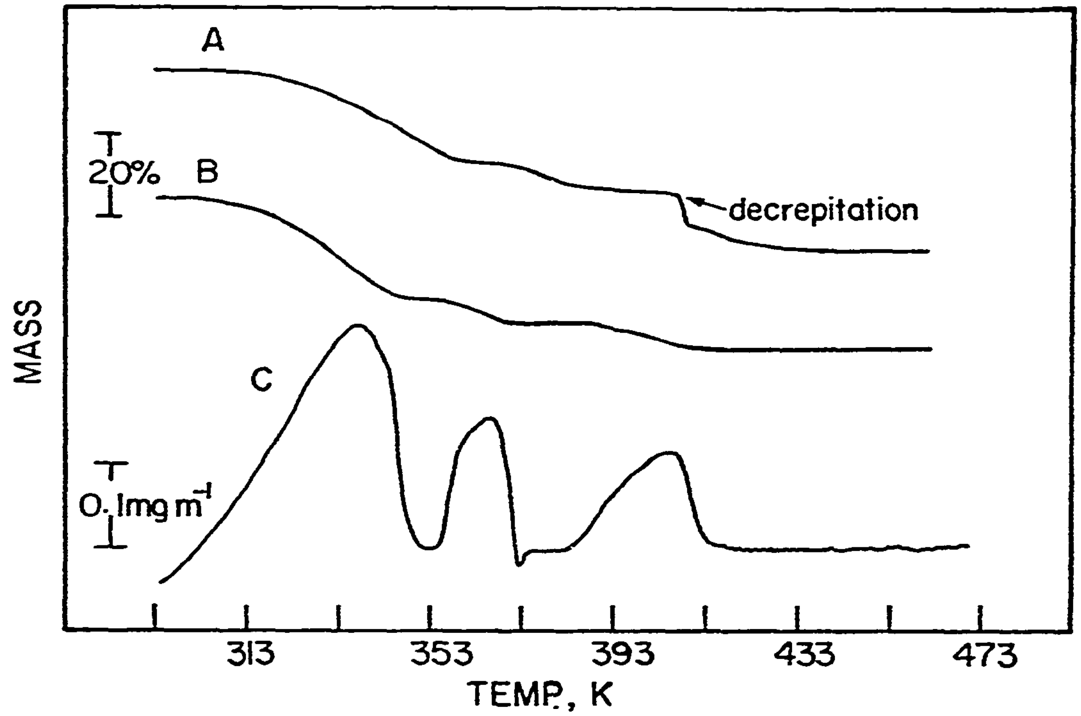

Fig. 1. TG and DTG curves of $SrCl_2 \cdot 6H_2O$ in N_2. (A) 10 K min^{-1}; (B) 5 K min^{-1}; (C) DTG curve at 5 K min^{-1}.

The temperature stability ranges of the intermediate hydrates show the usual heating rate dependence as do the T_i, T_f, and reaction interval $(T_f - T_i)$ temperatures[8]. For example, at a heating rate of 5 K min^{-1}, the 2-hydrate is stable over the temperature range from 348–356 K; at 10 K min^{-1}, it is shifted to 361–370 K. At the higher heating rate, decrepitation occurs at 408 K resulting in a non-reproducible curve in this temperature region. This decrepitation does not occur at slower heating rates. It is this region in the dehydration process that causes non-reproducibility in the DSC and DTA curves also. Peak maximum temperatures in the DTG curve, at 5 K min^{-1}, occur at 341, 369, and 410 K, respectively. These values are in goodagree ment with those reported by Buzagh-Gere et al.[4] for an open crucible type sample holder who reported: 333, 368, and 408 K, respectively.

DTA

The DTA curve of $SrCl_2 \cdot 6H_2O$, as obtained on the Mettler TA-2000 instrument, is shown in Fig. 2.

In agreement with previous studies[1,3,4], four endothermic peaks were observed in the DTA curve, with $(T_s - T_r)$ peak minima temperatures of 343, 378, 398, and 458 K, respectively. A shoulder peak was also observed in the 398–408 K temperature range, which corresponded to the decrepitation region found in the TG curve. As previously discussed, the curve was not very reproducible in this region.

