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THE TERNARY DIAGRAM OF SYSTEM $\text{Na}_2\text{O}-\text{CdO}-\text{H}_2\text{O}$

AT ROOM TEMPERATURE

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ABSTRACT

The ternary diagram of system $\text{Na}_2\text{O}-\text{CdO}-\text{H}_2\text{O}$ at room temperature has been investigated. CdO and NaOH solids were used to prepare starting reactional systems. They were slowly hydrated by water vapor. Cadmium and sodium were analyzed in saturated solutions, at each step of the hydration process, using an ICP spectrometer. The solubility curves of $\gamma\text{-Cd}(\text{OH})_2$ and $\text{Na}_2\text{Cd}(\text{OH})_4$ were drawn, and a value of the solubility product of $\gamma\text{-Cd}(\text{OH})_2$ is proposed: $K_{\text{sp}} = 4 \cdot 10^{-14}$ at room temperature.

KEYWORDS: A. Inorganic compound, B. Chemical synthesis, D. Phase equilibria.

INTRODUCTION

Cadmium hydroxide $\text{Cd}(\text{OH})_2$ is the active anodic material of the nickel–cadmium battery in discharged state. Since 1930, many studies have been carried out on ternary systems:

$\text{M}_2\text{O}-\text{CdO}-\text{H}_2\text{O}$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$), in which $\text{Cd}(\text{OH})_2$ can be prepared [1–4]. Reports on these studies have often been published without any indication of the allotropic variety β or γ of the hydroxide. In addition, the reacting systems have been constituted from cadmium salts (nitrate and chloride). Such salts are difficult to eliminate by washing; anionic species introduced can cause equilibria to be perturbed. The most reliable studies on the system $\text{Na}_2\text{O}-\text{CdO}-\text{H}_2\text{O}$ have been performed by Scholder and co-workers [1,2]. In a paper published in 1941 [1], Scholder and Staufienbiel proposed a diagram at 373 K. Reacting systems were composed of the solid phase $\beta\text{-Cd}(\text{OH})_2$ and a concentrated solution of sodium hydroxide. Two solid phases containing cadmium exist in this diagram: $\text{Cd}(\text{OH})_2$ and $\text{Na}_2\text{Cd}(\text{OH})_4$. Chemical analyses of cadmium in saturated solutions have been performed by a volumetric method using cadmium dipyridinrhodanid complex [5]. The β variety of cadmium hydroxide (brucite-type structure) as a starting material does not allow diagram study at room temperature because of its high stability.

More recently, we have shown [6–8] that the use of LiOH or KOH gives rise to the β variety, whereas $\gamma\text{-Cd}(\text{OH})_2$ is obtained with NaOH after the formation of disodium tetrahydroxocadmiate $\text{Na}_2\text{Cd}(\text{OH})_4$. We have described a new way to prepare cadmium hydroxide. It consists of a very

slow hydration, at room temperature, of a mixture containing CdO and NaOH solids (similar conditions as these are used in the nickel–cadmium battery).

The aim of this study was the determination, at room temperature, of the solubility curves of γ -Cd(OH)₂ and Na₂Cd(OH)₄. A better understanding of the ternary diagram is of great interest in the synthesis of one of the active materials in the Ni–Cd battery.

