FORMATION OF A DOUBLE SALT AND MIXED CRYSTALS IN THE $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O SYSTEM

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By solubility method in the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 25 and 50 °C, the formation of a double salt $CaCd(HCOO)_4$ and mixed crystals $Ca_{1-x}Cd_x(HCOO)_2$ was established. The double salt formation is explained by the electronic configuration of the metal ions involved. Formation of the mixed crystals, possessing the α-$Ca(HCOO)_2$ structure, is attributed to the ability of the Cd^{2+} ions to accept the coordination environment, characteristic of the Ca^{2+} ions in α-$Ca(HCOO)_2$.

Key words: Solubility diagrams; Calcium/cadmium formate double salt; Calcium/cadmium formate mixed crystals; Calcium; Cadmium.

In our previous paper[1], formation of the $CdSr(HCOO)_4 \cdot H_2O$ double salt in the $Cd(HCOO)_2$–$Sr(HCOO)_2$–H_2O system at 50 °C has been established. In the literature, there are also data on a double salt with the composition $BaCd(HCOO)_4 \cdot 2\,H_2O$, which has been obtained in the corresponding ternary system at 25 °C (ref.[2]). It was of interest to study the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at different temperatures because a thorough investigation would give more complete information on the solid phases formed in the system.

The purpose of the present work was to study the solubility diagram of the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 25 and 50 °C and to characterize the solid phases obtained. There are no literature data on the cocrystallization of calcium and cadmium formates.

EXPERIMENTAL

The calcium and cadmium formates were prepared by neutralization of dilute formic acid (1 : 1) with the corresponding carbonates at 70–80 °C. The metal formate solutions were filtered and concentrated. The crystals were obtained after cooling the solutions at room temperature, then recrystallized from distilled water and dried in air. Chemical and X-ray powder analysis showed that α-$Ca(HCOO)_2$ and $Cd(HCOO)_2 \cdot 2\,H_2O$ were obtained. The other reagents used were of analytical grade.

The solubility in the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system was studied by the Khlopin method of isothermal decrease of supersaturation[3]: aqueous solutions of both salts taken, in different ratios, were prepared at 60–70 °C, then were cooled in a thermostat at 25 and 50 °C and stirred until a constant concentration of the saturated solution, *i.e.* equilibrium, was achieved. Preliminary experiments showed that the equilibrium in the system was attained in about 15–20 h. The suspension was then filtered and the liquid and the wet solid were analyzed. The solubility in the system was investigated in the presence of a 2% excess of formic acid to prevent hydrolysis. The concentration of the metal ions in both phases was determined complexometrically as follows: Cd^{2+} at pH 6 using Xylenol Orange as indicator, the sum Ca^{2+}–Cd^{2+} at pH 10 using Eriochrome Black T as indicator, and the Ca^{2+} concentration was calculated by difference. The solid phase composition was determined by the graphic method of Schreinemakers for wet residues[4].

Thermal investigations were carried out on a Paulik–Paulik Erday MOM OD-102 derivatograph. DTA and TG curves were obtained in static air atmosphere with a sample mass of 300 mg, at a heating rate of 10 °C min^{-1} from ambient temperature to 600 °C using a standard corundum crucible. The reference substance was pure α-Al_2O_3. X-Ray diffraction analysis was carried out with a DRON-3 powder diffractometer using CuKα radiation with nickel filter.

RESULT AND DISCUSSION

The solubility data for the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 25 °C are listed in Table I, the solubility diagram is shown in Fig. 1. Three crystallization fields are seen in the solubility diagram: of simple salt $Cd(HCOO)_2 \cdot 2\,H_2O$, of double salt $CaCd(HCOO)_4$ and mixed crystals with composition $Ca_{1-x}Cd_x(HCOO)_2$. The double salt crystallizes from solutions containing 14.16 wt.% calcium formate and 3.70 wt.% cadmium formate up to solutions containing 8.94 wt.% calcium formate and 10.98 wt.% cadmium formate.

