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Solubility of Calcium Carbonate Hexahydrate

Ljerka Brečević[a,*] and Arne Erik Nielsen[b]

[a]Laboratory for Precipitation Processes, Ruđer Bošković Institute, PO Box 1016, HR-41000 Zagreb, Croatia and [b]Panum Institute, Department of Chemistry, University of Copenhagen, DK-2200 Copenhagen N, Denmark

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Calcium carbonate hexahydrate ($CaCO_3 \cdot 6H_2O$) has been synthesized, and the procedure is reported. The crystals were characterized by means of optical microscopy, thermogravimetry and IR-spectroscopy. The solubility was found by recording the pH during the dissolution of the hexahydrate in water, preventing the entrance of carbon dioxide. The solubility product was calculated from the final constant pH value, taking all known calcium and carbonate species into account. Between 10 and 40 °C the solubility product (or equilibrium constant), $K_s(CaCO_3 \cdot 6H_2O)$, could be expressed by:

$$-\log K_s = 7.1199 + 0.011\,756t + 0.000\,075\,556t^2$$

where t is in °C. The solubility product decreases with increasing temperature, and is (5.7, 3.5 and 1.9) $\times 10^{-8}$, at 10, 25 and 40 °C, respectively.

Most research on calcium carbonate has dealt with anhydrous crystalline polymorphs (calcite, aragonite and vaterite). The hydrates have been examined much less, probably because of their low stability at ordinary conditions. The most unstable form is amorphous calcium carbonate, containing less than one molecule of water per molecule of $CaCO_3$,[1] which undergoes rapid transformation to more stable anhydrous forms. $CaCO_3 \cdot 6H_2O$ and $CaCO_3 \cdot H_2O$ seem to be somewhat more stable. These forms can be kept for a few days at temperatures below 0 °C before they transform into calcite.

In supersaturated solutions hydrated forms often appear before the precipitation of the more stable anhydrous forms. A knowledge of the properties of these hydrates is valuable in studies of the mechanisms and kinetics of their formation and transformation.

Calcium carbonate hexahydrate was first prepared and described by Pelouze.[2] Later its crystallographic properties,[3] density[4] and crystal structure[5] were reported. In this study crystals of the composition $CaCO_3 \cdot 6H_2O$ were prepared, and their solubility in water was determined at different temperatures.

Experimental

Preparation of $CaCO_3 \cdot 6H_2O$. Stock solutions were prepared from analytical-grade chemicals and deionized water, and were standardized by conventional analytical methods. Three reactant solutions were used: solution A, 90 ml of 4 mol l^{-1} sodium chloride and 10 ml of 1 mol l^{-1} calcium chloride; solution B, 90 ml of 4 mol l^{-1} sodium chloride and 10 ml of 1 mol l^{-1} sodium carbonate; solution C, 50 ml of 0.5 mol l^{-1} calcium chloride.

All the solutions, as well as the reactant vessel, were cooled to −10 to −15 °C (by means of an ice–NaCl–water bath in a refrigerated room kept at 5 °C). Solutions A and B were poured together. Solution C was then added at constant speed (12 ml h^{-1}) by means of a motor-driven syringe. The precipitate was filtered through a Millipore membrane filter and dried by means of ethanol and ether. The whole procedure was accomplished in a refrigerated room. $CaCO_3 \cdot 6H_2O$ decomposes if the temperature exceeds 6 °C, for which reason the crystals were kept at −15 °C in a refrigerator. As soon as a trace of the hexahydrate has been transformed the rest changes relatively fast.

Characterization of $CaCO_3 \cdot 6H_2O$. The calcium carbonate hexahydrate crystals were characterized by means of optical microscopy (Leitz Orthoplan), thermogravimetry (Mettler TG 50 thermobalance with TC 10 TA processor and Print Swiss matrix printer) and infrared spectroscopy (Perkin-Elmer IR-spectrophotometer 225) before each set of solubility experiments. The IR spectra were recorded at room temperature in the region 4000–200 cm^{-1} using KBr pellets, if not otherwise stated.

