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On Solid Solution Formation in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O System

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Solubility in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system has been studied at 25 and 50°C. Three series of solid solutions are formed in the system at 50°C: solid solutions having the $Co(HCOO)_2 \cdot 2H_2O$ crystal structure as a matrix and solid solutions having the $Cu(HCOO)_2 \cdot 2H_2O$ crystal structure as a matrix. It was established that the crystal structure of the monoclinic $Cu(HCOO)_2 \cdot 2H_2O$ undergoes a change into a new crystal structure (solid solutions) in the concentration range $Cu_{0.83}Co_{0.17}(HCOO)_2 \cdot 2H_2O$–$Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$. The same phenomenon was observed in the $Cu(HCOO)_2$–$Mg(HCOO)_2$–H_2O system at 50°C. The X-ray diffraction spectra of the samples $Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$ and $Cu_{0.73}Mg_{0.27}(HCOO)_2 \cdot 2H_2O$ are proved to be identical. Since the new crystal phase contains a copper formate dihydrate as a main component a hypothesis has been made that a new polymorphous modification of $Cu(HCOO)_2 \cdot 2H_2O$ is probably formed due to included cobalt and magnesium ions in the copper formate dihydrate crystal structure. The new polymorphous modification of $Cu(HCOO)_2 \cdot 2H_2O$ is supposed to be built up by the structural element $Cu(HCOO)_4(H_2O)_2$. Two type of solid solutions are formed in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system at 25°C: solid solutions based on $Cu(HCOO)_2 \cdot 4H_2O$ and solid solutions based on $Co(HCOO)_2 \cdot 2H_2O$. Cobalt formate dihydrate retains its crystal structure up to a maximum of 50 mol% copper formate.

Introduction

The present paper continues our previous studies on the cocrystallization of copper formate dihydrate and formate dihydrates of magnesium, cadmium, and zinc (*1–3*). The metal formate dihydrates $Me(HCOO)_2 \cdot 2H_2O$ (Me = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd) crystallize in the monoclinic system, space group $P2_1/c$. The metal ions occupy two sets of nonequivalent centers of symmetry: the metal ion at the Me(1)-site is coordinated by six oxygen atoms from formate groups; the metal ion at the Me(2)-site is coordinated by four water molecules and two oxygen atoms from formate groups (*4–12*). The same crystal structure of the salts defines the possibility for the formation of continuous series of solid solutions during their cocrystallization from aqueous solutions. However, the experimental results for the isostructural pairs $Cu(HCOO)_2 \cdot 2H_2O/Mg(HCOO)_2 \cdot 2H_2O$ and $Cu(HCOO)_2 \cdot 2H_2O/Zn(HCOO)_2 \cdot 2H_2O$ show some deviation from the classical isomorphous theory rules. Two series of solid solutions are formed in the $Cu(HCOO)_2$–$Zn(HCOO)_2$–H_2O system at 50°C (*3*). Three series of solid solutions are formed in the $Cu(HCOO)_2$–$Mg(HCOO)_2$–H_2O system at 50°C: the $Mg(HCOO)_2 \cdot 2H_2O$ matrix includes a maximum of 50 mol% copper formate and the $Cu(HCOO)_2 \cdot 2H_2O$ matrix–includes a a maximum of about 2 mol% magnesium formate. The obtained solid solutions retain the crystal structure of the salts $Mg(HCOO)_2 \cdot 2H_2O$ and $Cu(HCOO)_2 \cdot 2H_2O$, respectively. A new type solid phase (solid solutions) is formed within the narrow concentration range $Cu_{0.75}Mg_{0.25}(HCOO)_2 \cdot$

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$2H_2O$–$Cu_{0.70}Mg_{0.30}(HCOO)_2 \cdot 2H_2O$ having a crystal structure which is different from those of the simple formate dihydrates (*1*).

