JOURNAL OF SOLID STATE CHEMISTRY 57, 260–266 (1985)

Role of the Crystal Field Stabilization Energy in the Formation of Metal(II) Formate Mixed Crystals

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Received November 21, 1983; in revised form August 17, 1984

A relationship between the distribution coefficient values and the factors determining the isomorphous substitution of some metal(II) formates (Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd) has been found, given by

$$D_{2/1} = \left[\frac{M_{1.0}}{M_{2.0}}\right]^2 \exp \frac{a \cdot f\left[\frac{\Delta R}{R}\right] + b \cdot \varphi(\Delta\varepsilon) + c \cdot \psi(\Delta s)}{RT},$$

where $\Delta R/R$ is the relative difference in the ionic radii of the intersubstituting ions, $\Delta\varepsilon$ is the difference in the Me–O bond energy, Δs is the difference in the crystal field stabilization energy. The preexponential term represents the balance in bonding factors between the ions in the crystal and in the aqueous solution, in the case of ideally mixing in the solid state. The exponential term takes into account the enthalpy of mixing in the solid state. For the isostructural formate salts in which the substitution of a given cation by another one occurs in equivalent octahedral positions, the difference in the crystal field stabilization energy exerts the most important influence on the enthalpy of mixing.

Introduction

Under ordinary conditions, the metal(II) formates crystallize from aqueous solutions as dihydrates with the general formula $Me(HCOO)_2 \cdot 2H_2O$, where Me(II) = Mg, Mn, Fe, Co, Ni, Cu,[1] Zn, and Cd. These salts dihydrates are monoclinic with space group $P2_1/c$ and possess nearly identical lattice parameters; hence, they should form mixed crystals. It was shown previously (*1–3*) that separate pairs of the formate combinations form, in most cases, a continuous series of mixed crystals. The series becomes discontinuous only for large differences in the ionic radii of the participating metal ions (Mg^{2+} and Cd^{2+}, for example: the ionic radii differ by about 0.2 Å) or when one of the ions is a Jahn–Teller ion for example, Cu^{2+} (*4*). The quantitative measure for the degree of mixing is the distribution coefficient for the components between the mixed crystals, and the solutions from which the mixed crystals are obtained.

The purpose of the present work is to find a relationship between the distribution coefficient values and the factors determining the isomorphous substitution.

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[1] Cupric formate crystallizes as dihydrate from aqueous solution in the temperature range 42–60°C.

0022-4596/85 $3.00

The available data on the distribution coefficients of isomorphous formate cocrystallization were insufficient for our purposes; for this reason we have studied the following three-component systems by the method of the physicochemical analysis: $Fe(HCOO)_2$–$Mn(HCOO)_2$–H_2O, $Fe(HCOO)_2$–$Co(HCOO)_2$–H_2O, $Fe(HCOO)_2$–$Zn(HCOO)_2$–H_2O, $Mn(HCOO)_2$–$Co(HCOO)_2$–H_2O, $Mn(HCOO)_2$–$Ni(HCOO)_2$–H_2O, and $Mn(HCOO)_2$–$Zn(HCOO)_2$–H_2O at 25°C.

Experimental

The Mn, Co, Ni, and Zn formates were prepared by neutralization of diluted formic acid solutions with the corresponding normal or basic metal carbonates. Iron(II) formate was prepared by dissolving powdered iron in diluted formic acid (*5*). The reagents used were of *pro analysis* grade.

Equilibrium in these systems was attained by the Khlopin method of isothermal decrease of supersaturation (*6*). The solubility of the salt components was determined in a slight excess of formic acid (about 2%) so as to suppress salt hydrolysis. In order to establish the time necessary to attain the equilibrium in the systems, kinetic curves have been drawn. The constancy of the distribution coefficient values with the time was used as a criterion for attaining thermodynamic equilibrium between the liquid phases and the solid phases. It has been shown that the equilibrium between the liquid and solid phases is attained in about 15–20 hr. The liquid-phase and wet-solid residue compositions were determined as follows: the Fe^{2+} concentration was determined by complexonometry at pH 1.5 using sulfosalicylic acid as indicator after preliminary oxidation of Fe^{2+} by hydrogen peroxide. The sum of Fe^{2+} and Mn^{2+}, or Co^{2+}, or Zn^{2+}, was also determined complexonometrically at pH 5.5 using xylene orange as indicator after preliminary oxidation of Fe^{2+} by hydrogen peroxide. The Mn^{2+} concentration was determined in the presence of Co^{2+}, Ni^{2+}, and Zn^{2+} complexonometrically at pH 9.5–10 using Eryochrome black as indicator, after masking Co^{2+}, Ni^{2+}, and Zn^{2+} in advance, as cyanides. The sum of Mn^{2+} and Co^{2+}, or Ni^{2+}, or Zn^{2+} was also determined complexonometrically at pH 5.5 using xylene orange as indicator (*7*). The composition of the ideally dried solid phase was calculated by the variant of Schreinemakers' method for algebraic indirect identification of the solid-phase composition (*8*). The systems with Fe^{2+} formate were studied in an argon atmosphere so as to prevent Fe^{2+} oxidation.