Solubility measurements. 20 ml of freshly deionized water (Milli-Q reagent water system, Millipore) was placed in a conical plastic vessel covered with a Teflon cover (Fig. 1). A combined glass–calomel electrode

* To whom correspondence should be addressed.

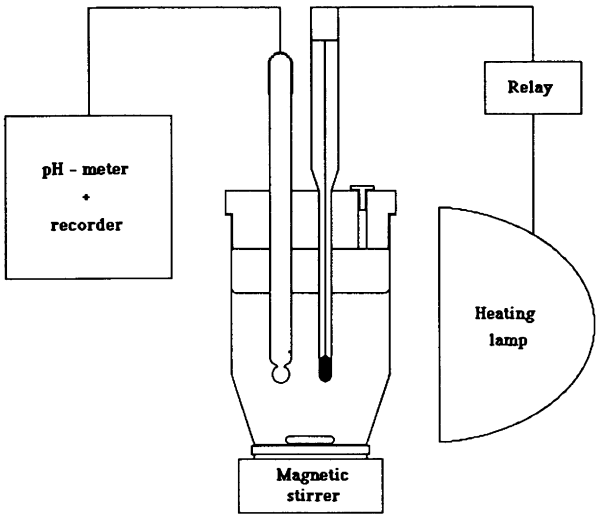

Fig. 1. Schematic drawing of the experimental set-up.

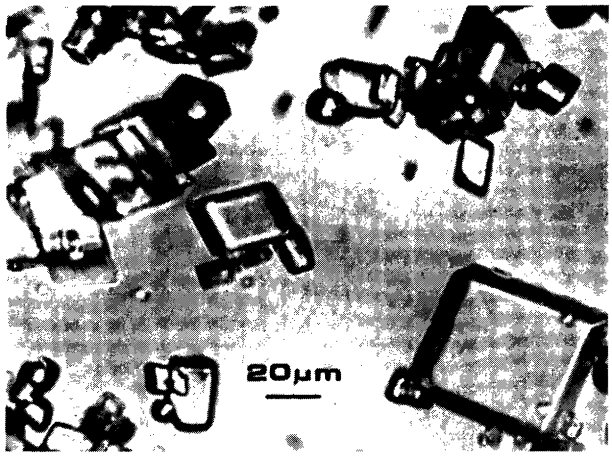

Fig. 2. Micrograph of the calcium carbonate hexahydrate crystals precipitated and preserved as described in the experimental section.

(Radiometer GK 2401C) and a contact thermometer (previously adjusted to the required temperature) were immersed in the water through the cover. When the required temperature was reached, a given amount of calcium carbonate hexahydrate crystals was added to the water through a hole in the cover. The hole was closed again with a stopper to prevent carbon dioxide entering the vessel. The temperature was maintained within 0.1 °C by means of a thermostat-controlled heating lamp or by cooling in a water bath using a Heto Hetofrig cryostat with a circulating pump. The system was continuously stirred at a constant rate by means of a Teflon-coated magnetic stirring bar, and the change of pH was recorded on a Radiometer Servograph Rec 80.

Commercial standard buffer solutions (Radiometer) were used to adjust the instrument (pH 7.01, 9.18 and 10.01 at 25 °C).

The solubility product was calculated from the pH values measured when solubility equilibrium was reached, i.e. at the maximum pH.

Results

Well defined rhombohedral cyrstals (Fig. 2) in the size range 10–40 μm were obtained.

Thermogravimetric analysis showed that a loss of weight started at about 40 °C and continued until about 140 °C, when nearly all the water had been released. The peak temperature was found to be 125 °C at the rate of heating of 10 °C min^{-1}. The total loss of weight up to 300 °C corresponded to between 5.9 and 6 molecules of water per molecule of calcium carbonate (Fig. 3).