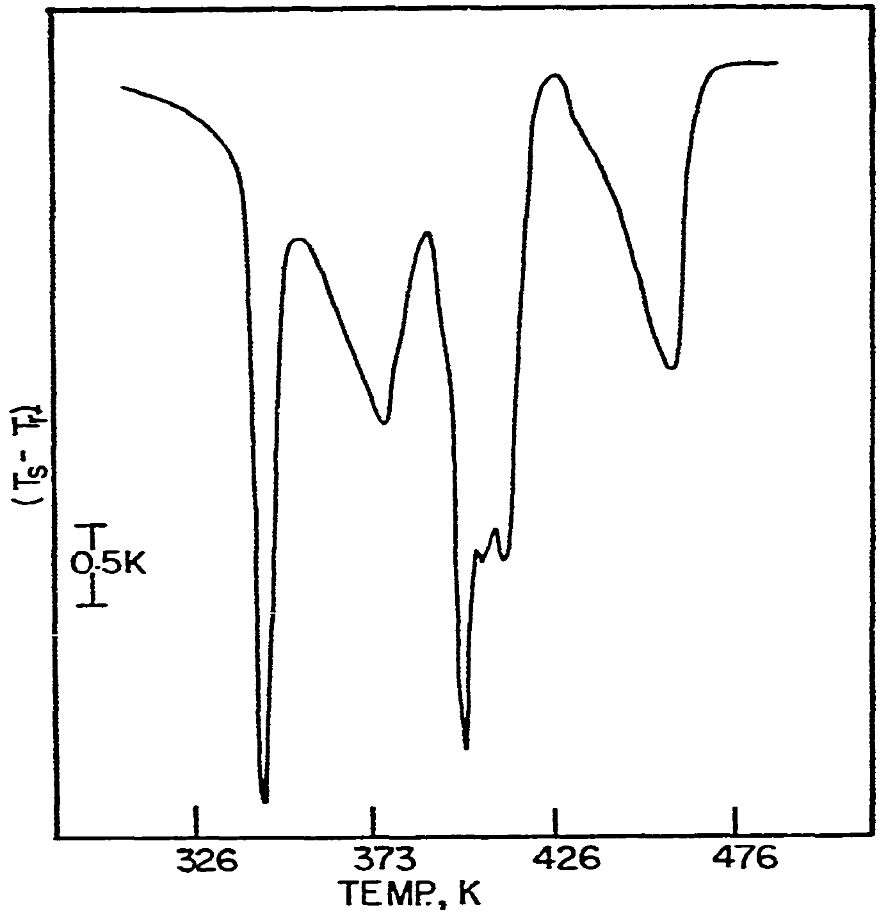

Fig. 2. DTA curve of $SrCl_2 \cdot 6H_2O$ in a self-generated atmosphere at 10 K min^{-1}.

Based on the TG curve previously reported and the DTA results obtained by others, the interpretation of the curve peaks is the same as reported by Borchardt and Daniels[1]. The DTA curve obtained here was obtained under conditions of high sensitivity compared with the latter[3,4] and indicates, as expected, overlapping curve peaks. For example, the first peak is caused by the liberation of a liquid water phase and the formation of the next lower hydrate, $SrCl_2 \cdot 2H_2O$. Under the dynamic conditions of temperature increase (10 K min^{-1}), water is evolved before the curve can return to the ($T_s - T_r$) baseline with maximum vaporization occurring at the curve minimum of 373 K. In a sealed tube DTA system[9], only the first peak is observed in the DTA curve. The remaining two endothermic peaks are due to the transitions, 2 → 1 hydrate and 1 → anhydrous. There was no evidence from the curve for the appearance or dissociation of a 0.5 hydrate, $SrCl_2 \cdot 0.5H_2O$, as previously reported[4] on the basis of DTG curve data.

