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The $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 25 and 50°C

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Abstract

The solubility in the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system has been studied by the method of physico-chemical analysis at 25 and 50°C. It has been established that only simple salts crystallize in the system at 25°C. A congruent double salt with composition $CdSr(HCOO)_4.H_2O$ is formed in the system at 50°C. The thermal dehydration and decomposition of the new compound have been investigated by TG, DTA and DSC. The enthalpy of dehydration of $CdSr(HCOO)_4.H_2O$ has been determined. © 1997 Elsevier Science B.V.

Keywords: Solubility diagram; Cadmium/Strontium formate double salt; DTA; DSC; Heat of dehydration

1. Introduction

It is known that the single crystals of $Sr(HCOO)_2$ and $Sr(HCOO)_2.2H_2O$ exhibit nonlinear optical properties [1]. The same properties have been observed with some double salts, such as $NaCd(HCOO)_3$ [2] and $BaCd(HCOO)_4.2H_2O$ [3,4]. In this connection it was of interest to investigate the interaction in the ternary system $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O at different temperatures in order to establish the existence of compounds (double salts) formed by cadmium and strontium formates.

The purpose of the present work was to study the solubility diagram of the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 25 and 50°C and to characterize the phases obtained. There are no literature data on the cocrystallization of cadmium and strontium formates and no double salts of the type $Cd_xSr_y(HCOO)_z.nH_2O$ are known from the literature.

2. Experimental

The formates of cadmium and strontium were prepared by neutralization of dilute formic acid (1 : 1) with the corresponding carbonates at 70–80°C and crystallization of the salts at room temperature; then the crystals were purified by recrystallization in water and dried in air. The reagents used were 'p.a.'

The solubility in the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system was studied by the Khlopin method for isothermal decrease of supersaturation [5]: aqueous solutions of both salts taken in different ratios were prepared at 60–70°C, then cooled in a thermostat at 25 and 50°C, respectively, and stirred until a constant concentration of the saturated solution, that is, equilibrium was achieved. The preliminary experiments

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showed that the equilibrium in the system was attained in about 10 to 15 h. Then the suspension was filtered and the liquid and the wet solid phases were analysed. 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 Cd^{2+}–Sr^{2+} at pH = 10 using eryochrome black T as indicator; Sr^{2+} concentration was calculated by difference. The solid phase composition was determined by the graphic method of Schreinemakers for wet residues [6].

The 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 sample mass 330 mg, at a heating rate of 10°C min^{-1} from ambient temperature to 600°C using standard corundum crucible. The reference substance was pure α-Al_2O_3. The DSC measurements were recorded on a Perkin–Elmer DSC-4 instrument up to 500°C in dynamic air atmosphere using standard Al pans. The sample mass was 10.80 mg and the heating rate was 5°C min^{-1}. The temperature and sensitivity were calibrated using indium (purity > 99.9%) as a standard substance. The X-ray diffraction analysis was carried out with a DRON-3 diffractometer using Ni filtered CuK_α radiation.

3. Results and discussion

3.1. Solubility diagrams

The $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 25°C, the experimental results of which are listed in Table 1. The solubility diagram is shown in Fig. 1. It is seen from the table that only simple salts crystallize in the studied system. Two crystallization fields of solid phases are observed in the solubility diagram, namely, the crystallization fields of the simple salts $Cd(HCOO)_2.2H_2O$ and $Sr(HCOO)_2.2H_2O$. The eutonics has a composition 12.52 mass % cadmium formate and 12.80 mass % strontium formate. The salts obtained were identified by chemical analysis and the X-ray powder diffraction method. Consequently, the formates of cadmium and strontium do not interact in aqueous solutions at the temperature of 25°C.

The $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 50°C, the solubility data for which are presented in Table 2 and Fig. 2. Three crystallization fields of solid phases are observed in the solubility diagram, the crystallization fields of the simple salts $Cd(HCOO)_2.2H_2O$ and $Sr(HCOO)_2.2H_2O$, and a crystallization field of a congruent double salt with composition $CdSr(HCOO)_4.H_2O$. The double salt crystallizes from solutions containing 26.45 mass % cadmium formate and 12.19 mass % strontium formate up to solutions containing 12.61 mass % cadmium formate and 17.71 mass % strontium formate.