Results

The results of the systems: $Fe(HCOO)_2$–$Mn(HCOO)_2$–H_2O, $Fe(HCOO)_2$–$Co(HCOO)_2$–H_2O; $Fe(HCOO)_2$–$Zn(HCOO)_2$–H_2O, $Mn(HCOO)_2$–$Co(HCOO)_2$–H_2O, $Mn(HCOO)_2$–$Ni(HCOO)_2$–H_2O, and $Mn(HCOO)_2$–$Zn(HCOO)_2$–H_2O at 25°C are listed in Tables I–VI. The experimental results show that continuous series of mixed crystals are formed in these systems. The formation of continuous series of mixed crystals in the formate systems was proven using X-ray diffraction method. As an example in Fig. 1, stick diagrams of the simple salts and the mixed crystals formed in the $Mn(HCOO)_2$–$Zn(HCOO)_2$–H_2O system are shown.

Discussion

It was shown (*9*) that when mixed crystals are formed on the basis of isodimorphous substitution, the distribution coefficient obey, with a high degree of accuracy, the relation

$$D_{2/1} = \left[\frac{M_{1,0}}{M_{2,0}}\right]^2 \frac{f_1}{f_2} \exp\left[\frac{-\Delta G_{\mathrm{II}\to\mathrm{I}}}{RT}\right], \qquad (1)$$

TABLE I

SOLUBILITY IN THE $Fe(HCOO)_2$–$Mn(HCOO)_2$–H_2O SYSTEM AT 25°C

Liquid phase, wt%		Ideally dried solid phase, wt%			
$Fe(HCOO)_2$	$Mn(HCOO)_2$	$Fe(HCOO)_2$	$Mn(HCOO)_2$	$D_{Fe/Mn}$	$D_{Mn/Fe}$
4.20	—	—	—	—	—
3.64	0.63	74.37	5.83	2.32	0.43
3.16	1.33	63.91	16.29	1.64	0.61
2.96	1.67	61.32	18.88	1.82	0.55
2.26	2.87	47.06	33.14	1.80	0.56
1.56	3.87	33.85	43.01	1.95	0.51
0.67	5.15	13.59	66.62	1.57	0.64
—	6.28	—	—	—	—

TABLE II

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

Liquid phase, wt%		Ideally dried solid phase, wt%			
$Fe(HCOO)_2$	$Co(HCOO)_2$	$Fe(HCOO)_2$	$Co(HCOO)_2$	$D_{Fe/Co}$	$D_{Co/Fe}$
4.20	—	—	—	—	—
3.51	0.44	66.78	13.39	0.62	1.61
2.47	0.97	48.15	32.05	0.59	1.70
2.01	1.25	39.69	40.51	0.61	1.64
1.51	1.57	27.56	52.64	0.54	1.85
1.17	1.74	22.04	58.15	0.56	1.79
0.90	1.79	15.90	64.30	0.49	2.04
0.51	2.45	8.81	71.38	0.52	1.92
—	2.44	—	—	—	—

TABLE III

SOLUBILITY IN THE $Fe(HCOO)_2$–$Zn(HCOO)_2$–H_2O SYSTEM AT 25°C

Liquid phase, wt%		Ideally dried solid phase, wt%			
$Fe(HCOO)_2$	$Zn(HCOO)_2$	$Fe(HCOO)_2$	$Zn(HCOO)_2$	$D_{Fe/Zn}$	$D_{Zn/Fe}$
4.20	—	—	—	—	—
3.72	0.78	64.96	14.91	0.92	1.09
3.09	1.53	53.40	16.56	1.00	1.00
2.36	2.37	39.13	41.55	0.94	1.06
1.52	3.33	28.45	53.23	1.18	0.85
1.07	4.04	18.09	62.73	1.09	0.92
0.64	4.52	11.09	73.07	1.08	0.92
—	5.38	—	—	—	—

