ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2006, Vol. 51, No. 5, pp. 814–818. © Pleiades Publishing, Inc., 2006.
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PHYSICOCHEMICAL ANALYSIS
OF INORGANIC SYSTEMS

Reactions in the $M(HCOO)_2$–$CS(NH_2)_2$–H_2O (M = Mg, Mn, Cd) Systems at 25°C

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Received September 10, 2005

Abstract—Complex formation in the $M(HCOO)_2$–$CS(NH_2)_2$–H_2O (M = Mg, Mn, Cd) systems at 25°C is studied using the isothermal solubility method. In the $Cd(HCOO)_2$–$CS(NH_2)_2$–H_2O system, a congruently dissolving compound $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ is found and characterized by X-ray powder diffraction and IR spectroscopy. The $Mg(HCOO)_2$–$CS(NH_2)_2$–H_2O and $Mn(HCOO)_2$–$CS(NH_2)_2$–H_2O systems are eutonics at this temperature. Data on carbamide and thiocarbamide complexes of divalent metal formates are systematized.

DOI: 10.1134/S0036023606050226

Thiocarbamide complexes of inorganic salts are well studied [1–10]. These compounds are attractive for their nonlinear-optical properties [5–8]. They are also promising precursors for sulfide preparation [9, 10]. Thiocarbamide compounds of metal formates are poorly studied. Compound $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ (1 : 2) was synthesized by a preparative technique [11, 12]. Compound $Zn(HCOO)_2 \cdot CS(NH_2)_2$ (1 : 1) was reported to crystallize at 40°C [13]. We studied solubility in the $Zn(HCOO)_2$–$CS(NH_2)_2$–H_2O system at 25°C and found compound $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$ in [14]. The $Co(HCOO)_2$–$CS(NH_2)_2$–H_2O system at 25°C does not form compounds [15].

In this work, we study the $Mg(HCOO)_2$–$CS(NH_2)_2$–H_2O and $Mn(HCOO)_2$–$CS(NH_2)_2$–H_2O systems at 25°C. Our goals were to determine the mutual solubilities of the components and to elucidate whether new compounds are formed. We also study the $Cd(HCOO)_2$–$CS(NH_2)_2$–H_2O system in order to determine crystallization conditions for $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$. These systems have not yet been studied. Solubility data for magnesium, manganese, and cadmium formates and thiocarbamide solubilities were borrowed from [16–18].

EXPERIMENTAL

The starting formates were prepared by reacting cadmium carbonate or basic magnesium and manganese carbonates (all of analytical grade) with dilute aqueous formic acid. The formates were recrystallized. The compositions of the recrystallized formates were $Mg(HCOO)_2 \cdot 2H_2O$ [19], $Mn(HCOO)_2 \cdot 2H_2O$ [20], and $Cd(HCOO)_2 \cdot 2H_2O$ [21] as derived from chemical analysis and X-ray powder diffraction. Analytical grade thiocarbamide was used.

Solubility in the $Mg(HCOO)_2$–$CS(NH_2)_2$–H_2O and $Mn(HCOO)_2$–$CS(NH_2)_2$–H_2O systems was studied using the Khlopin supersaturation release method [22]. Aqueous solutions of two components of a system taken in various proportions were prepared at (80–90)°C; then, the solution was cooled in a thermostat to the working temperature (25°C) and vigorously stirred until achieving a constant concentration of the saturated solution, i.e., until equilibration. The equilibration time was 15–20 h. The $Cd(HCOO)_2$–$CS(NH_2)_2$–H_2O system at 25°C was studied using the isothermal solubility method, because cadmium sulfide is evolved when cadmium formate is heated in the presence of thiocarbamide. The equilibration time in this system was about 3–4 days. Temperature maintenance accuracy was within ±0.1 K. Then, the suspension was filtered, and the resulting liquid phase and wet solid phase (residue) were analyzed. A 2% excess of formic acid was in the solution to preclude hydrolysis. The Mg^{2+}, Mn^{2+}, and Cd^{2+} concentrations in the liquid phases and wet residues were determined complexometrically at pH 10 (ammonia buffer) in the presence of Eriochrome Black T [23]. Thiocarbamide was determined gravimetrically as sulfate ions after oxidizing it with hydrogen peroxide [24]. The composition of the solid phase was determined using the Schreinemakers method of wet residues [25].

