Some Factors Influencing Distribution Coefficients of Trace Amounts of M²⁺ Ions During the Crystallization of Mn(CH₃COO)₂·4H₂O

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ABSTRACT

Distribution coefficients, $D_{2/1}$ (Henderson – Kraček, Khlopin) of trace amounts of Ni^{2+}, Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, and Sr^{2+} have been determined during the crystallization of $Mn(CH_3COO)_2 \cdot 4H_2O$. Their dependencies on several properties of co-crystallizing acetate hydrates $M(CH_3COO)_2 \cdot nH_2O$ as well as co-crystallizing M^{2+} ions have been analyzed. The $D_{2/1}$ values fall in the range from 0.011 (D_{Cu}) to 0.28 (D_{Co}) and indicate the possibility of effective removal of trace amounts of most investigated ions during the crystallization of $Mn(CH_3COO)_2 \cdot 4H_2O$ at 25 °C. They generally do not depend directly on most investigated factors, but those of Mg^{2+}, Ni^{2+} and Co^{2+} ions, which form acetate tetrahydrates like $Mn(CH_3COO)_2 \cdot 4H_2O$, closely depend on electronegativity of the elements as well as solubility and η parameter and may be estimated on the basis of the mentioned properties using simple formulae.

KEYWORDS

Crystallization, manganese(II) acetate tetrahydrate, Henderson-Kraček, Khlopin distribution coefficients, D.

1. Introduction

Co-crystallization coefficients $D_{2/1}$ (Henderson – Kraček, Khlopin) are important indicators of the effectiveness of crystallization as a method of purification. Therefore they are needed in preparation of high-purity salts. However, their calculation using the general thermodynamic equation relating $D_{2/1}$ to the solubility of co-crystallizing salts $Mn(CH_3COO)_2 \cdot 4H_2O$ and $M(CH_3COO)_2 \cdot nH_2O$‡:

$$D_{2,II/1,I} = \left(\frac{\gamma_{01} \cdot \gamma_{m01}}{\gamma_{02} \cdot \gamma_{m02}} \right)^3 \cdot \left(\frac{\gamma_{m2}}{\gamma_{m1}} \right)^3 \cdot \frac{f_1}{f_2} \cdot \exp\left(-\frac{\Delta\mu^0_{II \to I}}{RT} \right) \qquad (1)$$

is not possible because of a lack of the suitable data (mainly $\Delta\mu_{I \to II}$ as well as $f_1(f_2)$). Hence the effect of chemical, physicochemical and crystal-chemical factors on $D_{2/1}$ values is sought. Such dependences have already been established[1] in sulfate ($MSO_4 \cdot nH_2O$), nitrate ($M(NO_3)_2 \cdot nH_2O$), chloride ($MCl_2 \cdot nH_2O$) and formate ($M(HCOO)_2 \cdot nH_2O$) crystallization systems.

However acetate crystallization systems ($M(CH_3COO)_2 \cdot nH_2O$) have been less well studied and $D_{2/1}$ coefficients of trace amounts of M^{2+} ions have only been determined in the case of $Ni(CH_3COO)_2 \cdot 4H_2O$,[2] $Co(CH_3COO)_2 \cdot 4H_2O$,[3] as well as $Mg(CH_3COO)_2 \cdot 4H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ crystallization.[4]

In the case of $Mn(CH_3COO)_2 \cdot 4H_2O$ only four co-crystallization coefficients $D_{2/1}$ for comparable amounts of other acetates are available: for Mg^{2+} ($D_{2/1} = 0.07$), for Zn^{2+} ($D_{2/1} = 0.30$), for Co^{2+} ($D_{2/1} = 0.28$) and for Ni^{2+} ($D_{2/1} = 1.3$).[5]

The purpose of this work was to determine the co-crystallization coefficients $D_{M/Mn(CH3COO)2.4H2O}$ of trace amounts (10^{-3}–10^{-1} %) of M^{2+} ions ($M^{2+} = \{Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+} Sr^{2+}\}$) with $Mn(CH_3COO)_2 \cdot 4H_2O$ as well as to analyze the influence of some physicochemical and crystal-chemical properties of $Mn(CH_3COO)_2 \cdot 4H_2O$ and $M(CH_3COO)_2 \cdot nH_2O$ as well as Mn^{2+} and M^{2+} ions on $D_{M/Mn(CH3COO)2.nH2O}$ ($D_{2/1}$) coefficients.

