Solubilities of Calcium Acetates in the Temperature Range 0–100 °C

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The solubilities of calcium acetate monohydrate and hemihydrate in aqueous solution decrease with increasing temperature, the former and latter phases being stable below and above 58 °C, respectively. The phase transition from either compound into the other one is solution mediated and takes place by a dissolution–recrystallization process which can be followed by X-ray diffraction and optical microscopy.

Introduction

Formerly named brown acetate of lime, calcium acetate was employed in the past as raw material for the production of acetone by decomposition at 400 °C (*1*). This was its main utilization. Accordingly, only a few studies deal with its physical and chemical properties. A recrudescence of interest for this material took place between 1960 and 1970 when it was added to some lubricants of large marine diesel engines. These engines burn fuels containing sulfur derivatives which generate corrosive acid products subsequently neutralized owing to the alkalinity of calcium acetate.

Actually, there are three phases of calcium acetate between room temperature and about 180 °C (*2*): a monohydrate (triclinic, space group $P\bar{1}$), a hemihydrate (structure unknown), and an amorphous phase. The solubilities of the two former phases were investigated only once in 1902 (*3*), but it appears now that both the solubilities and nature of the solid phases in equilibrium with solution were not properly determined. For this reason, we carried out new solubility experiments in order to support our investigations on the crystallization of these materials.

Experimental Section

The solubilities of $(CH_3COO)_2Ca{\cdot}H_2O$ and $(CH_3COO)_2Ca{\cdot}0.5H_2O$ decrease with increasing temperature. We used this property for the solubility measurements. Saturated aqueous solutions of calcium acetate were prepared at 5 °C and pH 7.8, poured into a thermostated vessel at constant temperature, and stirred with a magnetic stirrer at 500 rpm until crystallization occurred and equilibrium was achieved. In all cases equilibrium between the new formed crystals and solution was achieved within 24 h. The calcium content in the supernatant was analyzed by a complexometric method (EDTA titrimetric method, AFNOR NF T 90-016). The accuracy of the measurement is about 0.5%.

To determine the nature of the crystalline phases, the crystals were removed from the solution, dried at room temperature, and analyzed by recording X-ray diffraction patterns with an INEL diffractometer equipped with a curved position sensitive detector. The interreticular distances (*d* spacings) measured for both monohydrate and hemihydrate are in agreement with those found in an earlier work (*2*).

Results and Discussion

Solubilities. The solubility values are given in Table I and displayed in Figure 1. As they are often expressed in different units according to whether they are used for laboratory or industrial aims, we also measured the solution densities which must be known for unit conversion (Table II). We determined this density by an oscillation measurement (AFNOR NF T 60-172 method).

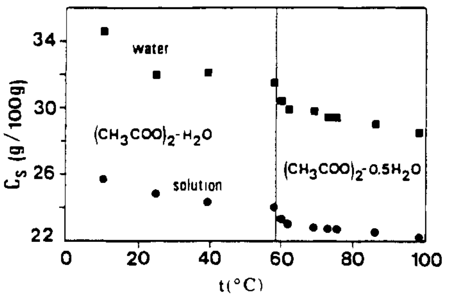

Figure 1. Solubilities (C_s) of calcium acetates, monohydrate and hemihydrate, expressed in terms of anhydrous calcium acetate per 100 g of water or solution versus temperature.

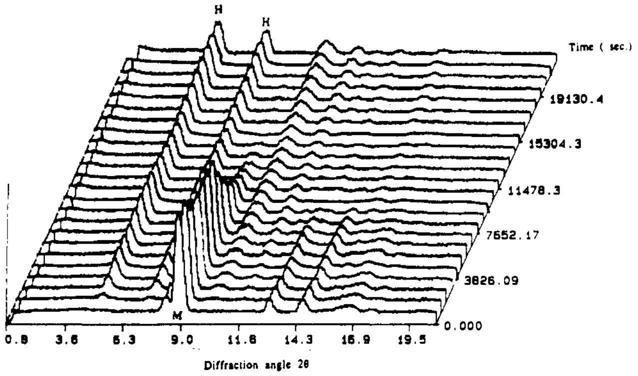

Figure 2. Evolution of the diffraction patterns of calcium acetate monohydrate transforming into hemihydrate in the presence of water (*t* = 70 °C).

