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Crystallizations and Transformations of SrCl_2 -Hydrates in H_2O -Solutions in Quartz Flasks

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The search for materials suitable for energy storage has aroused an interest in the kinetics of nucleation and the growth of salt hydrates.¹ In a previous paper² it was shown that $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ can, if properly treated, be heated above 61.3 °C – the temperature of transition for the system $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{sat. solution}$ – without transforming into dihydrate; $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ is formed at approx. 71 °C.

The system, $\text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{sat. solution}$, can be supercooled approx. 100 °C in quartz flasks if treated as described below; the temperature of transition for $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{sat. solution}$ is approx. 135 °C. The limit of supercooling – approx. 30 °C where hexahydrate is generated – depends probably on the quartz container used but not on the monohydrate crystals.

The system, $\text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{sat. solution}$, can also be supercooled – from 61.3 °C down to approx. 20 °C – and the limit, where hexahydrate is formed, depends probably also on the container used and not on the supercooled system (*cf.* results obtained with CaCl_2 -hydrates³).

Experimental details and results. Sample SrCl_2 , El-chemical, from Merck, Germany. The analysis of the sample and the experimental arrangement is described earlier.² The cleaning of the quartz flasks which contained the SrCl_2 -system has been modified as follows: the vacuum grease (Apiezone H) was first removed; the last residue was thoroughly washed away by chloroform. Then the flask was washed with alcohol and water and filled with conc. H_2SO_4 which contained 25 g NaClO_4 per 1 H_2SO_4 (analysed reagents). The flask was left for 12 h at 100 °C, and then thoroughly washed with distilled water (sp. conductivity less than $5 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$).

A SrCl_2 -solution was filtered through a filter, type VSWP 04700, white, plain, pore size 0.025 μm ; stainless pressure filter holder, type XX4004700. Filter and filterholder from Millipore Corp. U.S.A.; before use they were washed repeatedly with distilled water until the sp. cond. was less than $10^{-6} \Omega^{-1} \text{cm}^{-1}$. The washing and the filtration of the SrCl_2 -solution into a quartz flask was performed in a laminar air flow cabinet; the pore sizes of the air filter were less than 0.6 μm .

Before starting an experiment, a SrCl_2 -solution was heated to 100 °C, cooled and then exhausted four or five times. It proved to be

advantageous to have a stopcock between a quartz flask and the pyrex glass apparatus; thus it was possible to mount two flasks on each apparatus. Although the system was thoroughly and repeatedly exhausted, a trace of foreign gases was left: small air bubbles could always be seen on the bottom of a flask after having dissolved monohydrate crystals. Foreign gases are, strictly speaking, a part of the system. For further details the reader is referred to the previous paper.¹

The vapour pressure is indicative of the supersaturation; one notices that the curve for the supersaturated system, $\text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{sat. solution}$ (above 45°C), lies below the curve for the system which consists of two solid phases: $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot 2\text{H}_2\text{O}$. By using below mentioned vapour pressure measurements to prolong curve 3, Fig. 2, Ref. 2, the obtained results may be illustrated.

The system, $\text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{sat. solution}$, was supercooled down to approx. 30°C where hexahydrate was formed. The limit of supercooling was reached if and only if the monohydrate crystals were generated and grown as follows: the monohydrate was generated by heating the system, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} + \text{sat. solution}$, from 69.5 to 71.2°C in less than 5 min, then staying for 1 min before the system was cooled (in 2 min) to 70.3–70.4°C. The system was kept at this temperature for 3–4 h; then it was slowly cooled (10 min) to 69.9°C, and thereafter it was slowly heated, 0.02°C/h, up to 71.0°C before supercooling.

The procedure has the following background: the temperature of transition for the system, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O}$ (sat. solution), is 70.2°C.² The first seeds of monohydrate crystals were found to be formed at approx. 70.6°C; at 70.35° the crystals are slowly growing while the hexahydrate crystals are slowly dissolving; at temperatures below 70.2°C the process is reversed.

The limit (30°C) at which hexahydrate was formed depended apparently slightly on the rate of cooling. When the rate was 2°C/h the hexahydrate was formed at $29 \pm 2^\circ\text{C}$ in eight experimental runs using four different quartz flasks; but when the rate was 0.25°C/h then hexahydrate was formed at $31 \pm 2^\circ\text{C}$ (four runs).

Monohydrate crystals, not generated and grown as described above but more rapidly, could previously be supercooled only down to a temperature which lay slightly below 70°C.² This phenomenon was now found to be due to the nucleation and growth conditions above 70.2°C; it was eliminated by following precisely the above described procedure.