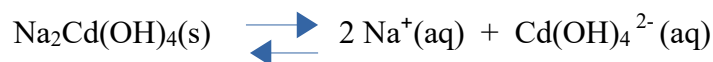
EXPERIMENTAL

For the study of the ternary diagram of the system Na₂O–CdO–H₂O, two starting materials were prepared, using CdO and NaOH. The first material, denoted by line **r1** in Figure 1, contains 62.2 moles of NaOH for 1 mole of CdO. The second, denoted by line **r2**, contains 12.8 moles of NaOH for 1 mole of CdO. These homogeneous starting materials are slowly hydrated by water vapor, because of the hygroscopic character of sodium hydroxide, sheltered from carbon dioxide. During the hydration process, their representative points in the diagram follow a straight line from their starting composition towards the figurative point of pure water (Fig. 1). The evolution was controlled by weighting, to determine the amount of water and then the new composition of the system. In order to reach equilibrium, chemical analyses were performed several days after the completion of each hydration step. Analyses of sodium and cadmium were carried out on the saturated solutions, using inductively coupled plasma (ICP) spectrometer. Samples corresponding to the ten systems situated either on **r1** (62.2) for the most concentrated in Na₂O or on **r2** (12.8) could be analyzed. They were taken out of the saturated solution using a syringe equipped with a 0.2 μ m filter. The sample weight was approximately 300 mg, while the weight of the whole system was about 40 g. Moreover, a visual observation of the reacting system in evolution allowed for confirmation of the limits of crystallization domains of the solid phases.

RESULTS AND DISCUSSION

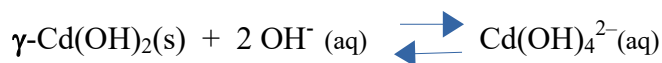
The results (in weight percent) of the chemical analyses are reported in Table 1 and shown in Figure 2, and the ternary diagram is presented in Figure 1. Two solid phases containing cadmium are represented in the diagram (Fig. 1): Na₂Cd(OH)₄ and γ -Cd(OH)₂. Their solubility curves are located very near the baseline H₂O–Na₂O, due to their weak solubility (Fig. 2). The solution saturated in both Na₂Cd(OH)₄ and γ -Cd(OH)₂ is located at 27.8 wt% Na₂O and 7.4×10^{-3} wt% CdO (point N°4). This point corresponds to the intersection of the two solubility curves and permits the limits of the domains of pure solids, Na₂Cd(OH)₄ and γ -Cd(OH)₂, to be accurately defined. These domains are denoted by the dotted areas in Figure 1. The part of the domain of Na₂Cd(OH)₄ beyond 45 wt% Na₂O was not investigated because the systems were too concentrated for solution sampling. Moreover, hydrates of sodium hydroxide can exist in this region.

In Figure 2, the solubility curve located beyond 27.8 wt% Na₂O corresponds to the following equilibrium:

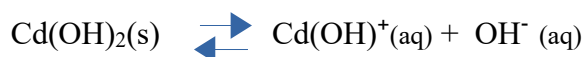


When the concentration of Na⁺ decreased, an increase of solubilized cadmium was observed (see Fig. 2). However, the determination of the solubility product of Na₂Cd(OH)₄ was not possible because of the very strong concentration of sodium hydroxide, which is larger than 12 mol.l⁻¹.

The second solubility curve, below 27.8 wt% Na₂O, corresponds to the solubility equilibrium of γ -Cd(OH)₂:



In this case, when hydroxide ion concentration decreases, solubilized cadmium decreases also (see Fig. 2). When the hydration process is finished, crystals of γ -Cd(OH)₂ obtained have a needle shape which size can reach several tenths of millimeter (Fig. 3). A powder X-ray diffraction pattern showed that the solid obtained was pure γ -Cd(OH)₂, without any trace of β -Cd(OH)₂ (Fig. 4). Therefore, the determination of the solubility product of γ -Cd(OH)₂ was allowed. After washing the crystals five times with pure water for one month, the concentration of cadmium in the saturated solution was determined. The solubility product found at room temperature is $K_{\text{sp}} = 4 \times 10^{-14}$. To our knowledge, this is the first time that K_{sp} for γ -Cd(OH)₂ has been determined. It is to be noted that the solubility of γ -Cd(OH)₂ increases with the different washings. This fact, as it has already been mentioned [4], is due to the formation of the complex Cd(OH)^+ when concentrations of NaOH are below 0.5 mol.l⁻¹.