The solid phase was isolated from the system by filtering, washing with alcohol and drying in air, and then identified by chemical analysis, X-ray powder diffraction and DTA.

Chemical analysis of the colorless double salt shows 60.58 wt.% calcium formate and 39.40 wt.% cadmium formate (theoretical composition 60.87 and 39.13 wt.%, respectively). There is no indication about the double salt in the literature.

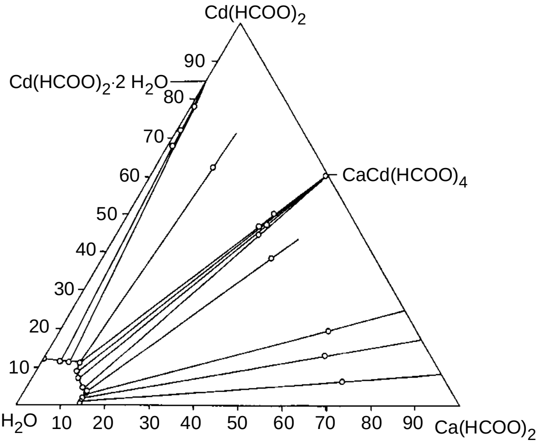

FIG. 1
Solubility diagram of the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 25 °C (in wt.%)

X-Ray diffraction phase analysis confirms the results of the solubility diagram data. As can be seen in Fig. 2, where diffraction patterns of different solid phases are compared, there are three solid phases in the system. The X-ray pattern of the double salt $CaCd(HCOO)_4$ differs from those of $Cd(HCOO)_2 \cdot 2\,H_2O$ (ref.[5]) and α-$Ca(HCOO)_2$ (ref.[6]) indicating the formation of a new solid phase in the system. The diffraction patterns of mixed crystals of different composition are very close to that of α-$Ca(HCOO)_2$, *i.e.*, the mixed crystals possess the α-$Ca(HCOO)_2$ crystal structure. As an example, the pattern of mixed crystals with composition $Ca_{0.88}Cd_{0.12}(HCOO)_2$ is shown in Fig. 2.

Thermal decomposition of $CaCd(HCOO)_4$ was studied by TG and DTA. The TG, DTA and DTG curves of the double salt are shown in Fig. 3. It can be seen in Fig. 3 that the decomposition begins at about 300 °C and ends at about 500 °C. Three effects are registered on the DTA curve: an exothermic effect with the maximum at 330 °C, an endothermic effect with the maximum at 360 °C and a strong exothermic effect with the maximum at 440 °C. The solid decomposition products at 500–600 °C are $CaCO_3$ and CdO (according to the X-ray analysis). The two processes, decomposition of the double salt and of $Ca(HCOO)_2$ and $Cd(HCOO)_2$, occur simultaneously.

TABLE I

Solubility in the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 25 °C

Liquid phase, wt.%		Wet solid phase, wt.%		Solid phase
$Ca(HCOO)_2$	$Cd(HCOO)_2$	$Ca(HCOO)_2$	$Cd(HCOO)_2$	
14.12	–	–	–	$Ca(HCOO)_2$
13.57	0.90	70.31	6.55	$Ca_{0.94}Cd_{0.06}(HCOO)_2$
13.67	2.18	62.90	13.28	$Ca_{0.88}Cd_{0.12}(HCOO)_2$
13.81	3.22	60.55	19.46	$Ca_{0.82}Cd_{0.18}(HCOO)_2$
14.16	3.70	38.72	38.47	transition point
12.53	4.84	44.77	32.51	$CaCd(HCOO)_4$
10.23	7.22	32.92	46.80	$CaCd(HCOO)_4$
9.45	8.91	31.15	46.19	$CaCd(HCOO)_4$
9.07	10.61	33.09	50.22	$CaCd(HCOO)_4$
8.94	10.98	12.90	62.64	eutonics
6.56	11.13	1.52	77.96	$Cd(HCOO)_2 \cdot 2\,H_2O$
4.00	11.38	1.03	68.03	$Cd(HCOO)_2 \cdot 2\,H_2O$
3.91	11.43	1.22	72.83	$Cd(HCOO)_2 \cdot 2\,H_2O$
–	12.45	–	–	$Cd(HCOO)_2 \cdot 2\,H_2O$