The present paper aims at studying cocrystallization in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system in order to establish the influence of copper ions on the Cu_xCo_{1-x} $(HCOO)_2 \cdot 2H_2O$ solid solution type. There are no literature data on the cocrystallization of the pair $Cu(HCOO)_2 \cdot 2H_2O/Co(HCOO)_2 \cdot 2H_2O$.

Experimental

The metal formates were prepared by reaction of the corresponding metal hydroxide carbonates with dilute formic acid solutions at 70–80°C. The crystals were obtained by slow evaporation of the solutions at room temperature, then recrystallized in water and dried in air. The reagents used were "p.a." (Merck). The solubility in the system was studied using the method of isothermal decrease of supersaturation. Aqueous solutions containing different quantities of the salts were prepared at 70–80°C. Then the solutions were cooled in a thermostat to 25 and 50°C and stirred. Preliminary experiments show that the equilibrium between the liquid and solid phases was reached in about 2 days. The experiments were carried out in the presence of a slight excess of formic acid (about 1–2 mass%) in order to suppress salt hydrolysis. The liquid phase and the wet solid phase concentrations were determined as follows: the sum of the copper and cobalt formate concentration was determined complexometrically at pH = 5.5–6 using xylenol orange as indicator; the copper formate concentration was determined iodometrically. The cobalt formate concentration was estimated by difference. A variation of the Schreinemaker method was used for to calculate the ideally dry solid phase concentration (*13*). The solid phases were washed with alcohol, dried in air, and analyzed as above. The X-ray powder analysis was carried out by means of a DRON-3 powder diffractometer using Fe-filtered Co*K*α radiation. The 2θ diffraction range was 10–60°. The lattice parameters were calculated from diffractometric data by least squares refinements using 25 reflections. The IR spectra were recorded on a UR-20 Zeiss spectrometer in the 500–3600 cm^{-1} region in Nujol and KBr mulls. The diffuse reflectance spectra of the powdery samples were recorded by a VSU-2P Carl Zeiss (Jena) spectrophotometer in the range of 1000–300 nm. MgO was used as a reference medium with a 100% reflection. The Kubelka–Munk function $F = (1 - R)^2/2R$ (R is relative reflectivity) characterizing the absorption coefficient was calculated over the whole range.

Results and Discussion

The experimental results on the solubility in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system at 50°C (the temperature at which the two salts crystallize as isostructural monoclinic dihydrates) are shown in Table I and Fig. 1. The distribution curve of the salt components in molar parts is shown in Fig. 2. It may be seen from Figs. 1 and 2 that three crystallization fields of solid solutions are observed. The $Co(HCOO)_2 \cdot 2H_2O$ matrix includes a maximum of 50 mol% copper formate and the $Cu(HCOO)_2 \cdot 2H_2O$ matrix includes a maximum of about 9 mol% cobalt formate. A middle crystallization field of solid solutions is observed in the concentration range of $Cu_{0.83}Co_{0.17}(HCOO)_2 \cdot 2H_2O$–$Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$. The crystallization fields are named I, II, and III, respectively. The distribution coefficients of the salt components between the liquid and solid phases are different in the three fields and have mean values of $D_{Co/Cu} = 8.00$ (crystallization field I); $D_{Co/Cu} = 3.57$ (crystallization field II); and $D_{Co/Cu} = 4.73$ (crystallization field III). The different branches of the distribution curve lie on one side of the diagonal due to the fact that the concentration of one component (copper formate) in the liquid phase remains higher than that in the solid phase for the whole concentration range.

TABLE I

SOLUBILITY IN THE $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O SYSTEM AT 50°C