The double salt has been isolated from the system by filtering, followed by washing with alcohol and drying in air. The $CdSr(HCOO)_4.H_2O$ forms colourless crystals. The chemical analysis shows 50.98 mass % $Cd(HCOO)_2$ and 44.52 mass % $Sr(HCOO)_2$ (theoretical composition, 50.87 mass % $Cd(HCOO)_2$ and 44.60 mass % $Sr(HCOO)_2$). The X-ray analysis confirms the results from physico-chemical analysis, that

Table 1
Solubility in the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 25°C

Liquid phase, mass %		Wet solid phase, mass %		Solid phase
$Cd(HCOO)_2$	$Sr(HCOO)_2$	$Cd(HCOO)_2$	$Sr(HCOO)_2$	
12.45	—	—	—	$Cd(HCOO)_2.2H_2O$
10.70	5.78	62.92	2.14	$Cd(HCOO)_2.2H_2O$
11.93	12.20	68.95	2.77	$Cd(HCOO)_2.2H_2O$
12.48	12.69	43.05	26.11	eutonics
12.52	12.80	36.55	32.33	eutonics
12.54	12.86.	20.27	43.63	eutonics
10.32	12.29	4.03	58.49	$Sr(HCOO)_2.2H_2O$
5.12	11.72	2.35	60.61	$Sr(HCOO)_2.2H_2O$
—	12.19	—	—	$Sr(HCOO)_2.2H_2O$

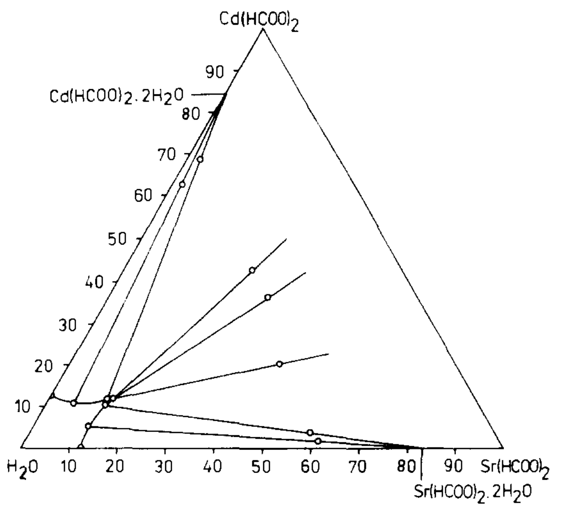

Fig. 1. Solubility diagram of the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 25°C (mass %).

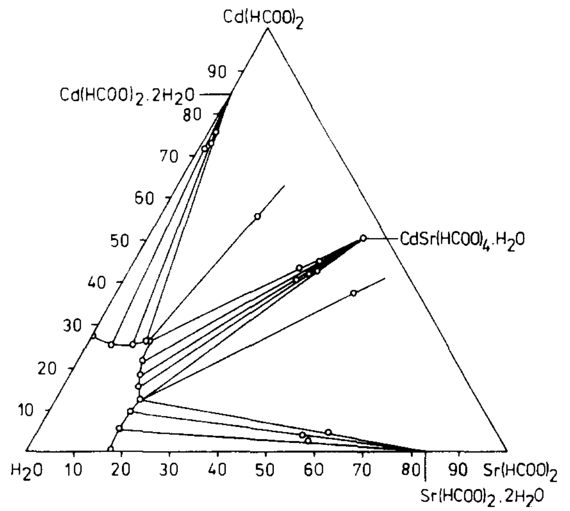

Fig. 2. Solubility diagram of the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 50°C (mass %).

is, formation of a new solid phase in the system at 50°C.