According to the precedent reacting scheme, when the OH⁻ concentration is decreased by washing, the concentration of Cd(OH)^+ and the solubility of Cd(OH)₂ increase. Nevertheless, for highest concentrations, the tetrahydroxocadmiate complex ion Cd(OH)_4^{2-} is formed. The experimental value of K_{sp} given in several tables for Cd(OH)₂ is about 10⁻¹⁴ and a value calculated from free enthalpies data is 5.3 x 10⁻¹⁵ [9], but although the variety is never specified, it is certainly the most stable: β -Cd(OH)₂. If we compare now our results at room temperature with those obtained by Scholder and Staufienbiel [1] at 373 K, we find that the main difference is the obtention of the γ -Cd(OH)₂ variety, instead of β -Cd(OH)₂. It is to be noted that solubilities are more important at 373 K, as would naturally be expected; for instance, for the disaturated solution, $[\text{Cd}^{2+}] = 10.8 \text{ mmol.L}^{-1}$ at 373 K and $[\text{Cd}^{2+}] = 0.80 \text{ mmol.L}^{-1}$ at room temperature.

A recent publication [10] reported the ternary diagram for system Na₂O–CuO–H₂O at room temperature. In this diagram, CuO (instead of Cu(OH)₂) and Na₂Cu(OH)₄ appear, but the point corresponding to the disaturated solution is nearly 30 wt% Na₂O. This is similar to the cadmium system. On the other hand, solubilities of copper compounds in the presence of hydroxide ions are more important, while K_{sp} of Cu(OH)₂ is smaller (10⁻¹⁹). This means that the complex Cu(OH)_4^{2-} is more stable than the complex Cd(OH)_4^{2-} .

CONCLUSION

This study confirms the results reported in previous publications [6,7]: solubility is more important for γ -Cd(OH)₂. This means that, under the same conditions, γ is less stable than β is, as it has been proved with the determination of decomposition enthalpies for γ and β , by DSC. Thus, γ transforms progressively into β , whose grain size may be important if the transformation is slow. This evolution has a harmful effect on the operating cycles of batteries. Consequently, the use of pure NaOH, which gives rise to the γ variety, must be prohibited.

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TABLE 1
Chemical Composition of Saturated Solutions

System	1	2	3	4	5	6	7	8	9	10
Na ₂ O (wt%)	40.2	37.5	30.1	27.8	26.0	22.9	20.0	14.9	6.8	0.064
NaOH (wt%)	51.9	48.4	38.9	35.9	33.6	29.6	25.8	19.2	8.8	0.083
Density (g/cc)	1.53	1.51	1.42	1.39	1.36	1.32	1.28	1.21	1.10	1.00
NaOH (mol/L)	19.8	18.3	13.8	12.5	11.4	9.8	8.3	5.8	2.4	0.021
CdO $\times 10^{-3}$ (wt%)	0.23	1.00	6.00	7.40	4.50	2.40	1.50	0.78	0.27	0.12
Cd ²⁺ (aq) $\times 10^{-5}$ (mol/L)	2.7	12	66	80	48	25	15	7.3	2.3	0.93