According to the literature data, gaseous decomposition products of metal formates always contain H_2, CO and CO_2 (refs[7–11]). This and the agreement between calculated and experimental values of the mass loss allow the assumption of the following thermal decomposition of $CaCd(HCOO)_4$:

$$CaCd(HCOO)_4\ (s) \xrightarrow{500–600\ °C} CaCO_3\ (s) + CdO\ (s) + H_2\ (g) + CO\ (g) + CO_2\ (g)$$

$\Delta m_{exp} = 31.17\%$; $\Delta m_{th} = 31.29\ \%$

In order to establish the type of the double salt, congruent or incongruent, the following experiment was carry out: saturated aqueous solution of the double salt was evaporated isothermally at 25 °C to dryness. X-Ray analysis of the dry residue showed two phases, $CaCd(HCOO)_4$ and α-$Ca(HCOO)_2$, which means that the double salt is incongruently soluble at 25 °C (ref.[12]).

Crystalline samples for investigation are mostly obtained by isothermal evaporation. It is known that only congruently soluble double salts can be obtained in this way. van't Hoff[13] has studied in detail the effect of temperature on the formation and decomposition of double salts from a viewpoint of physico-chemical analysis. According to the rule deduced by him, with rising temperature $CaCd(HCOO)_4$ should change from incongruent at 25 °C to congruent due to the broadening of its crystallization field. That is why the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system was also studied at 50 °C.

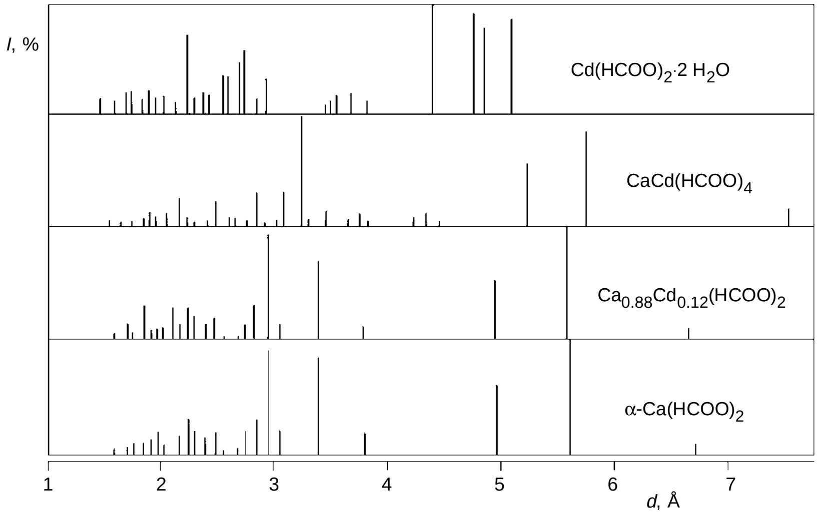

FIG. 2
X-Ray diffraction pattern of solid phases from the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 25 °C

The experimental results obtained at 50 °C are presented in Table II and Fig. 4. The solubility diagram is similar to that at 25 °C. The $CaCd(HCOO)_4$ crystallizes from solutions containing 14.04 wt.% calcium formate and 4.88 wt.% cadmium formate up to solutions containing 5.29 wt.% calcium formate and 22.58 wt.% cadmium formate. X-Ray analysis showed the same crystal structure of the solid phases in the system like at 25 °C. As expected, the double salt is congruently soluble, the X-ray analysis of a simple, obtained after isothermally evaporation at 50 °C of saturated aqueous solution of the double salt showed only one phase, $CaCd(HCOO)_4$ (ref.[12]).

