Russian Journal of Applied Chemistry, Vol. 76, No. 8, 2003, pp. 1221–1224. Translated from Zhurnal Prikladnoi Khimii, Vol. 76, No. 8, 2003, pp. 1260–1263.
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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Properties of Systems $Ba(HCOO)_2$–$M(HCOO)_2$–H_2O (M = Ca or Mg) at 25°C

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Received December 6, 2002

Abstract—The systems $Ba(HCOO)_2$–$Ca(HCOO)_2$–H_2O and $Ba(HCOO)_2$–$Mg(HCOO)_2$–H_2O were studied at 25°C by the solubility method. The effect of the ionic radii of doubly charged metals on the formation of double salts containing barium formate was considered.

Barium formate and its binary compounds possess interesting physical and chemical properties: $Ba(HCOO)_2$ and $BaCd(HCOO)_4 \cdot 2H_2O$ are nonlinear optical materials [1, 2], $Ba_2Cu(HCOO)_6 \cdot H_2O$ is paramagnetic material [3], and $BaY(HCOO)_5 \cdot 4H_2O$ and $Ba_2Cu(HCOO)_6 \cdot 4H_2O$ are suitable starting compounds for synthesis of superconductors [4, 5]. A study of salt systems containing barium formate is of interest because they show promise for practical application.

Barium formate is known to form double salts with formates of some doubly charged metals. $Ba_2M(HCOO)_6 \cdot 4H_2O$ (where M is Ni, Co, Cu, or Zn) (2 : 1 : 4) and $BaM(HCOO)_4 \cdot 2H_2O$ (where M is Cd) (1 : 1 : 2) [6, 7] were obtained by the preparative method. All these double salts (except that containing cobalt) were separated from the corresponding ternary water–salt systems [4, 8–10]. The double salt $Ba_2Fe(HCOO)_6 \cdot 4H_2O$ was separated from the $Ba(HCOO)_2$–$Fe(HCOO)_2$–H_2O system at 25°C. It was established that it is isostructural to the double salts of the isomorphic series. It is also known that manganese formate does not form a compound with barium formate. The $Ba(HCOO)_2$–$Mn(HCOO)_2$–H_2O system at 25°C is simple eutonic [11]. It was of interest to elucidate whether or not barium formate forms double salts with calcium and magnesium formates.

To determine the mutual solubility of the components and the possibility of formation of new phases from barium, calcium, and magnesium formates, we studied the systems $Ba(HCOO)_2$–$Ca(HCOO)_2$–H_2O and $Ba(HCOO)_2$–$Mg(HCOO)_2$–H_2O at 25°C. The systems have not been studied previously. Data on the solubility of barium, calcium, and magnesium formates were taken from [12, 13].

EXPERIMENTAL

The starting substances were obtained by reacting barium, calcium, and magnesium carbonates (all analytically pure) with a 50% solution of analytically pure formic acid, followed by recrystallization. According to chemical, derivatographic, and X-ray phase analyses, the resulting compounds have the compositions $Ba(HCOO)_2$ [14], α-$Ca(HCOO)_2$ [15], and $Mg(HCOO)_2 \cdot 2H_2O$ [16].

The solubility was studied by Khlopin's method of isothermal elimination of supersaturation [17]: aqueous solutions of two components of the system, taken in various proportions, were prepared at 80 – 90°C. Then the solution was cooled in a thermostat to the working temperature and vigorously stirred to constant concentration of a saturated solution (i.e., to attainment of equilibrium). The temperature was maintained constant to within ±0.1°C. The equilibration time was 15–20 h. After the suspension was filtered, the resulting liquid phase and the wet solid phase (residue) were analyzed. The Ba^{2+}, Ca^{2+}, and Mg^{2+} content in the liquid phases and residues was determined complexometrically [18]: the sum of Ba^{2+} and Ca^{2+} ions and of Ba^{2+} and Mg^{2+} ions was determined by back titration with zinc sulfate solution in ammonia solution in the presence of Eriochrome Black T indicator, Ca^{2+} was analyzed at pH 11 (NaOH solution) in the presence of calcone indicator, Mg^{2+} was analyzed in ammonia buffer solution after precipitating barium sulfate with a sulfuric acid solution, and the Ba^{2+} content was calculated as the difference between the two determinations. The solid phase composition was determined

Table 1. Solubility and solid phase composition in the systems $Ba(HCOO)_2$–$M(HCOO)_2$–H_2O (M is Ca or Mg) at 25°C

