STUDY OF THE CONVERSION OF $CaSO_4$ TO $CaCO_3$ WITHIN THE $CaSO_4$ + Na_2CO_3 = $CaCO_3$ + Na_2SO_4 FOUR-COMPONENT WATER–SALT SYSTEM

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The Pitzer ion-interaction model was employed to predict the conversion in the title quaternary water–salt system. The thermodynamic solubility products (K_s^0) were determined and the conversion of $CaSO_4$ to $CaCO_3$ in the $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ system was predicted. The standard molar Gibbs free energy $\Delta_r G^0$ of the conversion reaction was calculated to be –23.62 kJ mol^{-1}. A 98% degree of conversion of $CaSO_4$ was achieved by using calcium sulfate isolated from sea salt production waste brines. Suitable conditions were found for obtaining $CaCO_3$ exhibiting a high dispersity and whiteness.

All the four ternary subsystems of the $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ quaternary water–salt system have been described in the literature over a wide temperature range. A field of equilibrium crystallization of the 2 $NaSO_4$. Na_2CO_3 double salt, which actually is a phase with a varying composition[1], has been identified in the Na_2SO_4–Na_2CO_3–H_2O system. Crystallization of double salts of the k Na_2SO_4 . l $CaCO_3$. m H_2O (ref.[2]) and Na_2CO_3 . $CaCO_3$. n H_2O (ref.[3]) types ($k = 1, 2$; $l = 1, 5$; $m = 0, 1, 2$; $n = 2, 5$) has been established in the Na_2SO_4–$CaCO_3$–H_2O and Na_2CO_3–$CaCO_3$–H_2O ternary systems. The scarce data available in the literature on the $CaSO_4$–$CaCO_3$–H_2O system indicate the occurrence of a wide crystallization field of $CaCO_3$ (ref.[4]). The $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ quaternary system has been studied by physico-chemical methods[5,6], and conversion of $CaSO_4$ to $CaCO_3$ has been observed.

The purpose of the present work was to obtain high-quality $CaCO_3$ possessing a high dispersity and high whiteness, using $CaSO_4$ isolated from waste brine emerging from the production of sea salt.

EXPERIMENTAL

Conversion in the $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ four-component water–salt system was achieved by using $CaSO_4$. 2 H_2O isolated from waste brine from the production of sea salt. The conditions were as follows: duration of interaction, 4 h; temperature, 25 °C; reaction vessel, glass.

The reagents were ground before use. In order to remove Fe_2O_3 impurities, some of the $CaSO_4$ samples were treated with 5% H_2SO_4, filtered out and dried at 60 °C. The reagent mixture was added to distilled water in small portions with intense stirring. The Na_2CO_3 to $CaSO_4$ molar ratios lay within the limits of 1 ÷ 1.1. The use of excess Na_2CO_3 over $CaSO_4$ served obtaining a basic medium (pH 11) in which the conversion of $CaSO_4$ proceeds nearly completely.

The precipitated reaction product was washed with distilled water and alcohol and dried in air, and analyzed for $CaCO_3$ by the method of residual titration (Bulgarian State Standard 1820-71). The procedure is as follows: A weighed amount of the product is dissolved in distilled water, several drops of a 0.1% phenolphthaleine solution are added, and the solution is titrated with 1 M HCl to durable decolouration, after which excess HCl is added and the whole is heated gently on a flame to remove CO_2. Several drops of a 0.1% methyl orange solution are added, and the excess acid is titrated with 1 M NaOH.

A 98% degree of conversion of $CaSO_4$ to $CaCO_3$ was attained, while Na_2SO_4 remained in the solution. Colourless crystals of $Na_2SO_4 . 10\ H_2O$ were obtained by isothermal evaporation of the solution.

The dispersion and degrees of whiteness and yellowness of the $CaCO_3$ product were examined. The particle size distribution (in microns) was established by the sieve analysis method using a MALVERN 3600 apparatus, the colour measurements were made with an Elropho 2000 – Patacolor. The results are summarized in Table I. The quality of the product was found to be affected by the pre-treatment of the samples (grinding and washing with dilute H_2SO_4).

The best results were obtained if the two reagents had been ground but $CaSO_4 . 2\ H_2O$ had not been pre-treated with sulfuric acid. The product so obtained is first quality as far as its dispersion and whiteness are concerned (Bulgarian State Standard 1829-71) and can be used as filler in the cellulose industry.

The conversion of $CaSO_4$ to $CaCO_3$ was also evaluated when using sodium bicarbonate instead of carbonate. Even though a large excess of $NaHCO_3$ was added, the conversion degree was considerably lower (<90%) due to the buffer effect of this compound. Moreover, this conversion route is inconvenient because $NaHCO_3$ is considerably more expensive than Na_2CO_3.

TABLE I
Quantitative characteristics of the $CaCO_3$ obtained; *d* mean bulk diameter of particles

Exp. No.	$CaSO_4 . 2\ H_2O$ treated with 5% H_2SO_4(aq)	*d*, μm	Degree of whiteness, %	Degree of yellowness, %
1[a]	no	12.45	93.14	1.03
2[b]	no	10.03	94.18	1.43
3[b]	yes	35.44	87.55	4.42
4[b]	yes	31.89	84.00	3.25
5[c]	yes	31.34	86.78	4.47

[a] $m_{Na_2CO_3}/m_{CaSO_4} = 1$; [b] $m_{Na_2CO_3}/m_{CaSO_4} = 1.1$; [c] conversion of $CaSO_4$ to $CaCO_3$ is performed with sodium bicarbonate.