Solid phases were identified using X-ray powder diffraction and IR spectroscopy. The X-ray powder diffraction experiment was carried out on a DRON-3 diffractometer (CuK_α radiation, Ni filter). IR spectra were recorded as KBr pellets on a Bruker IFS 25 FTIR

Table 1. Solubilities in the $Mg(HCOO)_2$–$CS(NH_2)_2$–H_2O system at 25°C

In liquid phase, wt %		In wet residue, wt %		Solid phase
$Mg(HCOO)_2$	$CS(NH_2)_2$	$Mg(HCOO)_2$	$CS(NH_2)_2$	
11.99	–	–	–	$Mg(HCOO)_2 \cdot 2H_2O$
10.92	4.03	51.02	2.17	The same
10.10	7.15	53.92	3.25	″
10.63	10.54	57.21	4.01	″
10.57	10.80	39.60	29.13	$Mg(HCOO)_2 \cdot 2H_2O + CS(NH_2)_2$
10.51	10.87	18.14	58.94	The same
8.53	11.25	2.89	72.67	$CS(NH_2)_2$
4.78	12.15	2.13	67.88	The same
–	13.39	–	–	″

Table 2. Solubilities in the $Mn(HCOO)_2$–$CS(NH_2)_2$–H_2O system at 25°C

In liquid phase, wt %		In wet residue, wt %		Solid phase
$Mn(HCOO)_2$	$CS(NH_2)_2$	$Mn(HCOO)_2$	$CS(NH_2)_2$	
6.28	–	–	–	$Mn(HCOO)_2 \cdot 2H_2O$
5.33	3.78	53.52	1.51	The same
5.25	8.49	65.12	2.03	″
5.42	10.14	50.07	4.46	″
5.23	11.74	43.59	30.08	$Mn(HCOO)_2 \cdot 2H_2O + CS(NH_2)_2$
5.20	11.55	20.69	51.14	The same
5.16	11.60	2.10	72.06	$CS(NH_2)_2$
2.19	12.75	1.16	67.78	The same
–	13.39	–	–	″

Table 3. Solubilities in the $Cd(HCOO)_2$–$CS(NH_2)_2$–H_2O system at 25°C

In liquid phase, wt %		In wet residue, wt %		Solid phase
$Cd(HCOO)_2$	$CS(NH_2)_2$	$Cd(HCOO)_2$	$CS(NH_2)_2$	
12.45	–	–	–	$Cd(HCOO)_2 \cdot 2H_2O$
16.60	1.03	67.31	9.20	$Cd(HCOO)_2 \cdot 2H_2O + CS(NH_2)_2$
16.57	1.08	50.20	22.45	The same
9.41	1.23	43.25	31.52	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$
6.63	2.03	36.10	25.93	The same
3.44	4.60	49.76	38.05	″
2.72	5.56	38.51	30.03	″
3.09	12.00	42.06	34.11	″
3.71	13.90	35.81	31.20	″
4.62	17.85	44.25	37.12	″
5.55	24.53	30.17	57.18	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2 + CS(NH_2)_2$
5.60	24.77	9.35	77.38	The same
3.07	20.11	1.22	76.13	$CS(NH_2)_2$
–	13.39			The same

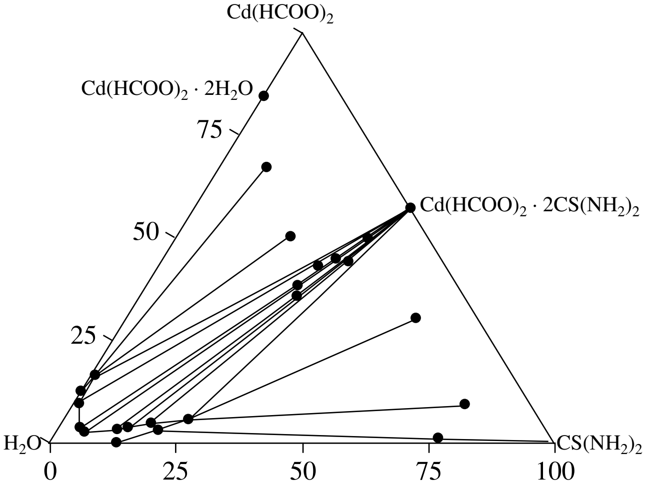

Fig. 1. Solubility diagram for the Cd(HCOO)$_2$–CS(NH$_2$)$_2$–H$_2$O system at 25°C.

instrument. A reaction with potassium bromide was not observed.

RESULTS AND DISCUSSION

System Mg(HCOO)$_2$–CS(NH$_2$)$_2$–H$_2$O. The results of our investigation of the system at 25°C (Table 1) show that chemical compounds are not formed at this temperature; i.e., the system is a simple eutonic. The solubility isotherm consists of two branches due to the crystallization of two phases: Mg(HCOO)$_2$ · 2H$_2$O [19] and CS(NH$_2$)$_2$ [26]. The composition of the eutonic solution is 10.51 wt % magnesium formate and 10.87 wt % thiocarbamide. Each component slightly decreases its solubility when the other is added, because of salting out.