3.2. Thermal behaviour of $CdSr(HCOO)_4.H_2O$

The thermal dehydration and decomposition of $CdSr(HCOO)_4.H_2O$ have been studied by TG, DTA and DSC. The TG and DTA curves of the double salt are shown in Fig. 3. It can be seen from Fig. 3, that under our conditions dehydration begins at about 160°C and ends at about 190°C. The mass loss, calculated from the TG curve, corresponds to the loss of one water molecule. The dehydration is registered on the DTA curve with a strong endo-effect with a maximum at 180°C. The TG curve indicates that the anhydrous product is stable in the temperature range 190–300°C. The X-ray diffraction spectra of the sample obtained after heating the crystal hydrate at 160°C for several hours gives evidence for one compound. The chemical analysis shows 53.35 mass %

Table 2
Solubility in the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system at 50°C

Liquid phase, mass %		Wet solid phase, mass %		Solid phase
$Cd(HCOO)_2$	$Sr(HCOO)_2$	$Cd(HCOO)_2$	$Sr(HCOO)_2$	
27.80	—	—	—	$Cd(HCOO)_2.2H_2O$
25.22	4.99	72.01	1.61	$Cd(HCOO)_2.2H_2O$
25.53	9.55	73.21	2.39	$Cd(HCOO)_2.2H_2O$
26.48	12.22	76.14	2.10	$Cd(HCOO)_2.2H_2O$
26.45	12.19	55.98	20.29	eutonics
26.15	12.25	43.29	35.05	$CdSr(HCOO)_4.H_2O$
21.92	13.32	45.06	38.57	$CdSr(HCOO)_4.H_2O$
18.35	14.54	41.02	36.34	$CdSr(HCOO)_4.H_2O$
15.59	16.03	42.35	37.89	$CdSr(HCOO)_4.H_2O$
12.49	17.97	42.89	38.95	$CdSr(HCOO)_4.H_2O$
12.61	17.71	37.55	49.63	eutonics
12.55	17.82	4.85	60.48	$Sr(HCOO)_2.2H_2O$
9.81	17.06	4.03	55.64	$Sr(HCOO)_2.2H_2O$
5.42	16.80	2.46	57.29	$Sr(HCOO)_2.2H_2O$
—	17.16	—	—	$Sr(HCOO)_2.2H_2O$

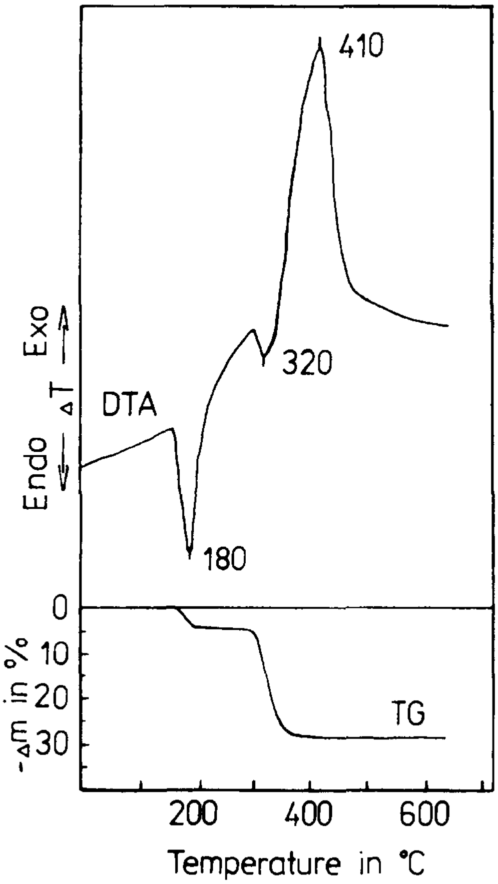

Fig. 3. TG and DTA curves of $CdSr(HCOO)_4.H_2O$ (330 mg, 10°C min^{-1}).