Liquid phase, wt.%		Solid phase calculated by (13), wt.%		Distribution coefficients	
$Cu(HCOO)_2$	$Co(HCOO)_2$	$Cu(HCOO)_2$	$Co(HCOO)_2$	$D_{Co/Cu}$	$D_{Cu/Co}$
25.17	—	—	—	—	—
23.91	0.20	78.84	2.14	3.24	0.31 II
23.50	0.25	77.77	3.19	3.85	0.26 field
23.10	0.60	73.95	6.98	3.63	0.28
22.81	1.00	67.76	13.13	4.42	0.23 III
21.80	1.05	65.28	15.57	4.95	0.20 field
21.47	1.50	60.46	20.34	4.81	0.21
20.42	2.89	42.27	38.49	eutonics	
19.42	2.52	38.76	41.97	8.33	0.12
14.12	2.50	35.45	45.27	7.21	0.14 I
11.29	2.55	26.24	54.42	9.09	0.11 field
7.16	2.73	20.04	60.58	7.69	0.13
4.04	3.30	11.31	69.30	7.69	0.13
—	3.33	—	—	—	—

Since the solid solutions from crystallization field III are formed in a narrow concentration range of the liquid phase the points corresponding to the solid solution compositions lie on the vertical part of the curve (Fig. 2).

The X-ray powder investigations of the samples show that the solid solutions formed in crystallization fields I and II retain the crystal structure of the simple salts $Co(HCOO)_2 \cdot 2H_2O$ and $Cu(HCOO)_2 \cdot 2H_2O$, respectively. The calculated lattice parameters are given in Table II. The deviations are given in parentheses. It is evident that the lattice constants do not change considerably with the change in the chemical composition. In Fig. 3 are shown both the X-ray spectrum of the solid solution $Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$ formed

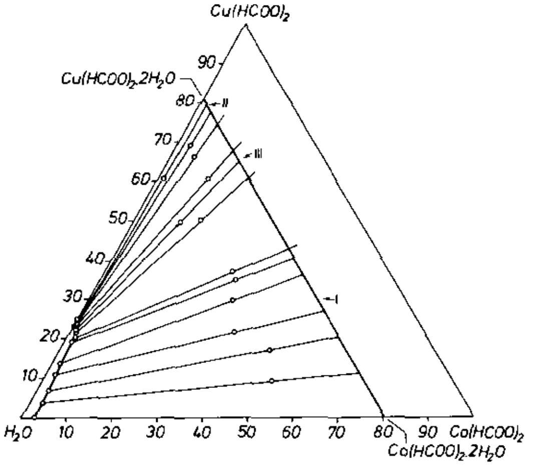

FIG. 1. Solubility diagram of the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system at 50°C.

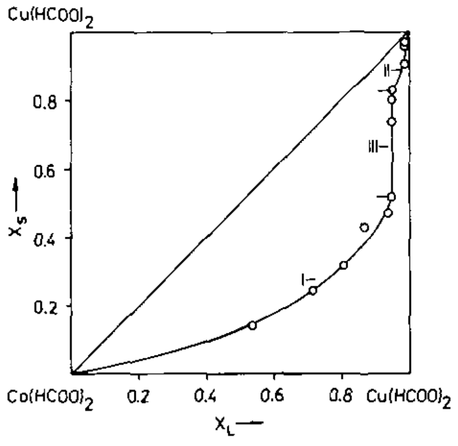

FIG. 2. Distribution curve of the salt components in the $Cu(HCOO)_2$–$CO(HCOO)_2$–H_2O system at 50°C.

TABLE II

LATTICE PARAMETERS OF $Cu_xCo_{1-x}(HCOO)_2 \cdot 2H_2O$ SOLID SOLUTIONS

Solid phase	a/Å	b/Å	c/Å	β/°
$Cu(HCOO)_2 \cdot 2H_2O$	8.49	7.12	9.34(1)	97.34
$Cu_{0.91}Co_{0.09}(HCOO)_2 \cdot 2H_2O$	8.50(1)	7.13	9.31(1)	97.22
$Cu_{0.47}Co_{0.53}(HCOO)_2 \cdot 2H_2O$	8.65(1)	7.16(1)	9.17(1)	96.42(1)
$Cu_{0.43}Co_{0.57}(HCOO)_2 \cdot 2H_2O$	8.67(2)	7.17(1)	9.18(1)	96.43(1)
$Cu_{0.32}Co_{0.68}(HCOO)_2 \cdot 2H_2O$	8.66(1)	7.16(1)	9.20(1)	96.52(2)
$Cu_{0.13}Co_{0.87}(HCOO)_2 \cdot 2H_2O$	8.64(2)	7.15(2)	9.22(1)	96.33(1)
$Co(HCOO)_2 \cdot 2H_2O$	8.66(2)	7.16(1)	9.22(1)	96.82(2)