2. Experimental

2.1. Reagents and Solutions

Solutions of Ni(II), Co(II), Cu(II), Cd(II), Zn(II), Mg(II), Ca(II) and Sr(II) acetates were prepared by dissolution of the acetate salt (POCh-Gliwice) in water. Ammonia solution (14 mole L⁻¹) was obtained by saturating distilled water with ammonia gas. Sodium versenate p.a. (POCh-Gliwice) – 0.1 mole L⁻¹ water solution, ascorbic acid p.a. (POCh-Gliwice), NH_3-NH_4Cl buffer solution of pH 10 and eriochrome black T ind. (POCh-Gliwice) were used.

2.2. Analytical Methods

The *macrocomponent:* manganese was determined (after addition of ascorbic acid) by complexometric titration with sodium versenate in NH_3-NH_4Cl buffer solution (pH 10) in the presence of eriochrome black T ind.[6] From the manganese(II) content of the mother solution and solution containing dissolved crystal the degree of $Mn(CH_3COO)_2 \cdot 4H_2O$ crystallization, α, was found, as well as the volumes of these solutions (containing 0.300 g of $Mn(CH_3COO)_2 \cdot 4H_2O$) calculated.

The *microcomponents* (Cu, Zn, Ni, Co, Mg, Cd, Ca and Sr) were determined by means of direct atomic absorption spectrometry (Perkin Elmer 3300) from solutions containing 0.300 g of

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‡Where $m_{01}(m_{02})$, $\gamma_{m01}(\gamma_{m02})$ = solubility/mol kg⁻¹/ of $Mn(CH_3COO)_2 \cdot 4H_2O(M(CH_3COO)_2 \cdot nH_2O)$ and mean molal activity coefficient of $Mn(CH_3COO)_2 \cdot 4H_2O(M(CH_3COO)_2 \cdot nH_2O)$ in its binary saturated solution; $m_1(m_2)$, $\gamma_{m1}(\gamma_{m2})$ = solubility/mol kg⁻¹/ and mean molal activity coefficient of $Mn(CH_3COO)_2 \cdot 4H_2O$ $(M(CH_3COO)_2 \cdot nH_2O)$ in the ternary solution being in equilibrium with $(Mn,M)(CH_3COO)_2 \cdot nH_2O$ solid solution; $x_1(x_2)$ = mole fraction of $Mn^{2+}(M^{2+})$ ion, and $f_1(f_2)$ = activity coefficient of ion $Mn^{2+}(M^{2+})$ in this solid solution; $\Delta\mu^0_{II \to I}$ = the molar partial Gibbs free energy of the phase transition of $(M(CH_3COO)_2 \cdot nH_2O)$ from its structure (II) into the structure (I) of $Mn(CH_3COO)_2 \cdot 4H_2O$; R = gas constant, T = temperature /K/.

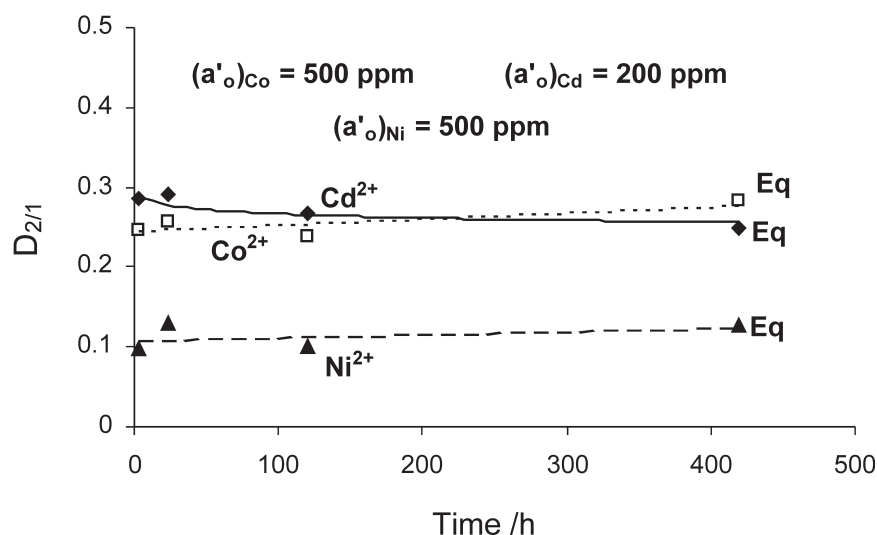* To whom correspondence should be addressed. E-mail: marek.smolik@polsl.pl

Figure 1 The dependence of co-crystallization coefficients $D_{2/1}$ of Co^{2+}, Cd^{2+}, Ni^{2+} on time of crystallization of $Mn(CH_3COO)_2\cdot 4H_2O$ at 25 °C; a'_o = initial concentration of M^{2+} in relation to $Mn(CH_3COO)_2\cdot 4H_2O$; Eq = equilibrium values of $D_{2/1}$, obtained by the second method.