TABLE IV

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

Liquid phase, wt%		Ideally dried solid phase, wt%			
$Mn(HCOO)_2$	$Co(HCOO)_2$	$Mn(HCOO)_2$	$Co(HCOO)_2$	$D_{Mn/Co}$	$D_{Co/Mn}$
6.28	—	—	—	—	—
5.38	1.29	51.42	18.53	0.24	4.17
3.95	1.00	41.35	39.16	0.27	3.74
3.84	1.11	39.62	40.88	0.28	3.57
2.28	1.49	19.12	61.61	0.21	4.93
—	2.44	—	—	—	—

TABLE V

SOLUBILITY IN THE $Mn(HCOO)_2$–$Ni(HCOO)_2$–H_2O SYSTEM AT 25°C

Liquid phase, wt%		Ideally dried solid phase, wt%			
$Mn(HCOO)_2$	$Ni(HCOO)_2$	$Mn(HCOO)_2$	$Ni(HCOO)_2$	$D_{Mn/Ni}$	$D_{Ni/Mn}$
6.28	—	—	—	—	—
4.59	0.46	53.59	26.52	0.20	5.00
3.55	0.76	44.42	35.69	0.27	3.75
1.77	1.34	21.31	58.81	0.27	3.75
—	2.13	—	—	—	—

TABLE VI

SOLUBILITY IN THE $Mn(HCOO)_2$–$Zn(HCOO)_2$–H_2O SYSTEM AT 25°C

Liquid phase, wt%		Ideally dried solid phase, wt%			
$Mn(HCOO)_2$	$Zn(HCOO)_2$	$Mn(HCOO)_2$	$Zn(HCOO)_2$	$D_{Mn/Zn}$	$D_{Zn/Mn}$
6.28	—	—	—	—	—
5.38	1.29	59.32	20.99	0.68	1.47
4.20	2.02	48.60	31.82	0.74	1.36
2.50	3.20	25.41	55.26	0.59	1.70
—	5.38	—	—	—	—

where $D_{2/1}$ is the distribution coefficient of component 2 between the solution and the crystal phase of component 1; $M_{1,0}$ and $M_{2,0}$ are the solubilities in molalities of the two salts in their binary solutions; f_1 and f_2 are the rational activity coefficients of the components in the mixed crystals; $\Delta G_{II \rightarrow I}$ is the free energy of the phase transition of the crystals of the component 2 with crystal lattice II into crystal lattice I, typical for com-

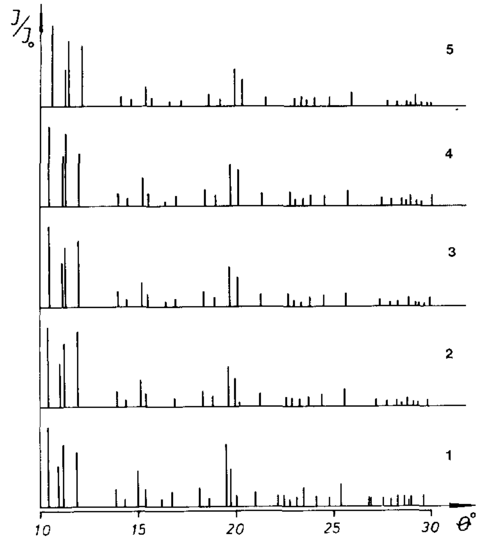

FIG. 1. Stick diagrams of the simple salts and the mixed crystals formed in the $Mn(HCOO)_2$–$Zn(HCOO)_2$–H_2O system. 1—$Mn(HCOO)_2 \cdot 2H_2O$; 2—59.32% $Mn(HCOO)_2$, 20.99% $Zn(HCOO)_2$; 3—48.60% $Mn(HCOO)_2$, 31.82% $Zn(HCOO)_2$; 4—25.41% $Mn(HCOO)$, 55.26% $Zn(HCOO)_2$; 5—$Zn(HCOO)_2 \cdot 2H_2O$.