Liquid phase				Residue, wt %		Solid phase composition
wt %		mol %				
$Ba(HCOO)_2$	$M(HCOO)_2$	$Ba(HCOO)_2$	$M(HCOO)_2$	$Ba(HCOO)_2$	$M(HCOO)_2$	
$Ba(HCOO)_2$–$Ca(HCOO)_2$–H_2O system						
23.21	–	2.34	–	–	–	$Ba(HCOO)_2$
20.59	3.25	2.09	0.58	71.17	1.55	"
18.05	6.35	1.84	1.13	76.13	2.23	"
16.38	8.50	1.67	1.52	74.25	3.10	"
14.93	10.66	1.54	1.92	70.54	3.50	"
15.03	10.23	1.54	1.83	52.06	37.11	Eutonic
15.14	10.38	1.56	1.86	16.43	70.15	$Ca(HCOO)_2$
13.25	10.08	1.33	1.76	70.45	4.30	"
8.90	10.67	0.85	1.79	68.75	2.80	"
4.92	11.29	0.45	1.82	66.12	1.94	"
3.02	12.37	0.28	1.98	73.09	2.10	"
–	14.12	–	2.23	–	–	"
$Ba(HCOO)_2$–$Mg(HCOO)_2$–H_2O system						
23.21	–	2.34	–	–	–	$Ba(HCOO)_2$
21.11	1.92	2.12	0.38	71.33	0.80	"
20.28	3.40	2.05	0.68	72.55	0.80	"
18.56	6.11	1.89	1.24	81.72	1.80	"
17.45	7.30	1.78	1.48	80.12	1.37	"
17.27	7.39	1.76	1.5	44.07	36.52	Eutonic
14.86	7.55	1.47	1.49	4.03	59.88	$Mg(HCOO)_2 \cdot H_2O$
11.45	7.63	1.09	1.45	3.25	51.79	"
7.80	8.32	0.72	1.53	2.27	55.32	"
4.20	9.80	0.38	1.76	1.57	60.38	"
–	11.99	–	2.10	–	–	"

by Schreinemaker's method of residues [19] and confirmed by chemical, thermal, and X-ray phase analyses. Thermal analysis was performed on an MOM-12 derivatograph (Hungary), and X-ray phase analysis, on a DRON-3 diffractometer (Cu_{K_α} radiation, Ni filter).

The results of a study of the system $Ba(HCOO)_2$–$Ca(HCOO)_2$–H_2O at 25°C are presented in Table 1, and the solubility isotherm is plotted in Fig. 1a. The system is simple eutonic at this temperature. The crystallizing solid phases are $Ba(HCOO)_2$ [14] and α-$Ca(HCOO)_2$ [15]. The composition of the eutonic solution is (wt %) 15.03 barium formate and 10.23 calcium formate. As either of the components is added, the solubility of the other decreases owing to salting-out.

Data on the solubility in the $Ba(HCOO)_2$–$Mg(HCOO)_2$–H_2O system are presented in Table 1 and Fig. 1b. The solubility isotherm is represented by the crystallization branches of anhydrous barium formate [14] and magnesium formate dihydrate [16], which intersect at the eutonic point of compositions (wt %): 17.27 $Ba(HCOO)_2$ and 7.39 $Mg(HCOO)_2$. The components exert the mutual salting-out effect. For example, the solubility of barium formate in the system decreases from 23.21 to 17.27 wt %, and that of manganese formate, from 11.99 to 7.39 wt %.

A study of the two systems showed that neither double salts nor mixed crystals are formed at 25°C. Thus, when barium formate is crystallized, the zinc and magnesium impurities are concentrated in the mother liquor. Barium formate free of calcium and

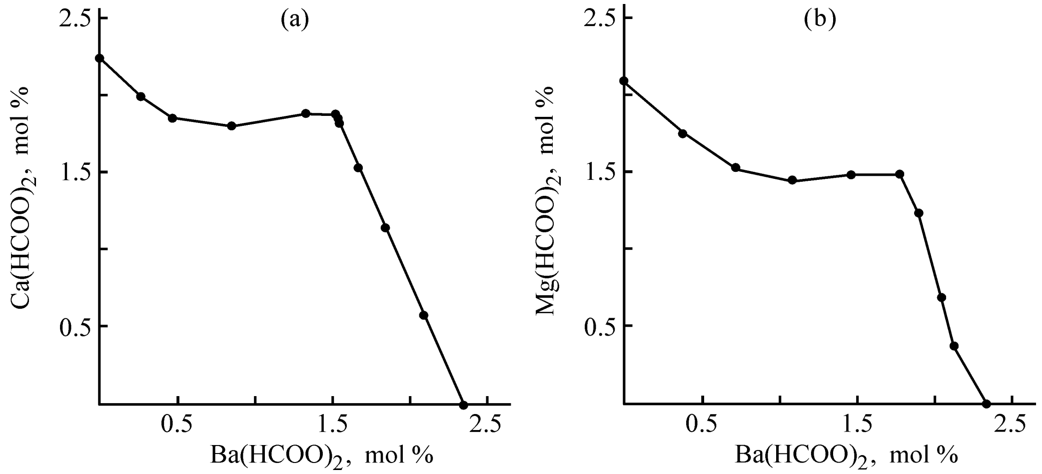

Fig. 1. Solubility isotherms of the systems (a) $Ba(HCOO)_2$–$Ca(HCOO)_2$–H_2O and (b) $Ba(HCOO)_2$–$Mg(HCOO)_2$–H_2O at 25°C.

magnesium impurities can probably be prepared by recrystallization.