$Mn(CH_3COO)_2\cdot 4H_2O$ in 25 mL of solution. Absorbances of the samples and of the sets of standards having the same concentrations of the matrix (manganese(II) acetate), were measured under the same conditions.

2.3. Methods of Determination of Distribution Coefficients

Distribution coefficients, $D_{M/Mn(CH3COO)2.4H2O}$ were determined at 25 ± 1 °C using the following two methods:

1) the method of isothermal leveling of supersaturation of manganese(II) acetate solutions by stirring its supersaturated solutions for 4–120 hours;

2) the method of long-time stirring of crushed $Mn(CH_3COO)_2\cdot 4H_2O$ crystals in their saturated solution – achieving the equilibrium 'from above' (D^o_{MAX}) and 'from below' (D^o_{min}).

Details of both methods as well as preparation of samples of crystals and mother solutions before analysis are described earlier[3,7] Determined by the above mentioned AAS method relative concentrations of microcomponents: $-a'_k$ (μg M/1g $Mn(CH_3COO)_2\cdot 4H_2O$ in the washed crystal in ppm) and $-a'_r$ (μg M/1g $Mn(CH_3COO)_2\cdot 4H_2O$ in the mother solution in ppm) were applied to calculate the homogeneous distribution coefficients –

$D_{2/1}$ (Henderson-Kraček, Khlopin) by means of the following equation:

$$D_{2/1} = D_{M/Mn(CH_3COO)_2\cdot 4H_2O} = \frac{a'_k}{a'_r}. \tag{2}$$

The results are given in Figs 1 and 2 (the first method) and in Table 1 (the equilibrium values).

3. Results and Discussion

Co-crystallization coefficients, $D_{2/1}$, of microcomponents with $Mn(CH_3COO)_2\cdot 4H_2O$ determined by the first method generally change with increasing time of stirring, and generally tend to the equilibrium $D_{2/1}$ values, obtained by the second method (Figs 1 & 2, Table 1). They had diverse values ranging from $D_{Cu/Mn(CH3COO)2\cdot 4H2O} = 0.011$ to $D_{Co/Mn(CH3COO)2.4H2O} = 0.28$.

These values indicate, that effective removal of trace amounts of most investigated ions (excepting Co^{2+}, Cd^{2+}, Ni^{2+}) is possible by means of crystallization of $Mn(CH_3COO)_2\cdot 4H_2O$ at 25 °C, and so may be used in the preparation of high purity manganese salts.

The dependences of the coefficients $D_{2/1}$ on various properties of the co-crystallizing salts ($Mn(CH_3COO)_2\cdot 4H_2O$ and
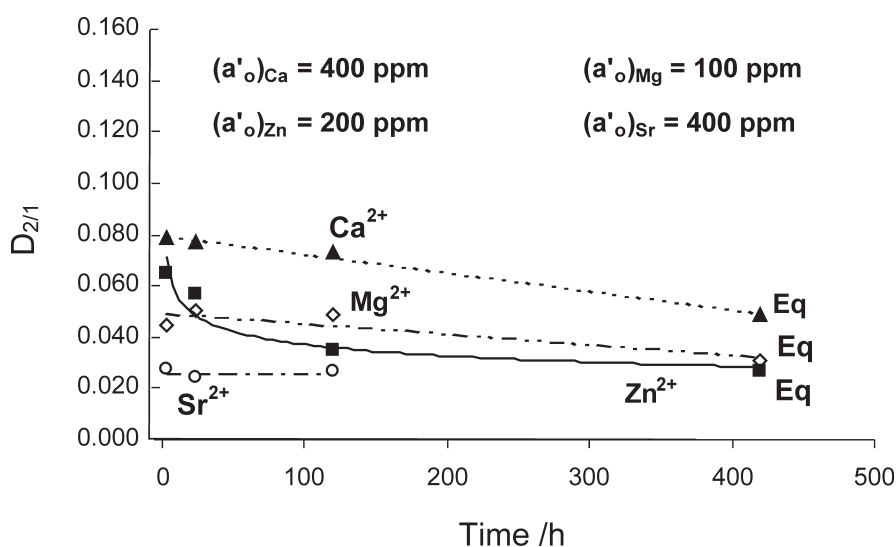

Figure 2 The dependence of co-crystallization coefficients $D_{2/1}$ of Ca^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+} on time of crystallization of $Mn(CH_3COO)_2\cdot 4H_2O$ at 25 °C; a'_o = initial concentration of M^{2+} in relation to $Mn(CH_3COO)_2\cdot 4H_2O$; Eq = equilibrium values of $D_{2/1}$, obtained by the second method.