Table I. Solubilities of Calcium Acetate Monohydrate ($t <$ 58 °C) and Hemihydrate ($t >$ 58 °C) Expressed in Terms of Anhydrous Calcium Acetate

	C_s		
t/°C	mol/L	g/100 g of solution	g/100 g of water
10.5	1.86	25.7	34.6
24.7	1.79	24.8	32.0
39.1	1.75	24.3	32.1
58.0	1.72	24.0	31.5
60.2	1.67	23.3	30.4
62.0	1.65	23.0	29.9
69.0	1.64	22.8	29.8
72.8	1.62	22.7	29.4
75.5	1.62	22.7	29.4
86.0	1.60	22.5	29.0

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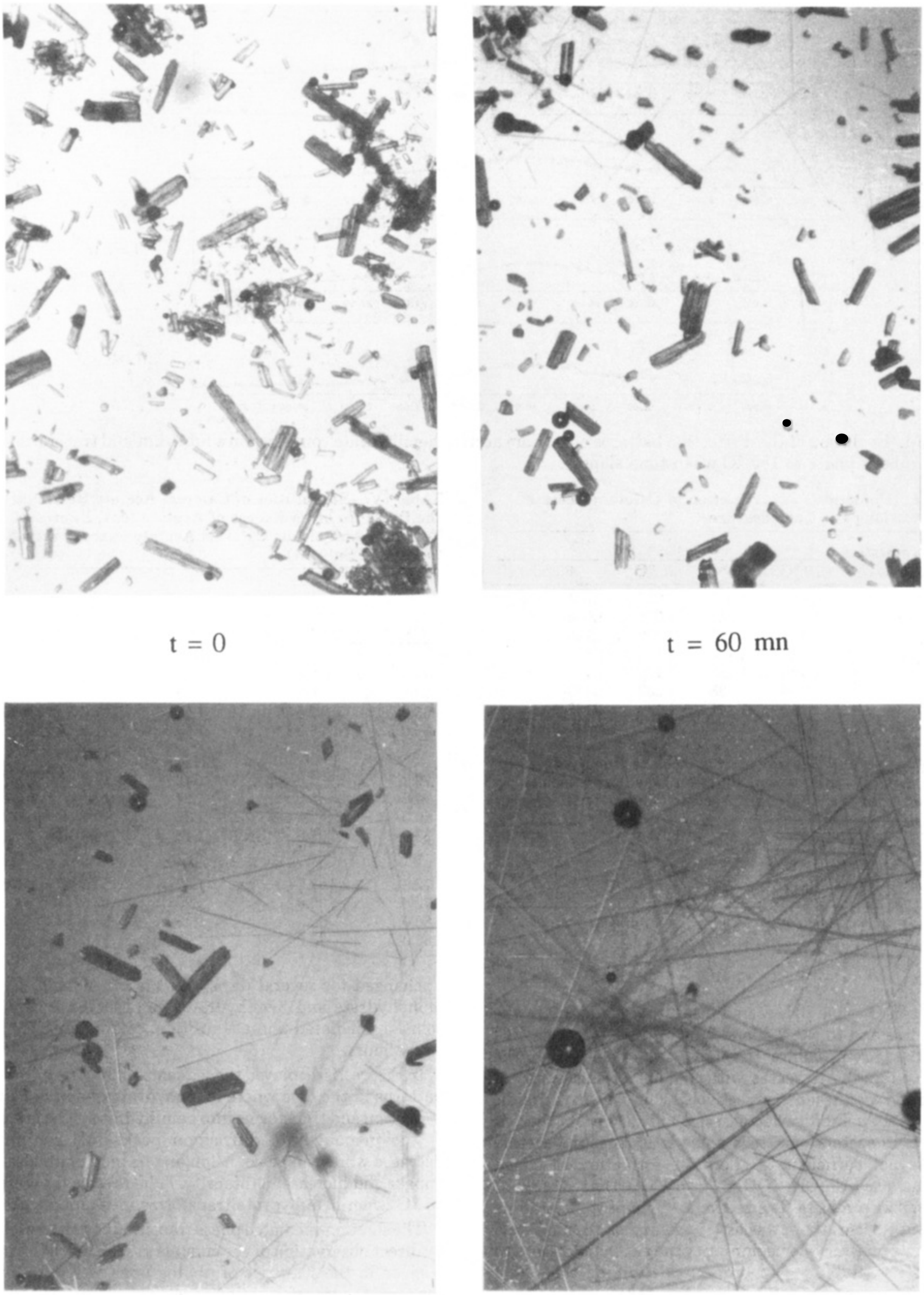

t = 0

t = 60 mn

t = 120 mn

t = 300 mn

Figure 3. Observation by optical microscopy of the phase transition $(CH_3COO)_2Ca\cdot 0.5H_2O \rightarrow (CH_3COO)_2Ca\cdot H_2O$.