High-pressure DSC

Previous studies with high-pressure DTA and DSC[10–12] have been extremely useful in the interpretation of the dehydration processes of metal salt hydrate systems. Indeed, this is the case here but the application of elevated pressures (to 50 atm) to this system also generates new curve peaks which cannot be interpreted with the limited data presently available.

The DSC curves of $SrCl_2 \cdot 6H_2O$ from 0.2 to 50 atm are shown in Figs. 3 and 4.

At sub-ambient atmospheric pressure, 0.2 atm, only three endothermic curve peaks are observed, which is similar to the curve obtained by Yamamoto et al.[3]. Apparently, the evolved liquid water vaporizes as soon as it is formed during the 6 → 2 hydrate transition. At 1 atm, the curve is similar to the DTA curve shown in Fig. 2 except that there is less separation in the first two curve peaks.

On application of pressure (dry N_2) to the system, the first endothermic peak, at a minimum temperature of 338 K, remains invariant of pressure. Since this peak is due to the 6 → 2 hydrate transition plus the liberation of liquid water, it is expected that it would be independent of pressure. The second peak (actually a shoulder peak), is due to the liquid → gas transition of the evolved water and would be expected to be pressure-dependent[12]. As can be seen, the peak minimum temperature does increase

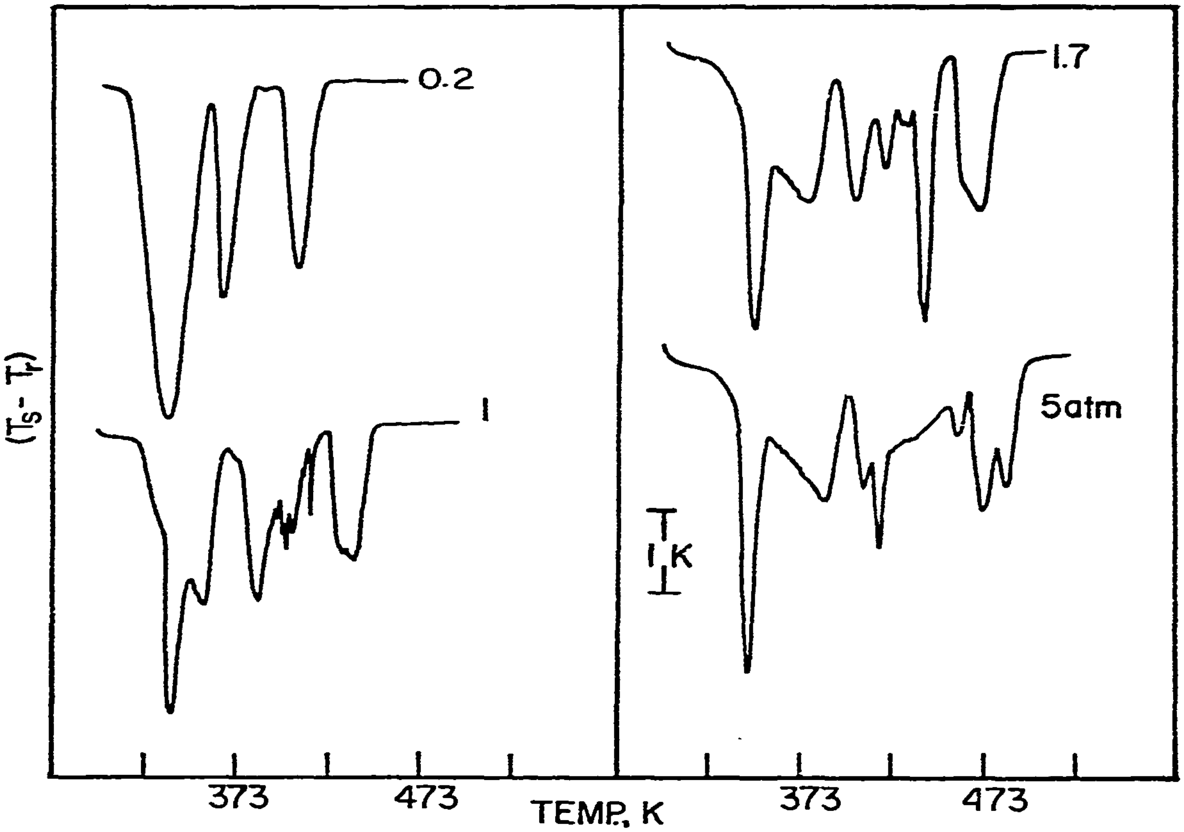

Fig. 3. DSC curves of $SrCl_2 \cdot 6H_2O$ at indicated pressures. Heating rate of 10 K min^{-1}.