Table 1 Equilibrium co-crystallization coefficients $D_{2/1}$ of trace amounts of M^{2+} ions with $Mn(CH_3COO)_2 \cdot 4H_2O$ at 25 °C.

Microcomponent M^{2+}	Initial distribution coefficient after long-time stirring		Average distribution coefficient		Average equilibrium distribution coefficient
			for D^o_{min}	for D^o_{MAX}	
	$D^0_{min} = \dfrac{a^{''}_{ko}}{a^{''}_{ro}}$	$D^0_{MAX} = \dfrac{a^{'}_{ko}}{a^{'}_{ro}}$	$\overline{D} \pm t_\alpha \dfrac{s}{\sqrt{n}}$	$\overline{D} \pm t_\alpha \dfrac{s}{\sqrt{n}}$	$\overline{D} \pm t_\alpha \dfrac{s}{\sqrt{n}}$
Ni^{2+}	0.040	0.40	0.113 ± 0.007	0.141 ± 0.036	0.127 ± 0.009
Mg^{2+}	0.025	0.30	0.028 ± 0.004	0.034 ± 0.006	0.031 ± 0.004
Cu^{2+}	0.005	1.00	0.012 ± 0.005	0.010 ± 0.004	0.011 ± 0.003
Co^{2+}	0.120	0.50	0.28 ± 0.02	0.28 ± 0.02	0.28 ± 0.01
Zn^{2+}	0.020	0.20	0.023 ± 0.008	0.031 ± 0.007	0.027 ± 0.005
Cd^{2+}	0.080	0.80	0.25 ± 0.01	0.26 ± 0.01	0.25 ± 0.01
Ca^{2+}	0.030	0.30	0.043 ± 0.004	0.054 ± 0.013	0.049 ± 0.007

$\overline{D}$ = mean value of $D_{M/Mn(CH3COO)2.4H2O}$; t_α = value of Student's t-test for (n –1) degrees of freedom and for the confidence level of $(1 – \alpha) = 0.95$; n = number of determinations; s = standard deviation; D^o_{min}, D^o_{MAX} = initial minimum and maximum values of $D_{M/Mn(CH3COO)2.4H2O}$, respectively.

$M(CH_3COO)_2 \cdot nH_2O$) as well as the metal ions Mn^{2+} and M^{2+} have been analyzed. These properties are presented in Table 2.

3.1. Effect of Solubility of Co-crystallizing Salts

The dependence of $\log D_{2/1}$ on $\log (m_{01}/m_{02})$ for all determined co-crystallization coefficients is not significant (correlation coefficient $\rho_{xy} = –0.3552$). Analogous correlation for coefficients $D_{Ni/Mn(CH3COO)2.4H2O}$, $D_{Mg/Mn(CH3COO)2.4H2O}$, $D_{Co/Mn(CH3COO)2.4H2O}$, that is, for monodentate-bonded acetates[15] that form monoclinic acetate tetrahydrates of similar structure to $Mn(CH_3COO)_2 \cdot 4H_2O$, is higher, but not significant as well ($\rho_{xy} = 0.7421$).

3.2. Effect of Ionic Radius

The effect of ionic radius on coefficients $D_{2/1}$ is presented in Fig. 3. They change irregularly as ionic radius increases and achieve the lowest values for Ca^{2+} and Sr^{2+} ($D_{2/1} < 0.06$), for which $r_{Mn2+} – r_{Ca(Sr)2+} /r_{Mn2+} > 0.22$.

3.3. Effect of Some Other Factors

Correlation coefficients (ρ_{xy}) of $y = \ln D_{2/1}$ or (where $\pi = \ln D_{2/1} – \ln(m_{01}/m_{02})^3$) and $x = \{\Delta\varepsilon, \Delta s, \Delta h$ and $\Delta n\}$ (where Δ are differences of: electronegativity, crystal field stabilization energy, hardness and number of molecules of crystallization water respectively) are presented in Table 3.