It was found possible to obtain IR spectra of the substance in spite of its tendency to decompose at room temperature. The KBr pellets were prepared immediately after the synthesis of calcium carbonate hexadrate crystals and dried to avoid decomposition. Fig. 4 shows the IR spectra. The absorption bands appear in the regions characteristic of the hydrated modifications of calcium carbonates.[6,7] The absorption in the region 4000–2000 cm^{-1} was recorded using a variable-temperature cell cooled by liquid nitrogen. Cooling was necessary in order to prevent a loss of lattice water during the scanning (Fig. 3). The three bands at 3360, 3215 and 3125 cm^{-1}, as well as the band at 1635 cm^{-1}, correspond to the vibrations of the water molecule, i.e. to the antisymmetrical and symmetrical O–H stretching and H–O–H bending, respectively. The region 1800–600 cm^{-1} was recorded at room temperature. The strong broad band in the region 1500–1400 cm^{-1} also originates from several (probably three) overlapping bands, two of which (at about 1470 and 1415 cm^{-1}) are the components of the antisymmetrical C–O stretching mode, ν_3. The symmetrical C–O stretching mode, ν_1, is represented by the band at 1088 cm^{-1}, which appears as a doublet. The absorption band at 747 cm^{-1} is due to the O–C–O in-plane deformation mode, ν_4, while the band at 876 cm^{-1} corresponds to the CO_3 out-of-plane deformation mode, ν_2. The lattice mode is represented by the absorption in the region 450–200 cm^{-1} observed with a CsI pellet. During the scanning calcium carbonate hexahydrate started to transform, which explains the absorption bands characteristic for calcite, at 713 and 228 cm^{-1}. The amount of calcite formed was less than a few percent.

The solubility measurements of calcium carbonate hexahydrate were performed at different temperatures. Fig. 5 shows the curves, pH as a function of time, obtained at 25 °C by stirring different amounts of the substance with water. When the solubility equilibrium was reached all further experiments with higher amounts of the crystals added showed an identical maximum pH value. This value was then used for the calculation of calcium carbonate hexahydrate solubility product, eqn. (1). The curves showing the maximum pH values at different temperatures are given in Fig. 6.

$$(Ca^{2+})(CO_3^{2-}) = K_s(CaCO_3 \cdot 6H_2O) \qquad (1)$$

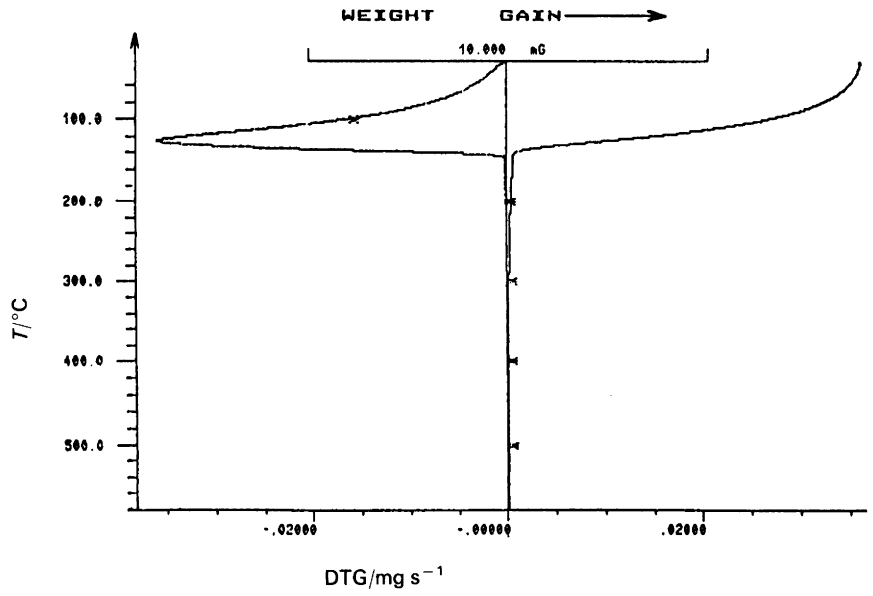

Fig. 3. Thermogram of calcium carbonate hexahydrate. Right-hand side: weight as a function of temperature. Left-hand side: differential quotient of the right-hand curve with respect to time.

In calculating the activities of calcium, (Ca^{2+}), and carbonate, (CO_3^{2-}), ions, the following species were taken into account: Ca^{2+}, $CaCO_3^0$, $CaHCO_3^+$, CO_3^{2-}, HCO_3^-, H^+, OH^-. The equilibrium constants used[8] and the corresponding relations between these constants and the species concentrations are given in Table 1.