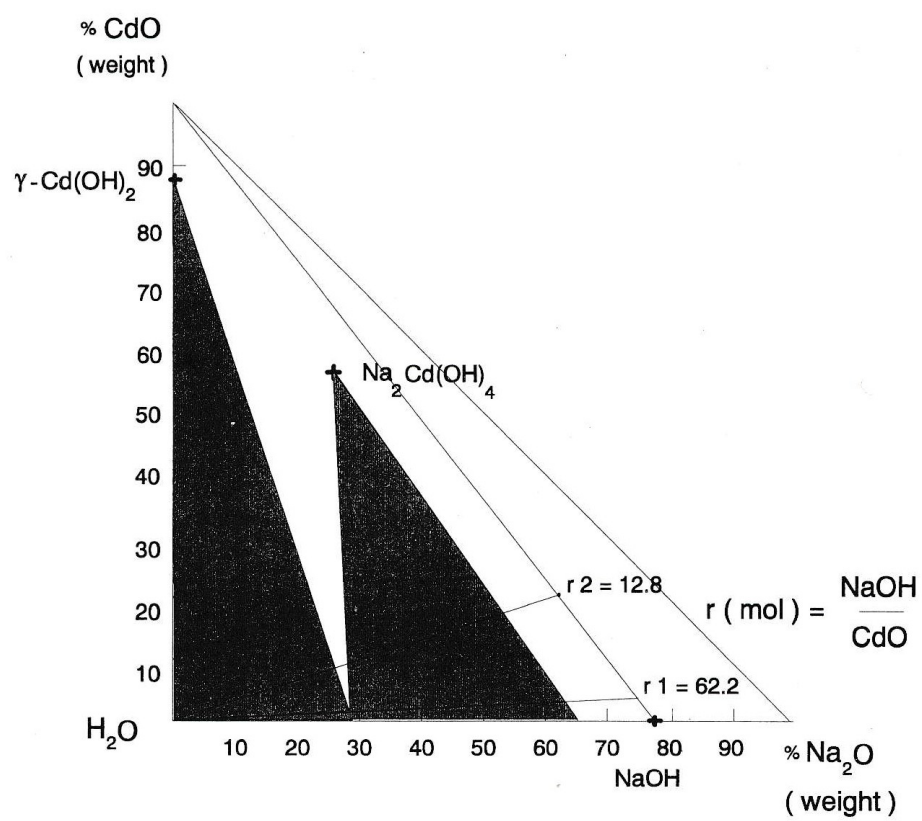


FIG. 1

The ternary diagram of system $\text{Na}_2\text{O}-\text{CdO}-\text{H}_2\text{O}$ at room temperature.

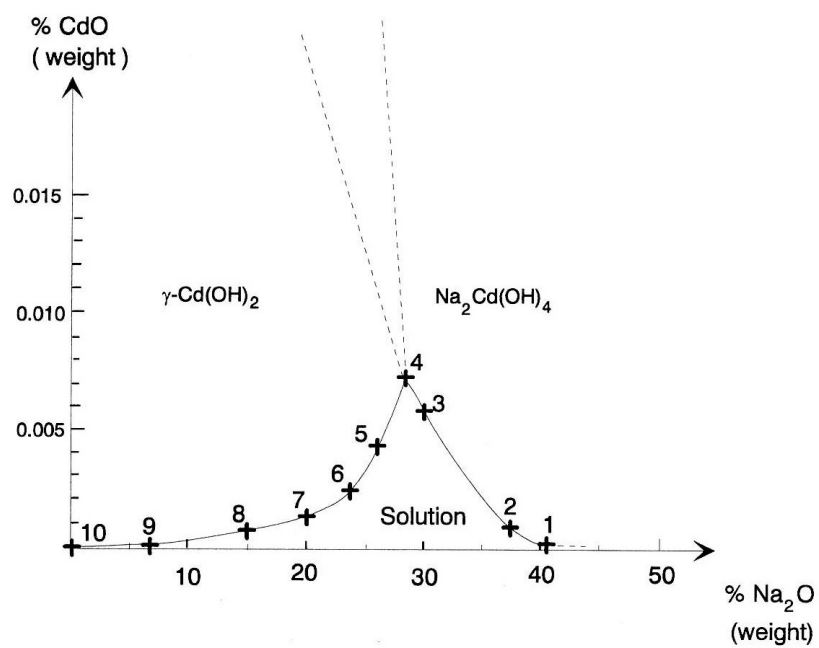


FIG. 2

The ternary diagram of system $\text{Na}_2\text{O}-\text{CdO}-\text{H}_2\text{O}$: solubility curves at room temperature.