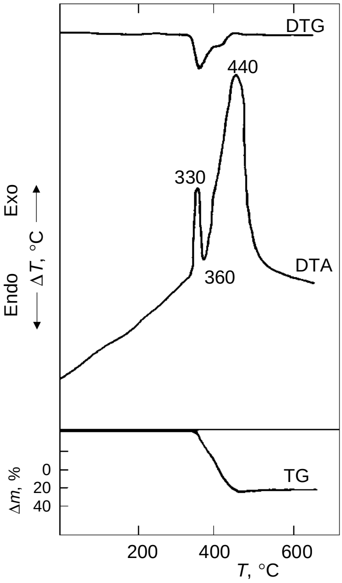

FIG. 3
TG, DTA and DTG curves of $CaCd(HCOO)_4$

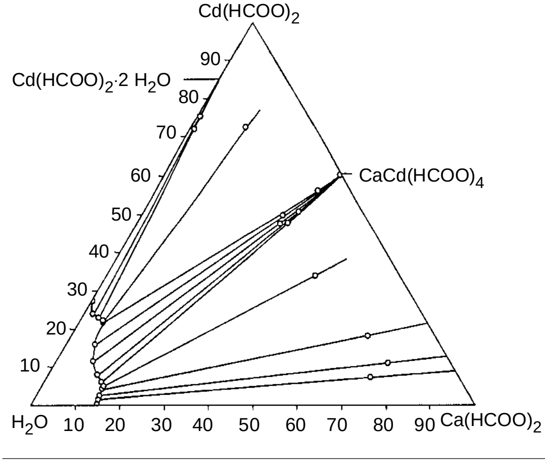

FIG. 4
Solubility diagram of the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 50 °C (in wt.%)

The formation of a double salt and mixed crystals in the same system is an interesting and rare phenomenon. It is known the assumption of Retgers[14] that formation of double salts and mixed crystals between the components of the same system exclude each other, *i.e.*, the interaction excludes the mixing. However, recent experimental data do not confirm this. For example, in the $Mn(CH_3COO)_2$–$Zn(CH_3COO)_2$–H_2O system at 60 °C, formation of a double salt and mixed crystals is observed[15]. In the $MgBr_2$–$ZnBr_2$–H_2O and $MnBr_2$–$ZnBr_2$–H_2O systems at 25 °C, coexistence of a double salts and mixed crystals has also been established[16]. However, this has not yet been found with a formate system.

The existence of a double salt of calcium and cadmium formate can be explained by the rule on the correlation between the electronic configuration of participating metal ions and the possibility of formation of double salt in the system of the type salt–salt–water. It has been established that, similarly to the chloride[17], bromide[18] and acetate[19] systems, double salts are formed in formate systems when both or at least one of the cations have ns^2, np^6 or $(n-1)d^{10}$ configuration of valence electrons[20]. For each of the cations and CFSE = 0, the metal–ligand bonds do not require a definite spatial orientation[17]. This allows strong deformation of their coordination polyhedra, which favours

TABLE II
Solubility in the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system at 50 °C

Liquid phase, wt.%		Wet solid phase, wt.%		Solid phase
$Ca(HCOO)_2$	$Cd(HCOO)_2$	$Ca(HCOO)_2$	$Cd(HCOO)_2$	
15.07	–	–	–	$Ca(HCOO)_2$
14.39	1.44	72.82	7.13	$Ca_{0.94}Cd_{0.06}(HCOO)_2$
14.20	2.25	75.02	11.19	$Ca_{0.91}Cd_{0.09}(HCOO)_2$
13.97	4.03	66.85	18.29	$Ca_{0.85}Cd_{0.15}(HCOO)_2$
14.04	4.88	47.15	30.06	eutonics
12.92	5.89	34.14	47.49	$CaCd(HCOO)_4$
11.10	8.09	34.94	50.95	$CaCd(HCOO)_4$
8.41	11.61	32.52	47.35	$CaCd(HCOO)_4$
6.50	15.98	31.87	49.93	$CaCd(HCOO)_4$
5.37	21.78	37.09	55.78	$CaCd(HCOO)_4$
5.29	22.58	12.32	72.48	eutonics
4.14	22.92	1.16	72.08	$Cd(HCOO)_2 \cdot 2\ H_2O$
2.03	24.21	0.87	75.58	$Cd(HCOO)_2 \cdot 2\ H_2O$
–	27.80	–	–	$Cd(HCOO)_2 \cdot 2\ H_2O$