The ion activity coefficients were obtained from the Davies equation[9] [eqn. (2)], where y_z is the activity

$$\log y_z = -Az^2[\sqrt{I}/(1+\sqrt{I}) - 0.3I] \quad (2)$$

coefficient for an ion of charge z, A is the Debye–Hückel constant dependent on temperature,[10] and I is the ionic strength [eqn. (3)], where c_i is the molar concentration

$$I = 0.5 \sum c_i z_i \quad (3)$$

and z_i is the ionic charge of the ith ion in solution.

In order to calculate the species concentrations in the system, further equations are needed. The first is the mass balance equation [eqn. (4)], obtained from eqn. (5) for

$$[Ca^{2+}] = [CO_3^{2-}] + [HCO_3^-] \quad (4)$$

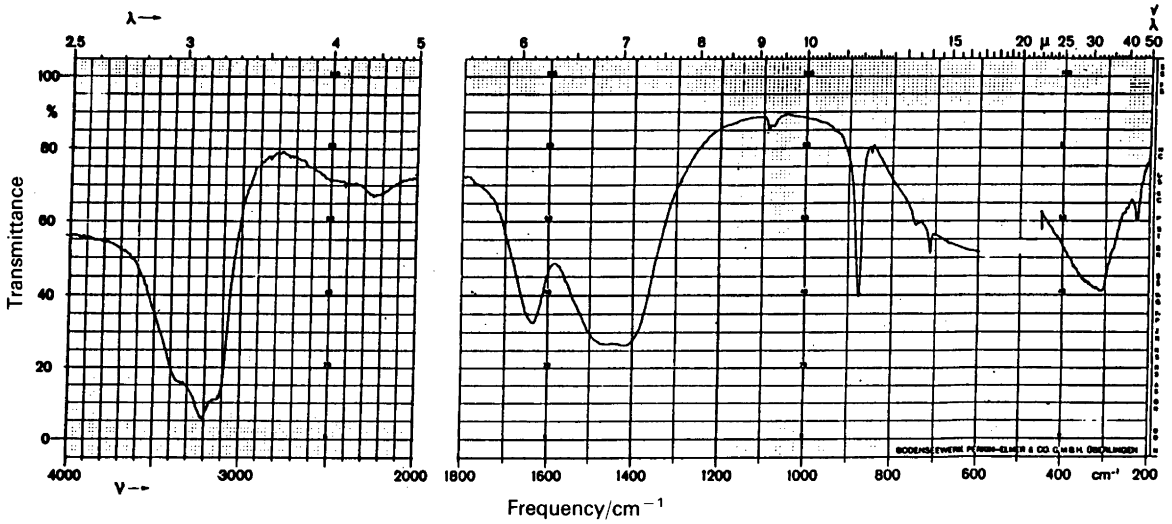

Fig. 4. Infrared spectrum of calcium carbonate hexahydrate in the region 4000–200 cm^{-1}. The region 4000–2000 cm^{-1} was recorded at liquid-nitrogen temperature. The part of the spectrum from 1800 to 200 cm^{-1} was recorded at room temperature using KBr (1800–600 cm^{-1}) and CsI (450–200 cm^{-1}) pellets.