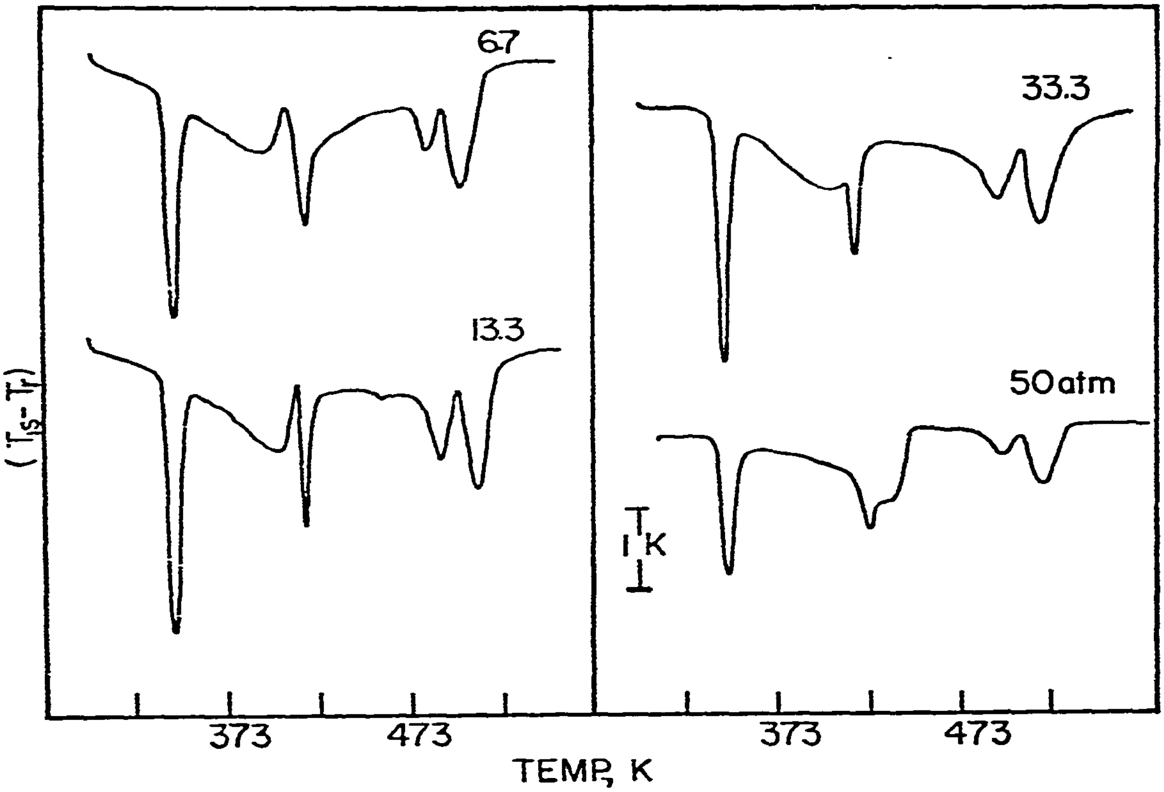

Fig. 4. DSC curves of $SrCl_2 \cdot 6H_2O$ at indicated pressures. Heating rate of 10 K min^{-1}.

with pressure, having values of 373 K (1.7 atm); 388 K (5 atm); 393 K (6.7 atm); 403 K (13.3 atm); 408 K (33.3 atm); and 433 K (50 atm). At 50 atm, the endothermic peak for the 2 → 1 hydrate transition overlaps with this transition making it difficult to determine the peak minimum temperature.