Since in industrial processes, calcium acetates are produced by reaction of acetic acid with lime wash, there is often an excess of calcium or acetate ions in the final solution. As solubility is influenced by an excess of either ion, we performed a few solubility measurements under nonstoichiometric conditions, for temperatures larger than 58 °C as we are especially interested in calcium acetate hemihydrate. Calcium was added as $CaCl_2\cdot 2H_2O$ whereas acetate was added as (CH3-

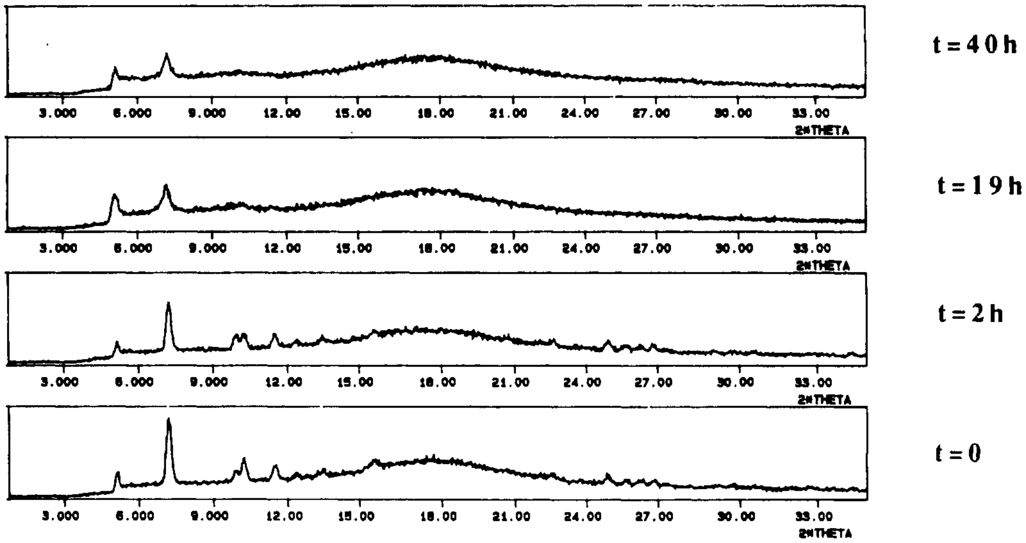

Figure 4. Evolution of the diffraction patterns of calcium acetate hemihydrate contained in a lubricant and transforming into an amorphous phase at 180 °C when time elapses.

Table II. Densities ρ as a Function of Calcium Acetate Concentrations and Temperature

calcium acetate concn/(mol/L)	$\rho/(g\cdot cm^{-3})$			
	10 °C	20 °C	25 °C	35 °C
0.35	1.031	1.029	1.027	1.024
0.72	1.060	1.059	1.055	1.053
1.36	1.115	1.113	1.109	1.106
1.50	1.124	1.123	1.120	1.115
1.65	1.134	1.131	1.128	1.124
1.72	1.138	1.138	1.132	1.130
1.73	1.142	1.141	1.137	1.133
1.77	1.146	1.144	1.140	crystallization

Table III. Solubilities of Calcium Acetate Hemihydrate in the Presence of an Excess of Calcium Ions, Expressed in Terms of Anhydrous Calcium Acetate (Excess with Respect to 100 g of Solvent)

t/°C	excess/(% mass)	C_s		
		mol/L	g/100 g of solution	g/100 g of water
73	1	1.54	21.3	27.1
73	2	1.43	19.7	24.6
87	1	1.52	21.1	26.7
87	2	1.41	19.5	24.2