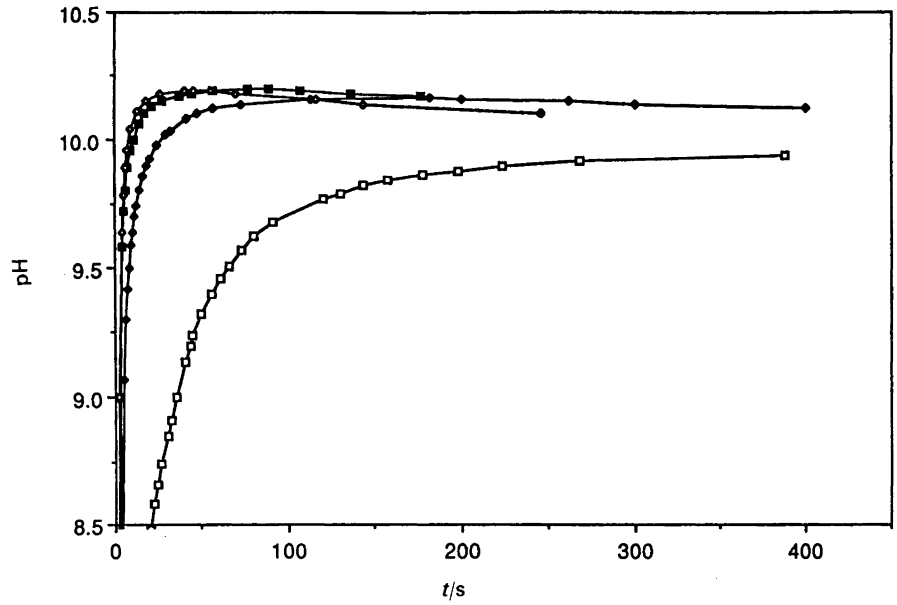

Fig. 5. Plots of pH as a function of time obtained by dissolving different amounts of calcium carbonate hexahydrate [1.31 (□), 9.84 (◆), 59.03 (■) and 91.35 (◇) mg] in 20 ml water at 25 °C. Only in the last two experiments was solubility equilibrium achieved.

total calcium species and eqn. (6) for total carbonic

$$Ca_{tot} = [Ca^{2+}] + [CaCO_3^0] + [CaHCO_3^+] \quad (5)$$

$$C_{tot} = [CO_3^{2-}] + [HCO_3^-] + [CaCO_3^0] + [CaHCO_3^+] \quad (6)$$

species in solution, assuming $Ca_{tot} = C_{tot}$ during dissolution of calcium carbonate hexahydrate. The second is the charge balance equation [eqn. (7)].

$$2[Ca^{2+}] + [CaHCO_3^+] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \quad (7)$$

Thus it was possible to calculate all the unknown variables from the measured pH, defined by eqn. (8). The

$$pH = -\log [H^+] \quad (8)$$

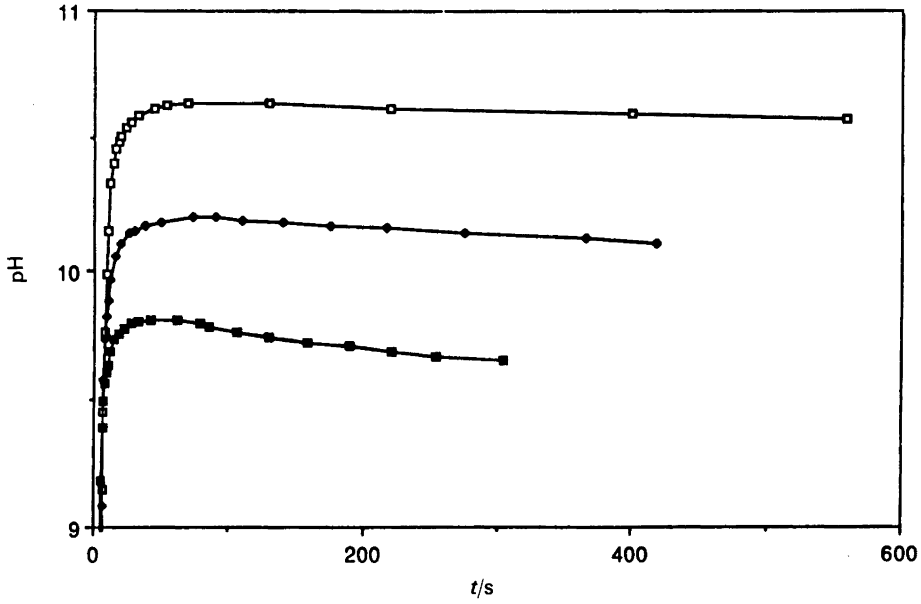

Fig. 6. Dissolution curves at 10 (□), 25 (◆) and 40 (■) °C. The maxima were taken to correspond to solubility equilibria with the hexahydrate, the later decrease being due to the formation of more stable forms of calcium carbonate.

Table 1. Equations and equilibrium constants used.