Another curve peak that is only slightly dependent on pressure is the 2 → 1 hydrate transition, which is observed at temperatures of 413–423 K at pressures of 1.7 to 50 atm. At lower pressures, 1.7 to 5 atm, there are also other peaks observed in this temperature region which cannot be interpreted. They may be due to decrepitation processes, or to saturated solution–liquid water–gaseous water equilibria.

At pressures of 5 atm and higher, the 1 → anhydrous transition peak is split into a doublet, indicating perhaps the formation of a 0.5 hydrate, $SrCl_2 \cdot 0.5H_2O$. With increasing pressure, the peak minima shift to higher temperatures, reaching a maximum value of 518 K at 50 atm pressure for the 0.5 → anhydrous transition.

EC and dilatometry

Electrical conductivity (direct current) and dilatometric data are useful for elucidating the presence of a liquid phase in a metal salt hydrate system. Wendlandt[6,13–15] has used EC to detect the presence of quadruple points in various metal salt hydrate systems and found the technique to be very useful for this determination.

The EC curve, as shown in Fig. 5, indicates the presence of a conducting phase starting at 323 K. This is, of course, expected because of the evolution of 4 moles of water per mole of metal salt and the formation of a saturated solution containing the 2-hydrate, $SrCl_2 \cdot 2H_2O$. Fluctuations in the EC curve are probably due to polarization or electrolytic reactions due to the use of direct current. These changes were not observed using alternating current[16] at 1 kHz frequency. The liquid water phase vaporizes rapidly in the 405–410 K temperature region forming a non-conducting phase. As seen in the TG curve in Figure 1, decrepitation occurs in this temperature region and this is also the region where non-reproducibility is found in the DTA and DSC curves.

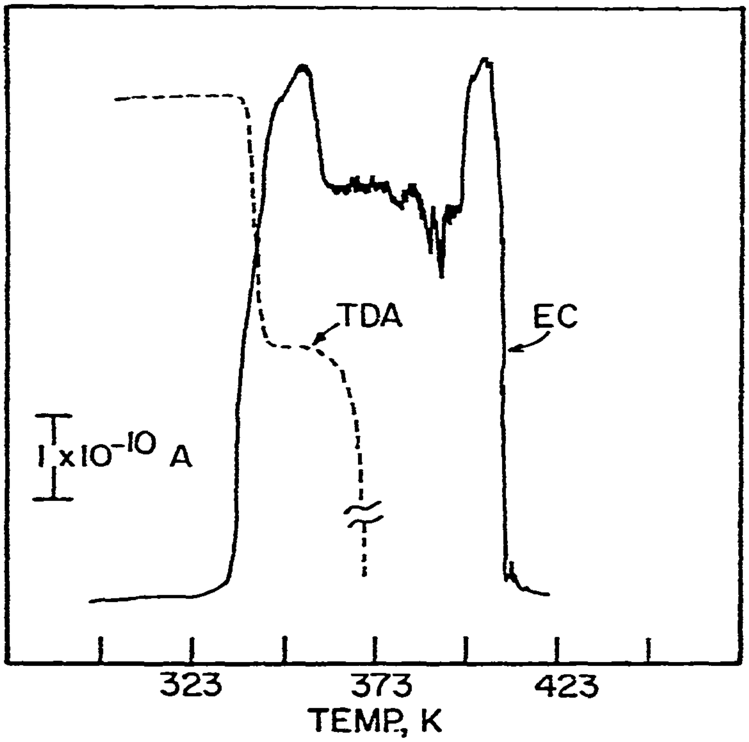

Fig. 5. EC and dilatometric curves of $SrCl_2 \cdot 6H_2O$. Heating rate of 5 K min^{-1} for EC curve and 10 K min^{-1} for the dilatometric curve.

The dilatometric curve, also shown in Fig. 5, indicates a volume decrease during the liquid water evolution. This is due to the push-rod of the dilatometer being immersed into the saturated solution. The curve went off-scale at about 370 K. As seen here, dilatometry can be used to detect the presence of liquid phases also.

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