$Cd(HCOO)_2$ and 46.68 mass % $Sr(HCOO)_2$, which corresponds to the theoretical composition of anhydrous $CdSr(HCOO)_4$, 53.29 mass % $Cd(HCOO)_2$ and 46.71 mass % $Sr(HCOO)_2$.

The decomposition of the double salt begins at about 300°C and ends at about 450°C. Two effects are registered on the DTA curve; a small endo-effect with maximum at 320°C and a strong exo-effect with maximum at 410°C. The solid decomposition products at 450–600°C are CdO and $SrCO_3$ (as the result of the X-ray analysis shows). The two processes, the decomposition of the double salt and the decomposition of the simple salts $Cd(HCOO)_2$ and $Sr(HCOO)_2$, occur simultaneously.

According to the literature data the gaseous decomposition products of the metal formates always contain CO_2, CO and H_2 [7–11]. This and the agreement between calculated and experimentally established

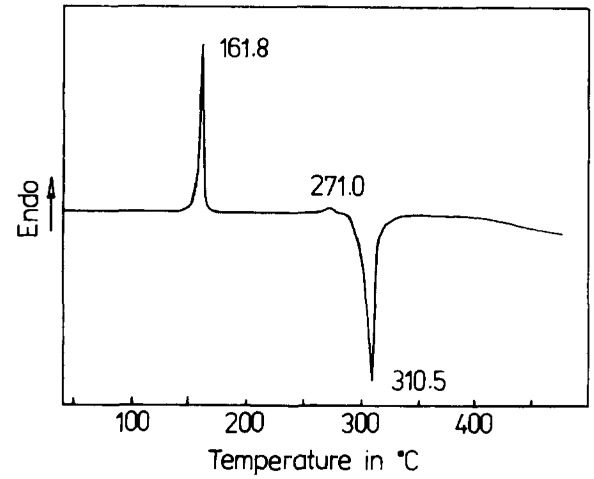

Fig. 4. DSC curve of $CdSr(HCOO)_4.H_2O$ (10.80 mg, 5°C min^{-1}).

values of the mass loss allow the assumption of the following equations for the thermal dehydration and decomposition of $CdSr(HCOO)_4.H_2O$:

$$CdSr(HCOO)_4.H_2O(s) \overset{160-190^\circ C}{\rightarrow} CdSr(HCOO)_4(s) + H_2O(g)$$

$$\Delta m_{exp} = 4.60\%, \Delta m_{th} = 4.53\%$$

$$CdSr(HCOO)_4(s) \overset{300-450^\circ C}{\rightarrow} CdO(s) + SrCO_3(s) + H_2(g) + CO(g) + CO_2(g)$$

$$\Delta m_{exp} = 27.08\%, \Delta m_{th} = 27.34\%$$

The DSC curve of $CdSr(HCOO)_4.H_2O$, presented in Fig. 4, shows an analogy with the DTA curve. The first endo-effect at $T_{onset} = 158.4$°C ($T_{max} = 161.8$°C) corresponds to the dehydration of the double salt. The enthalpy of dehydration of $CdSr(HCOO)_4.H_2O$ has been calculated, $\Delta_{deh}H = 64.10$ kJ mol^{-1}. The anhydrous $CdSr(HCOO)_4$ is stable in the temperature range 185–255°C. The thermal decomposition registered on the DSC curve by two effects; a small endo-effect at $T_{onset} = 263.1$°C ($T_{max} =$ 271.0°C) and a strong exo-effect at $T_{onset} =$ 302.8°*C* ($T_{max} = 310.5$°C).

4. Conclusion

The solubility diagram of the $Cd(HCOO)_2$-$Sr(HCOO)_2$-H_2O system has been investigated at 25 and 50°C showing a congruently soluble double salt with composition $CdSr(HCOO)_4.H_2O$ which crystallizes in the system at 50°C.

The thermal behaviour of $CdSr(HCOO)_4.H_2O$ has been studied by DTA and DSC methods. Equations for the thermal dehydration and decomposition have been proposed on the basis of the DTA data. The enthalpy of dehydration of the new double salt has been calculated from the DSC data.

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