in crystallization field III and the X-ray spectrum of the solid solution $Cu_{0.73}Mg_{0.27}(HCOO)_2 \cdot 2H_2O$ formed in the $Cu(HCOO)_2$–$Mg(HCOO)_2$–H_2O system at 50°C (*1*). It is seen that the X-ray spectra are identical and consequently the two solid solutions are isostructural. The X-ray spectrum of the solid solution $Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$ is considerably different from that of the copper formate dihydrate, indicating a new solid phase formation in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system at 50°C. The new solid phase (solid solutions) exists in the concentration range $Cu_{0.83}Co_{0.17}(HCOO)_2 \cdot 2H_2O$–$Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$.

The infrared spectra of the solid solutions were recorded in the range 500–3600 cm^{-1}. The assignments and interpretations are made according to (*14–19*). Six fundamentals are expected for the formate ion with C_{2v} symmetry (*16, 17, 19*). For the hydrated salts sharp absorption bands in the 3200–3600 cm^{-1}, 1650–1690 cm^{-1}, and 500–700 cm^{-1} regions are also recorded which can be assigned to crystallization water (*15*). The bands in the 720–920 cm^{-1} region were assigned to either the rocking vibrations of coordinated water molecules (*20*) or the bending mode vibrations of the coordinated carboxyl groups (*20, 21*). According to (*14*) the bands in the 820–910 cm^{-1} region are assigned to Me–H_2O rocking vibrations and the bands in the 750–785 cm^{-1} region are assigned to OCO bending. According to (*15, 16*) the bands in the 750–920 cm^{-1} region are assigned to ν_3—the bending mode vibrations of the coordinated formate groups. Our experimental results coincide well with those of Baraldi (*15*) and we use the same assignments. The solid solutions having cobalt formate dihydrate as a matrix exhibit similar spectra to that of $Co(HCOO)_2 \cdot 2H_2O$ (Table III). The bands at 870, 750, and 580 cm^{-1} are slightly shifted depending on the copper formate concentration. It is readily seen that the small cobalt concentration included in the Cu

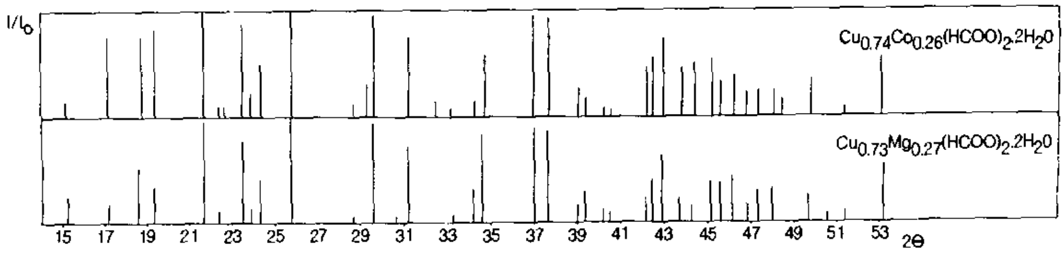

FIG. 3. Stick diagrams of the solid solutions (new crystal phase).