The vapour pressure of a solution saturated with respect to the monohydrate has been measured at 33, 40, and 50°C and found to be 16.85, 24.80, and 42.4 mmHg, respectively. With the aid of the Clausius-Clapeyron equation in the approximate form $d \ln p / (d1/T) = -Q/R$ it is found that Q is nearly constant between 30 and

70°C (10.6 kcal). This conforms with the fact that the solubility is practically constant in this interval.²

The procedure for determining the limit of supercooling for the system, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{sat. solution}$, has the same basic features as described above: dihydrate crystals are generated from hexahydrate crystals at a temperature slightly (1.5°C) above the temperature of transition (61.3°C) for $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$ (sat. solution) – here rapidly grown hexahydrate crystals are suitable only.³ After having cooled the system to 61.3°C it was slowly heated, 0.1°C/h, up to 63°C, then more rapidly, 0.5°C/h, up to 67–68°C before supercooling. The system $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{sat. solution}$, could be supercooled down to $20 \pm 2^\circ\text{C}$ (in eight experimental runs using four different flasks). The rate of cooling was 0.8°C/h.

The dihydrate can be generated and grown from the hexahydrate at any temperature between 61.3 and 70.2°C;² it was therefore an easy task to get rapidly generated and grown dihydrate crystals which could not be supercooled down to 20°C. Experience showed that too much solid substance in a flask (this is valid for all three types of crystals) had to be avoided when working with a thermodynamically instable system: crystals are stressed or even broken if space is lacking, and they may then initiate a process in the thermodynamically instable system.

Fig. 1 shows the results obtained when supersaturated SrCl_2 -solutions (without contact with crystals) were cooled in three of the four flasks (one broke). The points marked A, B, and C refer to the three flasks; a point shows the temperature and pressure (which is a measure

Fig. 1. Vapour pressure curves of saturated solutions of SrCl_2 -hydrates in comparison with vapour pressures and temperatures at which hexahydrate was formed.

of the SrCl_2 -concentration) at which hexahydrate is formed in a supercooled solution. The rate of cooling (from 70 °C) was 2 °C/h.

The flasks A and B were mounted on the same apparatus and therefore identically treated; for example, the SrCl_2 -conc. and the cooling rate were always identical for both during a run. It was always possible to supercool B more than A.

The results show that the nucleation is heterogeneous, not homogeneous. Foreign seeds – probably from the walls of the flasks – act as a catalyst for nucleation of hexahydrate. Fig. 1 shows that these foreign seeds determine most likely also the limits found for the systems represented by the curves 2 and 3 (cf. Fig. 2, Ref. 2); as mentioned before these limits were found to be approx. 20 and 30 °C, respectively. The results are analogous to those obtained when CaCl_2 -hydrates were studied.³

The transformation of hexahydrate into dihydrate above 61.3 °C, of dihydrate into hexahydrate below 61.3 °C, and of monohydrate into dihydrate below 135 °C are all found to depend either on foreign seeds or on proper nonequilibrium conditions. The influence of these factors can be minimized so that (1) a solution saturated with respect to and in contact with hexahydrate crystals can be heated above 61.3 °C without giving dihydrate (monohydrate is generated), (2) a solution saturated with respect to and in contact with monohydrate crystals can be supercooled without giving dihydrate, (3) a solution saturated with respect to and in contact with dihydrate crystals can be supercooled approx. 40 °C. Monohydrate or dihydrate crystals do not influence the limit of supercooling.

The SrCl_2 -systems exhibit large supersaturations as is often the case when salt hydrates are involved. For large supersaturation, the effects of foreign seeds have to be taken into consideration. The experiments indicate that it will be difficult to study homogeneous nucleation or the effect of a hydrate on the nucleation of a higher one: it is necessary to begin by getting the influence of foreign seeds under control, and this may be very difficult to realize. If the aim is to control in practice nucleation and growth of a hydrate exhibiting large supersaturation, it is probably more productive to study the catalytic effect of definite foreign seeds or of nonequilibrium conditions caused by ultrasonic waves.

The following phenomenon – which perhaps can be used to purify SrCl_2 – was observed: hexahydrate crystals in a sat. solution (kept on a table) crept rather rapidly up the glass wall. This resulted in a complete spatial separation of the phases. The phenomenon proved to be connected with a temperature radiation from a warm object, the crystals always creeping up the wall which faced the object.

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