System Mn(HCOO)$_2$–CS(NH$_2$)$_2$–H$_2$O. Experimental solubility data at 25°C, compiled in Table 2, likewise do not show compound formation in this system. The solubility isotherm of the system has two branches: the longer branch is due to Mn(HCOO)$_2$ · 2H$_2$O [20] (the least soluble component), and the short branch is due to thiocarbamide; the branches meet at a eutonic point, whose coordinates are 5.20 wt % Mn(HCOO)$_2$ and 11.55 wt % CS(NH$_2$)$_2$. Each component slightly decreases its solubility when the other is added, because of salting out. The manganese formate solubility drops from 6.28 to 5.20 wt %; the thiourea solubility drops from 13.39 to 11.55 wt %.

System Cd(HCOO)$_2$–CS(NH$_2$)$_2$–H$_2$O at 25°C. The solubility data for this system are compiled in Table 3. The solubility diagram is shown in Fig. 1. The following three phases crystallize in the system: Cd(HCOO)$_2$ · 2H$_2$O [21], CS(NH$_2$)$_2$ [26], and a congruently dissolving compound Cd(HCOO)$_2$ · 2CS(NH$_2$)$_2$. Cadmium formate dihydrate has a very narrow crystallization field. Most of the diagram is occupied by the crystallization field of the compound whose composition was found graphically using the Schreinemakers method. The concentration bounds of formation were determined for the compound from 16.60 to 5.60 wt % cadmium formate and from 1.03 to 24.77 wt % thiocarbamide in the liquid phase.

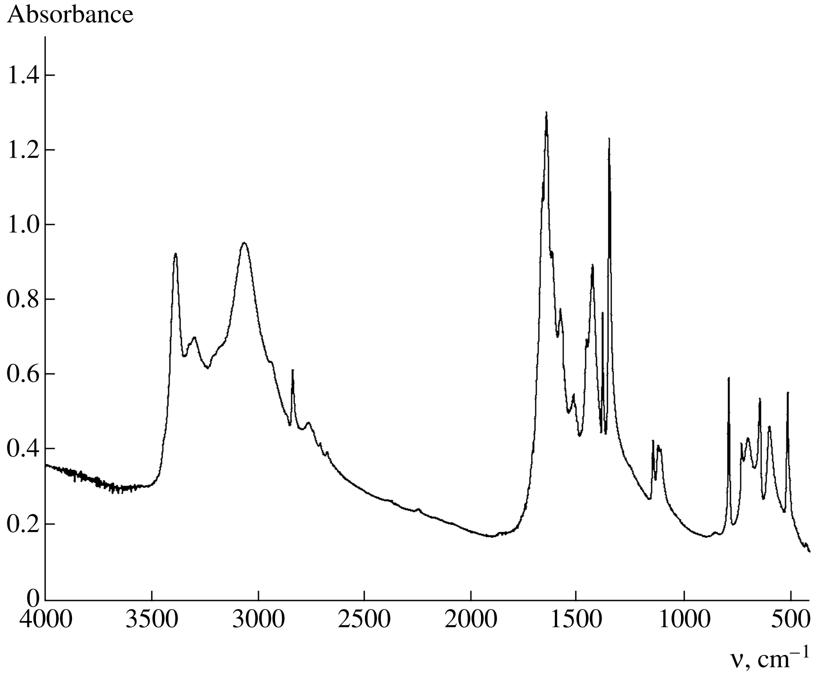

Fig. 2. IR spectrum of Cd(HCOO)$_2$ · 2CS(NH$_2$)$_2$ in the region 4000–400 cm^{-1}.

Table 4. Assignment of IR bands for $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$

ν, cm^{-1}	Assignment
3377 s	ν_{as} (N–H)
3295 m	
3183 sh	
3058 s	ν_s (N–H)
2927 sh	
2830 m	ν_1 (C–H)
2754 w	
2697 w	$2\nu_5$ $HCOO^-$
2665 w	
1657 v s	δ (NH_2)
1637 v s	
1630 s	ν_{4as} (COO)
1607 m	
1569 w	ν_{as} (C–N)
1510 m	ν_{as} (C–S)
1425 m	
1375 m	ν_5 (C–H)
1340 v s	ν_{2s} (COO)
1135 w	ν_s (C–N)
1110 w	ν_6 (C–H)
1098 w	
781 m	ν_{3s} (O–C–O)
720 w	ν_s (C–S)
690 w	
634 m	δ (NH_2)
589 m	δ_{as} (N–C–N)
502 m	δ_s (S–C–N)

Note: Band notation: v s, very strong; s, strong; m, medium intensity; w, weak; sh, shoulder.