TABLE III

IR SPECTRA OF THE $Cu_xCo_{1-x}(HCOO)_2 \cdot 2H_2O$ SOLID SOLUTIONS IN THE REGION 500–1700 cm^{-1}

Solid phase	ν_4	ν_5	ν_2	ν_3	γH_2O
$Co(HCOO)_2 \cdot 2H_2O$	1590s, b	1400s	1360s, b	870w	750sh
		1380s		845w	580m
				770s	
$Cu_{0.14}Co_{0.86}(HCOO)_2 \cdot 2H_2O$	1590s, b	1405s	1360s, b	890w	745sh
		1380s		845w	575m
				775s	
$Cu_{0.43}Co_{0.57}(HCOO)_2 \cdot 2H_2O$	1590s, b	1405s	1360s, b	890w	740sh
		1380s		850w	560m
				775s	
$Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$	1600s, b	1405s	1370s, b	885vw	715s
		1390s		860m	580s
New crystal phase				835m	500m
				770s	
$Cu_{0.80}Co_{0.20}(HCOO)_2 \cdot 2H_2O$	1600s, b	1405s	1370s, b	890vw	710s
		1390s		860m	580s
New crystal phase				830m	500m
				775s	
$Cu_{0.96}Co_{0.04}(HCOO)_2 \cdot 2H_2O$	1610s, b	1400s	1350s, b	9120vw	670m, b
		1380s		890vw	610m
				795s	
				785s	
$Cu(HCOO)_2 \cdot 2H_2O$	1610s, b	1400s	1340s, b	920vw	670m, b
		1380s		890vw	610m
				790s	
				785s	

Note. Mulls in kBr.

$(HCOO)_2 \cdot 2H_2O$ matrix does not effect on any shift of the bands. In the case of the solid solutions formed in crystallization field III the shape of the IR spectra is essentially different in the 500–900 cm^{-1} region. It is evident that the spectrum are not a superposition of the simple salt spectra. Since the new crystal phase contains a copper formate as a main component it is more correct to compare its IR spectrum with that of $Cu(HCOO)_2 \cdot 2H_2O$. $\gamma(H_2O)$ vibrations at 610 and 670 cm^{-1} characteristic for $Cu(HCOO)_2 \cdot 2H_2O$ disappear in the new crystal phase spectrum and three bands at 500, 580, and 710 cm^{-1} appear, respectively. The IR spectra of the solid solutions $Cu_xCo_{1-x}(HCOO)_2 \cdot 2H_2O$ in the high frequency region 3000–3600 cm^{-1} where the OH-stretch vibrations appear are shown in Fig. 4. It is seen that the spectra of Figs. 4 and 5 are essentially different from those of the simple salts (pp. 1, 7). Strong bands at 3380 (3390) and 3445 cm^{-1} and two broad bands at 3130 (3120) and 3220 (3240) cm^{-1} are characteristic for the new crystal phase. The same four bands at 3150, 3225, 3400, and 3480 cm^{-1} were observed in the IR spectrum of the solid solution $Cu_{0.75}Mg_{0.25}(HCOO)_2 \cdot 2H_2O$ (*1*). In conclusion, the results show that the IR spectrum of the new crystal phase differs from the IR spectra of the simple salts $Cu(HCOO)_2 \cdot 2H_2O$ and $Co(HCOO)_2 \cdot 2H_2O$ in the regions where the bands of the $\gamma(H_2O)$ vibrations and the OH-stretch vibrations appear.

Diffuse reflectance spectra in the visible range of some copper formates with known

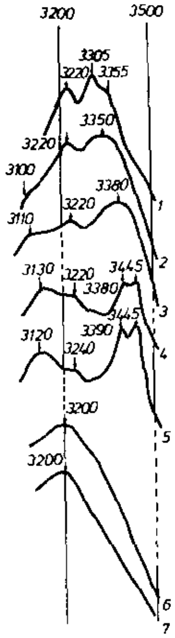

FIG. 4. IR spectra of the solid solutions formed in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system at 50°C in the region 3000–3600 cm^{-1}. Suspension in Nujol: 1. $Co(HCOO)_2 \cdot 2H_2O$; 2. $Cu_{0.14}Co_{0.86}(HCOO)_2 \cdot 2H_2O$; 3. $Cu_{0.43}Co_{0.57}(HCOO)_2 \cdot 2H_2O$; 4. $Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$; 5. $Cu_{0.80}Co_{0.20}(HCOO)_2 \cdot 2H_2O$; 6. $Cu_{0.96}Co_{0.04}(HCOO)_2 \cdot 2H_2O$; 7. $Cu(HCOO)_2 \cdot 2H_2O$.