Table IV. Solubilities of Calcium Acetate Hemihydrate in the Presence of an Excess of Acetate Ions, Expressed in Terms of Anhydrous Calcium Acetate (Excess with Respect to 100 g of Solvent)

t/°C	excess/(% mass)	C_s		
		mol/L	g/100 g of solution	g/100 g of water
		pH 5		
72.8	2.5	1.58	22.1	28.4
72.8	5.0	1.57	21.9	28.0
86.0	2.5	1.54	21.6	27.5
86.0	5.0	1.54	21.5	27.4
		pH 8		
72.7	2.5	1.42	19.9	24.7
72.7	5.0	1.24	17.4	21.0
86.0	2.5	1.36	19.1	23.6
86.0	5.0	1.18	16.6	19.9
		pH 10.5		
72.8	2.5	1.47	20.5	25.7
72.8	5.0	1.25	17.5	21.2
86.0	2.5	1.45	20.2	25.3
86.0	5.0	1.21	17.0	20.4

COO)Na·H_2O. The pH was adjusted to 7.8 and 9.0 in the former case and to 5.0, 7.8, and 10.5 in the latter with HCl or NaOH. From Tables III and IV it appears that the solubility rapidly decreases with and increasing excess of calcium and acetate ions, respectively. However, in the acidic pH range, the solubility decreases by only 2% when there is an excess in acetate ion. It is noteworthy that the acetate excess is not sufficient to allow the formation of mixed compounds as $n\mathrm{Ca(CH_3COO)_2}\cdot m\mathrm{(CH_3COOH)}\cdot k\mathrm{H_2O}$ (*3*).

Phases and Phase Transitions. Since two crystalline phases may occur, there was always some risk to nucleate a metastable phase at the beginning of the experiments and to measure its solubility. In order to determine the phase transition mechanism and evaluate the transformation rate, we recorded sequences of X-ray diffraction patterns. After the solubility measurements, the crystals were left, on the one hand, in their mother solutions or, on the other hand, removed from these solutions and dried. In both cases, the samples were then placed out of their temperature stability range. The transformation of the monohydrate was studied at 70 °C, while that of the hemihydrate was studied at 25 °C. With the dry crystals, we could never detect any solid-state phase transition, the X-ray diffraction patterns remaining unchanged for several days. On the other hand, for both monohydrate and hemihydrate, we observed a very quick solution-mediated phase transition, completely ended after a few hours.

In Figure 2 is displayed the sequence of the X-ray diffraction patterns in the case where monohydrate undergoes a phase transition and transforms into hemihydrate. The intensities of the monohydrate diffraction peaks (M) continuously decrease while the peaks belonging to the hemihydrate (H) appear and increase in intensity. The reverse is observed at 25 °C when hemihydrate transforms into monohydrate.

The solution-mediated phase transition can also be followed by direct observation of the crystals in solution. An example is given in the sequence of photographs of Figure 3 which concerns the transformation of calcium acetate hemihydrate into calcium acetate monohydrate. The hemihydrate crystals exhibit a rodlike habit whereas the monohydrate crystals exhibit a very elongated needlelike habit. In the unstirred solution where the sequence of photographs was taken the transformation took place within 6 h. Actually, the transformation rate increases very rapidly with increasing stirring rate. Accordingly, there is no doubt that after 24 h all our solutions were in equilibrium with a stable phase: either monohydrate below 58 °C or hemihydrate above 58 °C.

Amorphous Phase. Since an amorphous phase was observed above 140 °C (2) and due to the fact that the lubricant containing calcium acetate hemihydrate crystals may attain temperatures larger than 140 °C, we tried to check whether the amorphous phase may occur inside the lubricant and eventually at which rate the transformation takes place. For studying this phenomenon, we used a typical marine lubricant (mixture of base oils and additives) prepared in our laboratory. It was a dense suspension of hemihydrate crystals (75 wt %), the size of which ranged from 0.5 to 1.5 μm.

The sample was placed at constant temperature, 180 °C, and the evolution of the crystals was followed by removing small portions of lubricant and recording X-ray diffraction patterns. A sequence of four patterns is shown in Figure 4; they were recorded at time, 0, 2, 19, and 40 h. After this period of time, the hemihydrate inside the lubricant was almost completely transformed into the amorphous phase. Only its two main peaks were still observable on the diffraction pattern. A thermogravimetric method confirmed that 0.5 molecule of water per molecule of calcium acetate was lost during this transformation.

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