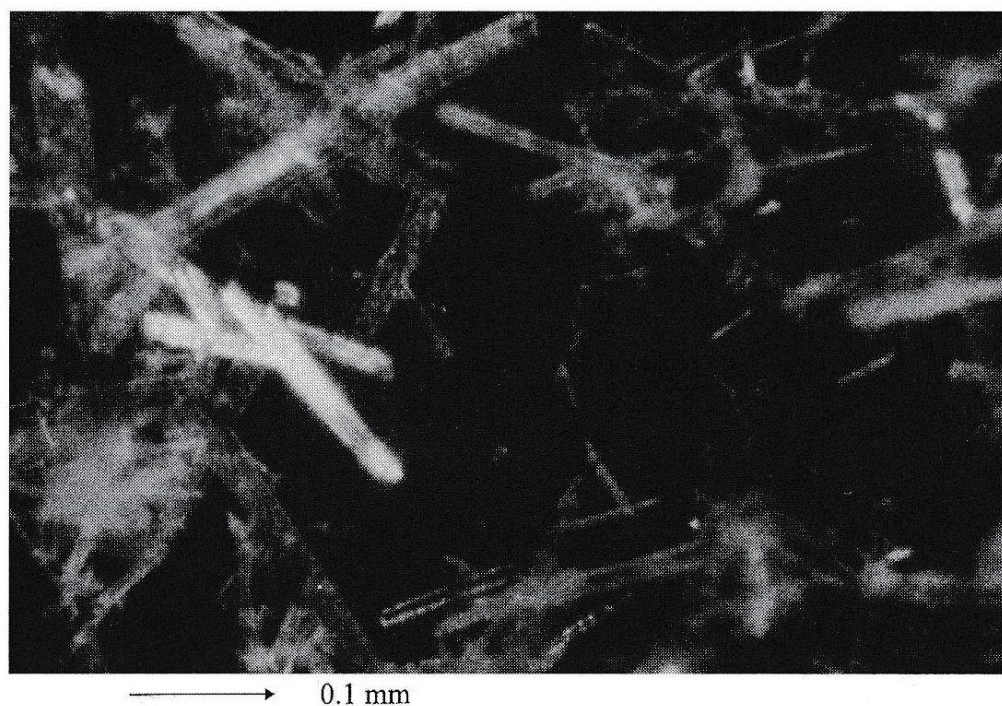


FIG. 3

Optical photograph: $\gamma\text{-Cd}(\text{OH})_2$ crystals.

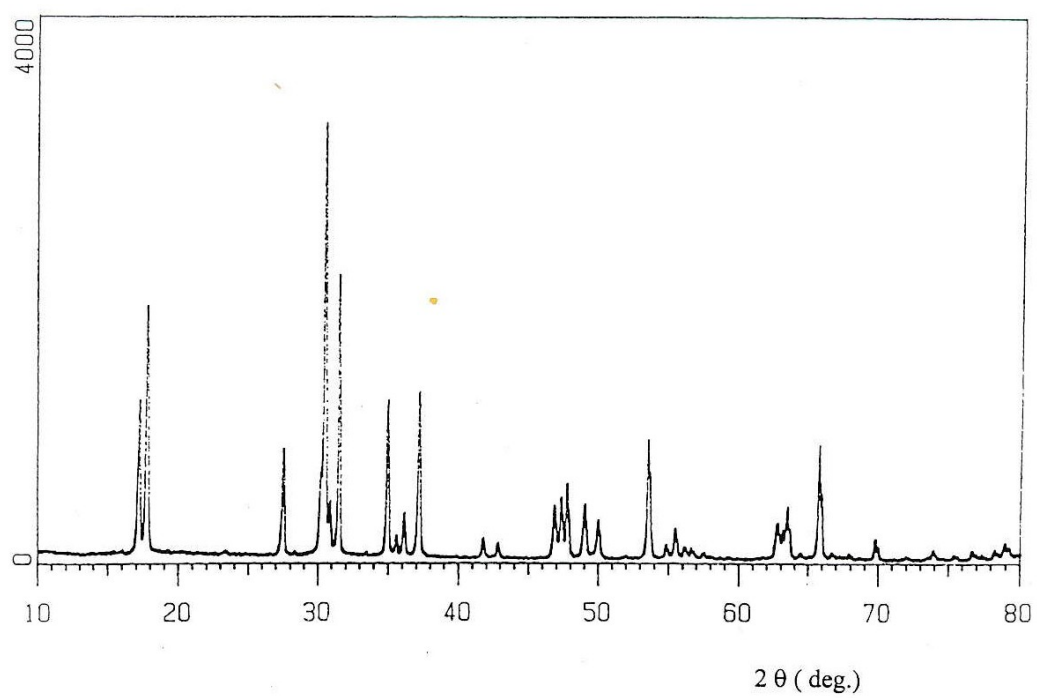


FIG. 4
Powder X-ray diffraction pattern of $\gamma\text{-Cd(OH)}_2$ (Cu $K\alpha$).