As can be seen, values of $\ln D_{2/1}$ for all investigated ions (k = 8) do not depend directly on crystal field stabilization energy (Δs), electronegativity ($\Delta\varepsilon$), hardness of cation (Δh) as well as on the number of molecules of crystallization water (Δn). Corresponding correlation coefficients are insignificant.

However, in the case of acetate tetrahydrates of Ni(II), Mg(II), Co(II) (with monodentate acetate ligands) $\ln D_{2/1}$ is correlated to $|\Delta\varepsilon|$ ($\rho_{xy} = 0.9820$) and π depends on $(\Delta\eta/\eta_M)^2$ ($\rho_{xy} = –0.9987$). Hence it is possible to estimate coefficients $D_{Ni/Mn(CH3COO)2.4H2O}$, $D_{Co/Mn(CH3COO)2.4H2O}$ and $D_{Mg/Mn(CH3COO)2.4H2O}$ by means of the two following empirical equations:

$$D_{2/1} = \left(\frac{m_{01}}{m_{02}}\right)^3 \cdot e^{-8272\left(\frac{\eta_1 - \eta_2}{\eta_1}\right) + 0.698} \tag{3}$$

(at an average relative error not exceeding 7.8 %); or

$$D_{2/1} = e^{-7.644|\varepsilon_1 - \varepsilon_2| - 0.687} \tag{4}$$

(at an average relative error not exceeding 15.6 %); where $m_{01}(m_{02})$ = solubility of $Mn(CH_3COO)_2 \cdot 4H_2O(M'(CH_3COO)_2 \cdot nH_2O)$, $M' = \{Co, Ni, Mg\}$; $\eta_1(\eta_2) = \eta_{Mn(CH3COO)2.4H2O}$ ($\eta_{M'(CH3COO)2.nH2O}$); $\varepsilon_1(\varepsilon_2) = \varepsilon_{Mn}(\varepsilon_{M'})$.

The average coefficient, $D_{2/1}$ for open shell ions (Cu^{2+}, Ni^{2+}, Co^{2+}) is almost twice as great as that for closed shell ions (Mg^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+} Sr^{2+}).

4. Conclusion

Co-crystallization coefficients, $D_{2/1}$ of trace amounts of M^{2+} ions with $Mn(CH_3COO)_2 \cdot 4H_2O$ range from 0.011 ($D_{Cu/Mn(CH3COO)2.4H2O}$) to 0.282 ($D_{Co/Mn(CH3COO)2.4H2O}$). Their values indicate the possibility

Table 2 Some properties of co-crystallizing salts ($M(CH_3COO)_2 \cdot nH_2O$) and ions (M^{2+}) where CS is the crystal system; m = solubility in water at 25 °C; EC = electronic configuration of M^{2+} ion; r = radius of M^{2+} ion[12]; h = cation M^{2+} hardness[13]; ε = electronegativity[14]; $\eta = 10^3 \cdot \sqrt[3]{\dfrac{M_x}{d \cdot N}}$, M_x = molar mass of $M(CH_3COO)_2 \cdot nH_2O/g \cdot mole^{-1}$, d = density/$g \cdot cm^{-3}$, N = Avogadro number; and s = crystal field stabilization energy of M^{2+} ion.

Salt	CS	m/mol kg^{-1}	M^{2+}	EC	r/Å	ε	h/eV	η/Å	s/Dq[e]
$Ni(CH_3COO)_2 \cdot 4H_2O$	monoclinic	0.747 [a]	Ni^{2+}	$[Ar]3d^8$	0.70	1.75	0.29	6.191	1.2
$Mg(CH_3COO)_2 \cdot 4H_2O$	monoclinic	4.608 [a]	Mg^{2+}	[Ne]	0.72	1.23	2.53	6.261	0.0
$Cu(CH_3COO)_2 \cdot H_2O$	monoclinic	0.284 [b]	Cu^{2+}	$[Ar]3d^9$	0.73	1.75	–0.55	5.583	0.6
$Co(CH_3COO)_2 \cdot 4H_2O$	monoclinic	1.453 [b]	Co^{2+}	$[Ar]3d^7$	0.735	1.70	0.44	6.232	0.8
$Zn(CH_3COO)_2 \cdot 2H_2O$	orthorhombic	1.688 [b]	Zn^{2+}	$[Ar]3d^{10}$	0.745	1.66	–1.02	5.929	0.0
$Mn(CH_3COO)_2 \cdot 4H_2O$	monoclinic	2.570 [c]	Mn^{2+}	$[Ar]3d^5$	0.82	1.60	0.69	6.369	0.0
$Cd(CH_3COO)_2 \cdot 2H_2O$	monoclinic	4.314 [c]	Cd^{2+}	$[Kr]3d^{10}$	0.95	1.46	–2.04	5.936	0.0
$Ca(CH_3COO)_2 \cdot H_2O$	monoclinic	2.172 [c]	Ca^{2+}	[Ar]	1.00	1.04	2.33	5.574	0.0
$Sr(CH_3COO)_2 \cdot 0.5H_2O$	hexagonal	1.954 [d]	Sr^{2+}	[Kr]	1.16	0.99	2.15	5.659	0.0