ponent 1. In the case of isomorphous salts such as the formate dihydrates $\Delta G_{II \to I} = 0$ and Eq. (1) assumes the form

$$D_{2/1} = \left[\frac{M_{1,0}}{M_{2,0}}\right]^2 \frac{f_1}{f_2}. \qquad (2)$$

For a number of metal(II) salt crystal hydrates, such as sulfates, acetates, nitrates, double salts—shoenites and alums, for example, it was found (*9*) that the activity coefficient ratio remains close to 1 and the mixed crystals of these salts may be considered as being close to ideal solid solutions. The calculated distribution coefficients are satisfactory if only the solubilities appear in the formula

$$D_{2/1} \approx \left[\frac{M_{1,0}}{M_{2,0}}\right]^2. \qquad (3)$$

Some deviations, however, are observed for the formates. The main experimental distribution coefficients values as well as the theoretical ones obtained by Eq. (3) are given in Table VII. In the table, the deviation of the highest and lowest distribution coefficients from the mean values are listed for every system.

In systems where deviation from the ideal behavior is observed, the activity coefficients differ substantially from unity. In cases where the activity coefficient are independent of the composition, i.e., where they maintain a constant value along the solubility isotherm, the ratio f_1/f_2 is also constant. For the formates studied here the

TABLE VII

INFLUENCE OF THE CFSE ON THE DISTRIBUTION COEFFICIENT VALUES

Impurity/host ion	D_{exp}	$\left[\frac{M_{1,0}}{M_{2,0}}\right]^2$	ΔS (kJ · mole^{-1})	D_{theor} ($c/2.3RT = 0.0034$)
Mg/Mn	0.12 ± 0.05	0.15	0	0.15
Mg/Co	0.02 ± 0.01	0.015	88.90	0.03
Mg/Ni	0.04 ± 0.01	0.015[a]	121.88	0.04
Mg/Zn	0.08 ± 0.03	0.09	0	0.09
Mn/Fe	0.54 ± 0.10	0.42[a]	49.71	0.61
Mn/Co	0.25 ± 0.03	0.13[a]	88.90	0.26
Mn/Ni	0.25 ± 0.04	0.10[a]	121.88	0.26
Mn/Zn	0.67 ± 0.08	0.63	0	0.63
Fe/Co	0.52 ± 0.10	0.31[a]	39.19	0.45
Fe/Zn	1.05 ± 0.13	1.49[a]	−49.71	1.00

[a] Cases in which the deviations of the distribution coefficients calculated from the solubilities of the salts do not lie within the experimental error limits.

distribution coefficients were found to be not changed considerably in the entire solubility diagram, which provides the basis to claim that the f_1/f_2 ratio remains constant. In such a case, assuming the regular solution approximation, the activity coefficients may be expressed by the partial molar enthalpy of mixing:

$$RT \ln f_1 = \Delta\overline{H}_1$$
$$RT \ln f_2 = \Delta\overline{H}_2$$

hence, we obtain

$$\frac{f_1}{f_2} = \exp\left[\frac{\Delta\overline{H}_1 - \Delta\overline{H}_2}{RT}\right]. \qquad (4)$$

Then the differences in the partial molar enthalpies of mixing $\Delta\overline{H}_1 - \Delta\overline{H}_2$ is also a constant value. In this case, a linear dependence of the ΔH_{mix} vs x_i $(i = 1,2)$ is required.

Substituting Eq. (4) into Eq. (2) we obtain

$$D_{2/1} = \left[\frac{M_{1,0}}{M_{2,0}}\right]^2 \exp\left[\frac{\Delta\overline{H}_1 - \Delta\overline{H}_2}{RT}\right]. \qquad (5)$$

Thus, the difference in the partial molar enthalpies of mixing should account for the difference in the coordination environment around the two intersubstituting ions. The current theory for the energetics of isomorphous mixing takes into account only the effect of ionic size differences, and of the M–L bond energy differences with respect to the enthalpy of mixing (*10*). For ions possessing nonzero crystal field stabilization energy (CFSE), the effect of the spatial M–L bond orientation in the crystal field should be taken into account (*9*). Then

$$\Delta\overline{H}_1 - \Delta\overline{H}_2 = a \cdot f\left[\frac{\Delta R}{R}\right] + b \cdot \varphi(\Delta\varepsilon) + c \cdot \psi(\Delta S). \qquad (6)$$

Here $\Delta R/R$ is the relative difference in the ionic radii, $\Delta\varepsilon$ is the chemical bond energy difference, and ΔS is the difference in CFSE. The constants a, b, c at this stage of our knowledge should be considered as empirical constants. The constant a is semiempirical since the effect of size differences of the isomorphic intersubstituting ions on the enthalpy of mixing has been studied on a theoretical basis in a number of investigations (*10*).