THERMODYNAMIC INVESTIGATION OF THE $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ SYSTEM USING THE PITZER MODEL

According to a rule formulated by Van't Hoff[7], the equilibrium in a quaternary water–salt system is shifted towards the formation of that pair of salts whose sum of solubility products (K_s^0) is smaller. For a theoretical examination of the conversion of $CaSO_4$ to $CaCO_3$ in the above quaternary system we simulated thermodynamically the Na_2CO_3–H_2O, Na_2SO_4–H_2O and $CaSO_4$–H_2O binary solutions at 25 °C using the Pitzer ion-interaction model[8,9]. The applicability of this model to the calculation of the thermodynamic characteristics of binary and multicomponent electrolyte solutions has been proved by many authors[10–16]. The ultimate purpose of the simulation was obtaining the thermodynamic solubility products of the crystalline hydrates ($Na_2CO_3 . 10\ H_2O$, $Na_2SO_4 . 10\ H_2O$ and $CaSO_4 . 2\ H_2O$) formed in the above saturated binary solutions.

The Pitzer binary parameters of the systems were taken from refs[16,17] (Table II). The decisive criterion for the choice of parameters was their applicability within the widest possible concentration range with a low standard deviation (σ).

Using the values of the binary parameters we calculated the activity coefficients ($\gamma_\pm$) and the water activity (a_w) in the saturated electrolyte solutions (with molality m). The values obtained are presented in Table III. Based on the overall reactions,

$$Na_2CO_3 . 10\ H_2O = 2\ Na^+ + CO_3^{2-} + 10\ H_2O \tag{A}$$

$$Na_2SO_4 . 10\ H_2O = 2\ Na^+ + SO_4^{2-} + 10\ H_2O \tag{B}$$

$$CaSO_4 . 2\ H_2O = Ca^{2+} + SO_4^{2-} + 2\ H_2O\ , \tag{C}$$

TABLE II

Pitzer binary parameters at 25 °C; σ is the standard deviation of the osmotic coefficients

System	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	c^φ	m^{max}	σ
Na_2CO_3–H_2O[a]	0.05306	1.29262	–	0.00094	2.75	0.00257
Na_2SO_4–H_2O[b]	0.04604	0.93350	–	–0.00483	1.75	0.00112
$CaSO_4$–H_2O[b]	0.20000	3.7762	–58.388	–	0.02	0.00460

[a] Ref.[16]; [b] ref.[17].

we calculated the logarithm of the thermodynamic solubility product of the crystalline hydrates. For $Na_2CO_3 . 10\ H_2O$ and $Na_2SO_4 . 10\ H_2O$:

$$\ln K_s^0 = \ln (4m^3\gamma_\pm^3 a_w^{10}) \ , \qquad (1)$$

and for $CaSO_4 . 2\ H_2O$:

$$\ln K_s^0 = \ln (m^2\gamma_\pm^2 a_w^2) \ . \qquad (2)$$

The results are given in Table III. Due to the very low solubility of $CaCO_3$ in water, no isopiestic data exist concerning the dependence of the water activity on the concentration of the $CaCO_3$–H_2O solution. For that reason, we were unable to determine the binary parameters of interionic interaction and calculate the thermodynamic solubility product of $CaCO_3$. The $\ln K_s^0$ value for $CaCO_3$ given in Table III was taken from ref.[18]. It is clear that the sum of the $\ln K_s^0$ values is much lower for $CaCO_3$ and $Na_2SO_4 . 10\ H_2O$ than for $CaSO_4 . 2\ H_2O$ and $Na_2CO_3 . 10\ H_2O$, so that, according to the Van't Hoff rule, $CaSO_4$ should dissolve and $CaCO_3$ precipitate in the quaternary system under consideration.

In agreement with the conditions of phase and chemical solid–liquid equilibria in water–salt systems, the chemical potential of the liquid phase is equal to the chemical potential of the solid phase. Owing to this, the standard molar Gibbs free energy of reaction $\Delta_r G^0$ of solid $CaSO_4 . 2\ H_2O$ with solid $Na_2CO_3 . 10\ H_2O$ could be derived from the calculated activities of the components in their saturated binary solutions (Table III). A similar scheme was used to determine the $\Delta_r G^0$ values of the reaction of synthesis of the double salts from the corresponding simple salts[10,11,13,15]. For the reaction

TABLE III

Calculated values of the logarithm of the thermodynamic solubility product K_s^0; m concentration of saturated binary solution; $\gamma_\pm$ activity coefficient; a_w water activity

Salt composition	m	$\gamma_\pm$	a_w	$\ln K_s^0$
$Na_2CO_3 . 10\ H_2O$	2.77	0.1734	0.8981	–1.889
$Na_2SO_4 . 10\ H_2O$	1.97	0.1548	0.9363	–2.834
$CaSO_4 . 2\ H_2O$	0.02	0.3042	0.9995	–10.205
$CaCO_3$[a]				–18.789

[a] Ref.[18].

$$\mathrm{CaSO_4 \,.\, 2\,H_2O(cr) + Na_2CO_3 \,.\, 10\,H_2O(cr) =}$$

$$\mathrm{= CaCO_3(cr) + Na_2SO_4 \,.\, 10\,H_2O(cr) + 2\,H_2O(l)} \qquad (D)$$

the change in the standard molar Gibbs free energy is

$$\Delta_r G^0 = RT[\ln a_{\mathrm{CaCO_3}} + \ln a_{\mathrm{Na_2SO_4\,.\,10\,H_2O}} + 2\ln a_{\mathrm{H_2O}} - \ln a_{\mathrm{CaSO_4\,.\,2\,H_2O}} - \ln a_{\mathrm{Na_2CO_3\,.\,10\,H_2O}}], \quad (3)$$

where a is the activity of the salt in its saturated solution at 25 °C and $\ln a_{H_2O} = 0$ (the activity of pure water is 1). The $\Delta_r G^0$ value so obtained is –23.62 kJ mol^{-1}.

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