Crystals of the compound isolated from the system were dried in air and characterized by chemical analysis, X-ray powder diffraction, and IR spectroscopy. Chemical analysis showed the following:

Calcd., wt %: $Cd(HCOO)_2$, 57.08; $CS(NH_2)_2$, 42.92. Found, wt %: $Cd(HCOO)_2$, 56.70; $CS(NH_2)_2$, 43.61.

The structure of $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ was studied comprehensively in [11, 12]. The crystals are orthorhombic, space group $P2_12_12_1$, with the unit cell parameters a = 8.00(0) Å, b = 17.87(8) Å, c = 3.93(3) Å, $Z = 2$. Each Cd atom is coordinated octahedrally by four S atoms lying in one plane, and two O atoms belonging to the formate groups in the *trans* position to the plane of the sulfur atoms. Our X-ray powder diffraction analysis showed that the compound isolated differs structurally from its precursors ($Cd(HCOO)_2 \cdot 2H_2O$ [21] and $Cs(NH_2)_2$ [26]). Interplanar distances and intensity ratios for $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ coincide with the data in [12].

The IR absorption spectra of thiocarbamide compounds of inorganic salts were studied in [27–29]. However, we failed to find data on the IR spectra of $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ in the literature. Our IR-spectroscopic investigation in the region 4000–400 cm^{-1} (Fig. 2) showed bands due to the vibrations in thiocarbamide molecules and formate groups. Band assignment was with reference to [27–29] for thiocarbamide and [30–32] for formate groups. The results of the IR investigation correlate with crystal data for $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ [12].

A comparative analysis of carbamide and thiocarbamide compounds with formates of several divalent metals was carried out. Table 5 summarizes data on carbamide and thiocarbamide complexes of Mg, Mn, Fe, Co, Ni, Zn, and Cd formates.

Both families of compounds have 1 : 2 formulas: $M(HCOO)_2 \cdot 2CO(NH_2)_2$ and $M(HCOO)_2 \cdot 2CS(NH_2)_2$. Carbamide or thiocarbamide molecules substitute for the two water molecules in formate dihydrates [19–21]. Carbamide forms compounds with all of the aforementioned formates [33–36]; thiocarbamide, with zinc and cadmium formates only [12, 14]. This holds for the reactions of carbamide and thiocarbamide with other inorganic salts [1]. It is known from the literature that carbamide has a stronger tendency toward complex formation than thiocarbamide. The

Table 5. Formation of carbamide and thiocarbamide complexes of Mg, Mn, Fe, Co, Ni, Zn, and Cd formates

$M(HCOO)_2 \cdot 2H_2O$	$M(HCOO)_2 \cdot 2CO(NH_2)_2$	$M(HCOO)_2 \cdot 2CS(NH_2)_2$
$Mg(HCOO)_2 \cdot 2H_2O$ [19]	$Mg(HCOO)_2 \cdot 2CO(NH_2)_2$ [33]	Not formed [this work]
$Mn(HCOO)_2 \cdot 2H_2O$ [20]	$Mn(HCOO)_2 \cdot 2CO(NH_2)_2$ [33–35]	The same
$Fe(HCOO)_2 \cdot 2H_2O$ [20]	$Fe(HCOO)_2 \cdot 2CO(NH_2)_2$ [33]	–
$Co(HCOO)_2 \cdot 2H_2O$ [20]	$Co(HCOO)_2 \cdot 2CO(NH_2)_2$ [33]	Not formed [15]
$Ni(HCOO)_2 \cdot 2H_2O$ [20]	$Ni(HCOO)_2 \cdot 2CO(NH_2)_2$ [33]	–
$Zn(HCOO)_2 \cdot 2H_2O$ [21]	$Zn(HCOO)_2 \cdot 2CO(NH_2)_2$ [33]	$Zn(HCOO)_2 \cdot 2CS(NH_2)_2$ [14]
$Cd(HCOO)_2 \cdot 2H_2O$ [21]	$Cd(HCOO)_2 \cdot 2CO(NH_2)_2$ [34–36]	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ [11, 12, this work]

higher complexing ability of zinc and cadmium ions compared to that of magnesium, manganese, and cobalt ions likely allows formates of these ions to form thiocarbamide complexes.

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