double salt formation. The two cations, Ca^{2+} and Cd^{2+}, participating in the $CaCd(HCOO)_4$, have $4p^6$ and $5s^24d^{10}$ configuration, respectively.

The formation of mixed crystals in the system can be explained using the theory of isomorphous and isodimorphous cocrystallization[21]. The formation of isomorphous and isodimorphous mixed crystals occurs when the admixed ion may assume the coordination environment of the substituted ion in the crystal structure of the host salt. If the stable crystal form of the admixed salt is not isomorphous with the host crystal under the experimental conditions (*i.e.* a crystallization into another space group or is of another chemical type, *e.g.* another crystal hydrate), the existence of mixed crystals may be interpreted as an indication of the existence of a polymorphous form of the admixed salt, which is metastable under the given conditions and which is isomorphous with the host crystal.

Calcium formate is known as an anhydrous salt crystallizing in several polymorphous forms: α, β, γ and δ (refs[6,22,23]). Under the experimental conditions used, temperature 25 and 50 °C, the α form (orthorhombic) is stable modification.

Cadmium formate crystallizes as a dihydrate from aqueous solutions at temperatures up to 66 °C being an anhydrous salt above this temperature[24]. One polymorphous form, monoclinic, of $Cd(HCOO)_2 \cdot 2\,H_2O$ is known[5]. Anhydrous cadmium formate has two polymorphous modifications – orthorhombic[25] and monoclinic[26]. According to Haussühl[25], the orthorhombic $Cd(HCOO)_2$ and α-$Ca(HCOO)_2$ are isostructural.

The inclusion of Cd^{2+} ions in the crystal lattice of α-$Ca(HCOO)_2$ is determined by the ability of Cd^{2+} ions to accept the coordination environment characteristic of the Ca^{2+} ions in α-$Ca(HCOO)_2$. The existence of $Cd(HCOO)_2$ (metastable under experimental conditions), isostructural with α-$Ca(HCOO)_2$, confirms this opinion. Formation of mixed crystals on the basis of $Cd(HCOO)_2 \cdot 2\,H_2O$ is not observed in the system. This means that Ca^{2+} cannot assume the coordination environment around the Cd^{2+} ions in its formate dihydrate.

CONCLUSION

The solubility diagrams of the $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O system have been investigated at 25 and 50 °C showing the existence of a double salt with composition $CaCd(HCOO)_4$, which is incongruent at 25 and congruent at 50 °C. Isodimorphous mixed crystals with composition $Ca_{1-x}Cd_x(HCOO)_2$ having the structue of α-$Ca(HCOO)_2$ is formed in the system together with the double salt.

The coexistence of a double salt and mixed crystals in the system $Ca(HCOO)_2$–$Cd(HCOO)_2$–H_2O can be considered rather an exception than a general case. The existence of $CaCd(HCOO)_4$ is associated with the electronic configuration of Ca^{2+} ions ($4p^6$) and Cd^{2+} ($5s^24d^{10}$), *i.e.*, the ions that allow strong deformation of their coordination polyhedra, which favours double salt formation. The formation of the mixed crystals $Ca_{1-x}Cd_x(HCOO)_2$

is related to the ability of the Cd^{2+} ions to assume the coordination environment typical of Ca^{2+} ions in α-$Ca(HCOO)_2$.

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