Equations	T/°C 10	25	40
$K_W = (H^+)(OH^-)$	$10^{-14.549}$	$10^{-13.998}$	$10^{-13.530}$
$K_2 = (H^+)(CO_3^{2-})/(HCO_3^-)$	$10^{-10.488}$	$10^{-10.329}$	$10^{-10.222}$
$K_I = (CaCO_3^0)/(Ca^{2+})(CO_3^{2-})$	$10^{3.134}$	$10^{3.224}$	$10^{3.383}$
$K_J = (CaHCO_3^+)/(Ca^{2+})(HCO_3^-)$	$10^{0.968}$	$10^{1.106}$	$10^{1.178}$

Table 2. Solubility of calcium carbonate hexahydrate.

T/°C	Solubility, c_s/mM	pK_s	Standard error in pK_s	No. of experiments
10	0.43	7.245	0.001	4
25	0.37	7.461	0.005	6
40	0.34	7.711	0.005	5

calculations were made by a simultaneous solution of eqns. (1)–(4), (7) and (8) and the equations from Table 1 by means of a program in MathCAD 2.5 of MathSoft Inc. for PC computers.

The solubility product was determined for each of the three examined temperatures. The results are summarized in Table 2 together with the standard error and the solubilities of $CaCO_3 \cdot 6H_2O$. The solubility was calculated on the basis of one of the two balance equations (9) and (10), where [ ] denotes the concentration of the species.

$$c_s = [Ca^{2+}] + [CaCO_3^0] + [CaHCO_3^+] \quad (9)$$

$$c_s = [CO_3^{2-}] + [HCO_3^-] + [CaCO_3^0] + [CaHCO_3^+] \quad (10)$$

The plot of solubility product against temperature between 10 and 40 °C gives a curve best represented by eqn. (11).

$$-\log K_s = 7.1199 + 0.011\,756t + 0.000\,075\,556t^2. \quad (11)$$

Discussion

The solubility of calcium carbonate hexahydrate was originally measured in a broader range of temperatures. The data obtained at temperatures >40 °C are not represented because of the irreproducibility of the results. The most probable reason for such behaviour is in a phase-transformation process which calcium carbonate hexahydrate undergoes when exposed to elevated temperatures. According to thermogravimetric analysis (Fig. 3) a gradual loss of structural water starts above 40 °C, so that a change in structure as well as in the apparent solubility of the material is to be expected.

The solubility values reported here show that calcium carbonate hexahydrate is more soluble (and thus thermodynamically less stable) than the three anhydrous polymorphs (calcite, aragonite and vaterite)[8] but less soluble than the amorphous calcium carbonate.[1] The only solubility data for calcium carbonate hexahydrate found in the literature were those published by Mackenzie,[11] who reported that at temperatures near 2 °C between 0.03 to 0.04 g l^{-1} could be dissolved.

The IR spectra of $CaCO_3 \cdot 6H_2O$ (Fig. 4) showed that the water molecule vibration in the region 3500–3000 cm^{-1} was composed of at least three bands, but it seems that there was an overlapping of more such bands. An additional study of the absorption in this region is needed.

The part of the spectrum corresponding to the normal vibrations of the carbonate ion, 1700–1500 cm^{-1}, shows some similarities to vaterite,[7,12] but the lattice mode, 450–200 cm^{-1}, is completely different from that of vaterite.[7]

Thus the absorption spectrum of calcium carbonate hexahydrate joins the series of calcium carbonate spectra which all show many similarities.

Conclusion

Calcium carbonate hexahydrate was prepared and characterized by means of optical microscopy, thermogravimetry and IR spectroscopy. The thermogram and the IR spectrum have been shown and discussed.

The hexahydrate crystallized in well defined rhombohedral crystals unstable at temperatures above 6 °C. The solubility product in aqueous solutions was determined in the temperature interval 10–40 °C. Above these temperatures the phase transformation of the hexahydrate into more stable calcium carbonates was too fast to allow reliable solubility values to be measured by the method used. The solubility was found to be higher than those of calcite, aragonite and vaterite, and lower than that of amorphous calcium carbonate. The solubility decreases with increasing temperature, as is the case with all known calcium carbonates.

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