structures were recorded in order to obtain some additional information for the new crystal phase structure. The strength of the ligand field depends on the coordination environment of the copper ion and as a consequence the maximum in the optical absorption varies correspondingly (Table IV). $Cu(HCOO)_2 \cdot 2H_2O$, containing two structural elements $Cu(H_2O)_4(HCOO)_2$ and $Cu(HCOO)_6$, displays a maximum in the spectra at 12,500 cm^{-1}. The salts $Cu(HCOO)_2 \cdot 4H_2O$ and $Ba_2Cu(HCOO)_6 \cdot 4H_2O$, containing the structural element $Cu(H_2O)_2(HCOO)_4$, display maxima in the spectra at 12,800 cm^{-1}. In the spectrum of the solid solution $Cu_{0.73}Mg_{0.27}(HCOO)_2 \cdot 2H_2O$ the maximum is observed at just the same energy (12,800 cm^{-1}) which could be an indication that the crystal structure is probably built up by the same structural element $Cu(H_2O)_2(HCOO)_4$. Taking into account the conclusion that the solid solutions $Cu_{0.73}Mg_{0.27}(HCOO)_2 \cdot 2H_2O$ and $Cu_{0.74}Co_{0.26}(HCOO)_2 \cdot 2H_2O$ are isostructural (Fig. 3) one could assume that the new crystal phase formed in the $Cu(HCOO)_2$–$Mg(HCOO)_2$–H_2O and $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O systems at 50°C has as a matrix $Cu(HCOO)_2 \cdot 2H_2O$ in which the copper ions are coordinated by two water molecules and four formate groups.

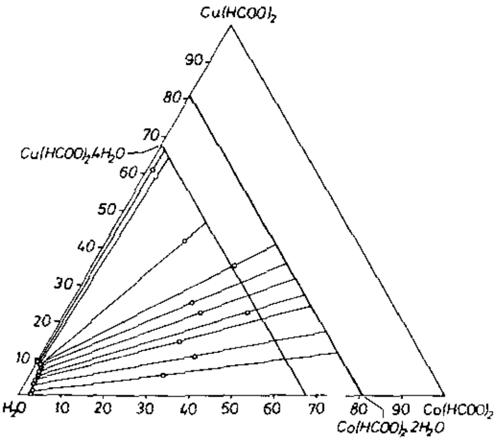

FIG. 5. Solubility diagram of the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system at 25°C.

The solubility in the $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O system has been studied at 25°C as well (Table V, Fig. 5). Two type of solid solutions are formed in the system—solid solutions having $Cu(HCOO)_2 \cdot 4H_2O$ as a matrix and solid solutions having $Co(HCOO)_2 \cdot 2H_2O$ as a matrix. The $Co(HCOO)_2 \cdot 2H_2O$ matrix in-

TABLE IV

Solid phase	Structural element	ν_{max}/cm^{-1}
$Cu(HCOO)_2$	$Cu(HCOO)_6$	14,700
$Cu(HCOO)_2 \cdot 4H_2O$	$Cu(HCOO)_4(H_2O)_2$	12,820
$Ba_2Cu(HCOO)_6 \cdot 4H_2O$	$Cu(HCOO)_4(H_2O)_2$	12,820
$Cu_{0.73}Mg_{0.27}(HCOO)_2 \cdot 2H_2O$	$Cu(HCOO)_4(H_2O)_2$	12,820
$Cu(HCOO)_2 \cdot 2H_2O$	$Cu(HCOO)_6$ $Cu(HCOO)_2(H_2O)_4$	12,500

TABLE V

SOLUBILITY IN THE $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O SYSTEM AT 25°C