Then, from Eqs. (5) and (6) we obtain

$$D_{2/1} = \left[\frac{M_{1,0}}{M_{2,0}}\right]^2 \exp\frac{a \cdot f\left(\frac{\Delta R}{R}\right) + b \cdot \varphi(\Delta\varepsilon) + c \cdot \psi(\Delta s)}{RT}. \qquad (7)$$

The first term of Eq. (7) represents the balance in bonding factors between the ions in the crystal and in the aqueous solution for the case of ideally mixing in solid state (Eq. (3)). The exponential term in Eq. (7) takes into account the enthalpy of mixing in the solid state.

From Table VII it is seen that the experimental distribution coefficients essentially coincide with those calculated by Eq. (3) for the Mg^{2+}/Mn^{2+} (ΔR has a maximum value), Mg^{2+}/Zn^{2+} ($\Delta\varepsilon$ has a maximum value) and Mn^{2+}/Zn^{2+} mixed formate crystals, i.e., for ions having p^6, d^5 (high spin), and d^{10} electronic configuration. In such cases, the CFSE is zero and consequently the electronic configuration of the metal ion should not affect additionally the distribution coefficient determined from the solubility ratio only (Eq. (3)). The systems in which the distribution coefficient values calculated by Eq. (3) differ from the experimental ones and do not lie within the experimental error limits are indicated by the footnote. It is obvious that in these systems at least one of the metal ions is an open-shell d-ion, for example, $Fe^{2+}(d^6)$, $Co^{2+}(d^7)$, or $Ni^{2+}(d^8)$.

The data in Table VII are an indication of an important contribution of the CFSE. It is probably connected with the crystal lattices of formates which represent two kinds of alternating metal octahedra linked by bridg-

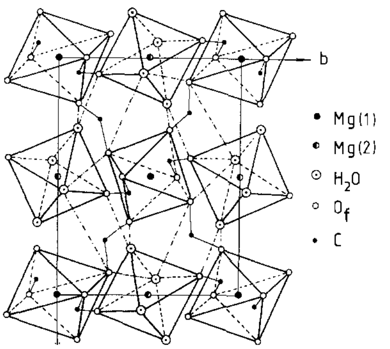

FIG. 2. Crystal structure of $Mg(HCOO)_2 \cdot 2H_2O$.

ing formate groups (Fig. 2). The structures are additionally stabilized by a network of hydrogen bonds (*11–18*). The presence of the formate bridges makes it difficult to distort the structure which may, in fact, be the reason for the isostructure of the formate salts. This fact shows that the differences in the dimensional factor ($\Delta R/R$) and M–L bond energy differences ($\Delta\varepsilon$) weakly affect the formate dihydrate crystal structure.

Thus, from Eq. (7) and assuming that the function ψ is linear, we obtain

$$\log D_{2/1} = \log \left[\frac{M_{1,0}}{M_{2,0}}\right]^2 + \frac{c}{2.3RT}\,\Delta s, \quad (8)$$

where Δs is the CFSE-difference for the host ion and the impurity ion, and c is an empirical constant.

The incorporation of Fe^{2+} (d^6), for example, into the $Zn(HCOO)_2 \cdot 2H_2O$ (Zn^{2+}, CFSE = 0) crystals would require more energy; as a result, the distribution coefficient of Fe^{2+} formate would be lower as compared with the one calculated from the solubilities only: $D^{\text{exp}}_{\text{Fe/Zn}} = 1.03$, $D^{\text{cal}}_{\text{Fe/Zn}} = 1.49$.

To calculate Δs, we have used the following CFSE values of the high-spin octahedral complexes (*19*):

Fe^{2+}	49.71 kJ mole^{-1}
Co^{2+}	88.90 kJ mole^{-1}
Ni^{2+}	121.88 kJ mole^{-1}.

Table VII lists the distribution coefficients calculated by formula (8). The value $c/2.3RT = 0.0034$ has been chosen because for this value, the coincidence between the experimental and calculated distribution coefficient values for every D_{exp} and Δs is greatest. It is seen from the table that the values thus obtained are very close to the experimental ones, and in all cases they do lie within the limits of the experimental error.

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