Table 2 summarizes data on the compositions of double salts formed in the $Ba(HCOO)_2$–$M(HCOO)_2$–H_2O system (where M is Ni, Co, Cu, Zn, Fe, Mn, Cd, and Ca) at 25°C and lists the M^{2+} ionic radii [20]. As can be seen, barium formate yields double salts of stoichiometric composition $Ba_2M(HCOO)_6 \cdot 4H_2O$ (2 : 1 : 4) and $Ba_2M(HCOO)_4 \cdot 2H_2O$ (1 : 1 : 2) with formates of doubly charged metals. Barium formate gives the first structural type (2 : 1 : 4) with Ni, Co, Cu, Zn, and Fe formates. Only the double salt of copper has crystal structure [3]. All these double salts crystallize in the triclinic system, space group $P\bar{1}$, and have close unit cell parameters, i.e., they are isostructural.

The composition of a double salt and the M^{2+} ionic radius correlate. The structural type (2 : 1 : 4) is formed at ionic radii larger than 0.69 and smaller than 0.75Å. These conditions are satisfied by nickel(II), cobalt(II), copper(II), zinc(II), and iron(II) ions. In the systems $Ba(HCOO)_2$–$Mg(HCOO)_2$–H_2O (this study) and $Ba(HCOO)_2$–$Mn(HCOO)_2$–H_2O [11] no double salts are formed. This is because the Mg^{2+} radius (0.65Å) is probably too small, whereas the Mn^{2+} radius (0.80Å) is too large to make this structure stable. Apparently, the decisive factor influencing the formation of double compounds of the (2 : 1 : 4) structural type containing barium formate is the M^{2+} radius. The double salt of the second type [(1 : 1 : 2)] (only $BaCd(HCOO)_4 \cdot 2H_2O$ is known) crystallizes from aqueous solution at 25°C with the ionic radius increasing further. According to the data obtained in this study, no double salt is formed in the $Ba(HCOO)_2$–$Ca(HCOO)_2$–H_2O system. The ionic radii of Cd^{2+} and Ca^{2+} are very close (0.97 and 0.99Å, respectively). All the data presently available for the water–formate systems, including calcium formate, confirm the formation of anhydrous salts [21]. This fact is accounted for by strong dehydrating action of calcium formate. Probably, no double salt containing crystallization water is formed between barium and calcium formates for this reason.

Table 2. Composition of double salts formed in the $Ba(HCOO)_2$–$M(HCOO)_2$–H_2O systems

M^{2+}	Ionic radius, Å	Double salt composition
Mg^{2+}	0.65	Pure salts
Ni^{2+}	0.69	$Ba_2Ni(HCOO)_6 \cdot 4H_2O$ [6–8]
Co^{2+}	0.72	$Ba_2Co(HCOO)_6 \cdot 4H_2O$ [6, 7]
Cu^{2+}	0.72	$Ba_2Cu(HCOO)_6 \cdot 4H_2O$ [4, 6, 7]
Zn^{2+}	0.74	$Ba_2Zn(HCOO)_6 \cdot 4H_2O$ [6, 7, 9]
Fe^{2+}	0.75	$Ba_2Fe(HCOO)_6 \cdot 4H_2O$
Mn^{2+}	0.80	Pure salts [11]
Cd^{2+}	0.97	$Ba_2Cd(HCOO)_6 \cdot 2H_2O$ [6, 7, 10]
Ca^{2+}	0.99	Pure salts

CONCLUSIONS

(1) The systems $Ba(HCOO)_2$–$M(HCOO)_2$–H_2O (where M is Ca or Mg) were studied at 25°C and the formation of pure salts was established.

(2) Barium formate can be prepared by crystallization from an aqueous solution of impurity-free magnesium and calcium salts.

(3) A correlation between the composition of double barium salts and the M^{2+} ionic radius was estab-

lished. Double salts of the (2 : 1 : 4) type are formed at the ionic radii within 0.69 – 0.75Å. Above 0.80Å, another structural type (1 : 1 : 2) is formed.

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