Liquid phase, wt.%		Solid phase calculated by (13), wt.%		Distribution coefficients	
$Cu(HCOO)_2$	$Co(HCOO)_2$	$Cu(HCOO)_2$	$Co(HCOO)_2$	$D_{Cu/Co}$	$D_{Co/Cu}$
8.80	—	—	—	—	—
8.40	0.50	66.61	1.44	2.78	0.36
8.20	0.70	64.78	3.25	1.69	0.59
8.15	1.02	47.20	20.65	eutonics	
8.00	1.01	40.92	39.85	0.12	8.33
8.05	1.03	35.37	45.33	0.10	10.00
6.77	1.29	31.69	49.09	0.12	8.33
5.83	1.35	26.98	53.78	0.12	8.33
4.10	1.50	23.65	57.01	0.15	6.67
3.30	1.80	18.40	64.11	0.15	6.67
1.19	2.33	11.31	69.32	0.08	12.50
—	2.44	—	—	—	—

cludes a maximum of 50 mol% copper formate, thus providing a wider crystallization field of solid solutions than that of solid solutions based on the copper formate tetrahydrate crystal structure. The distribution coefficients of the salt components between the liquid and solid phases in the crystallization field of solid solutions based on the cobalt formate crystal structure are close to those in the same system at 50°C (Table V).

Conclusion

On the basis of the previous and present studies it was established that the crystal structure of $Cu(HCOO)_2 \cdot 2H_2O$ undergoes a change into a new crystal structure due to included magnesium and cobalt ions. The concentration of the admixture which causes the crystal structure change could be used as a measure of the deforming effect of the included ions. Therefore, the magnesium ions have a stronger deforming effect on the copper formate dihydrate crystal structure than the cobalt ions, thus providing the narrower crystallization field of solid solutions based on the $Cu(HCOO)_2 \cdot 2H_2O$ matrix. Probably the smaller ionic radius of magnesium than of cobalt is the reason for the stronger deforming effect of the magnesium ions. On the other hand, the experimental results show that $Co(HCOO)_2 \cdot 2H_2O$ and $Mg(HCOO)_2 \cdot 2H_2O$ that include 50 mol% of copper formate retain their crystal structures. It is known that the coordination octahedra in the crystal structures of the cobalt and magnesium formate dihydrates are comparatively regular with respect to Me–O bond lengths and O–Me–O angles (close to 90°C). The copper ions (d^9) display a strong radical deformation of the coordination octahedra (large differences in the Me–O bond lengths as a consequence of the Jahn–Teller effect). When the copper ions replace the cobalt or magnesium ions they cause a strong radial deformation of the cobalt or magnesium octahedra. The distortion force created by this substitution, however, does not affect substantially the cobalt or magnesium formate lattice up to the copper formate concentration in the solid phase of 50 mol%.

Since the new crystal phase contains a copper formate dihydrate as a main component a hypothesis has been made that a new polymorphous modification of $Cu(HCOO)_2 \cdot 2H_2O$ is probably formed due to included Mg^{2+} and Co^{2+} ions. The results of the diffuse reflectance spectroscopy indicate that the coordination environment of the copper ions in the new phase consists of two water molecules and four oxygen atoms from formate groups. The same coordination environment is characteristic for the copper ions in the $Cu(HCOO)_2 \cdot 4H_2O$ crystal structure. Furthermore, it is known that $Mg(HCOO)_2 \cdot 2H_2O$ crystallizes in both the monoclinic (*9*) and the orthorhombic system (*18*). The orthorhombic crystals are built up by the structural element $Cu(H_2O)_2(HCOO)_4$. Some preliminary experiments were carried out in order to isolate a new polymorphous modification of the copper formate dihydrate. For example, it was established that when the dehydration process of $Cu(HCOO)_2 \cdot 4H_2O$ is carried out with alcohol at room temperature a mixture of two phases is obtained. The X-ray diffraction spectra of the dehydration product exhibit the peaks of the monoclinic copper formate dihydrate and some strong peaks which are characteristic for the new phase formed in the $Cu(HCOO)_2$–$Mg(HCOO)_2$–H_2O and $Cu(HCOO)_2$–$Co(HCOO)_2$–H_2O systems at 50°C. These results, however, need additional supports.

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