[a] From ref. 8; [b] From ref. 9; [c] From ref. 10; [d] From ref. 11; [e] Dq = natural theoretical unit for crystal-field splitting energies.
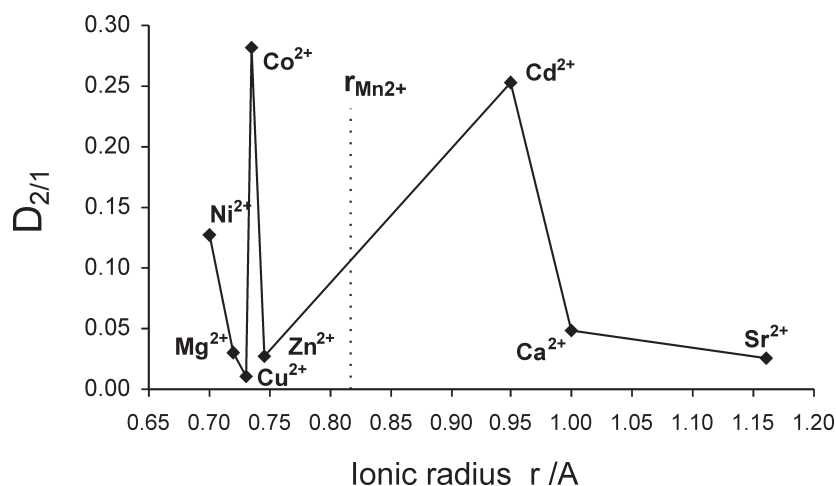
Figure 3 The effect of ionic radius of M^{2+} on co-crystallization coefficients $D_{2/1}$.

Table 3 Correlation coefficients (ρ_{xy}) of y = {ln$D_{2/1}$; π} and x = {r, $\Delta\varepsilon$; $\Delta\mu$, Δn, Δh} for co-crystallizing salts ($Mn(CH_3COO)_2 \cdot 4H_2O$ and $M(CH_3COO)_2 \cdot nH_2O$) and ions (Mn^{2+} and M^{2+}).

y	x	Correlation coefficient ρ_{xy}	Number of investigated ions k
ln $D_{2/1}$	r	−0.0479	8
ln $D_{2/1}$	$\Delta\varepsilon$	−0.3243	8
ln $D_{2/1}$	Δh	0.2845	8
ln $D_{2/1}$	Δn	−0.5379	8
ln $D_{2/1}$	Δs	−0.3242	8
ln $D_{2/1}$	$|\Delta\varepsilon|$	0.9820	3 (Mg^{2+}, Co^{2+}, Ni^{2+})
$\pi = \ln D_{2/1} - \ln (m_{01}/m_{02})^3$	$(\Delta\eta/\eta_M)^2$	**−0.9987**[†]	3 (Mg^{2+}, Co^{2+}, Ni^{2+})

[†]Significant correlation coefficient ρ_{xy} is indicated in bold.

of effective removal of trace amounts of most investigated ions during the crystallization of $Mn(CH_3COO)_2 \cdot 4H_2O$ at 25 °C. This may find application in preparation of high-purity manganese(II) salts.

Coefficients $D_{2/1}$ for Mg^{2+}, Ni^{2+} and Co^{2+} ions, which form (like $Mn(CH_3COO)_2 \cdot 4H_2O$) acetate tetrahydrates, closely depend on electronegativity of the elements as well as η and may be calculated using simple empirical formula.

M^{2+} ions, whose radii r_{M2+} fulfill the following condition: $|r_{Mn2+} - r_{M2+}|/r_{Mn2+} > 0.22$ have very low values of their co-crystallization coefficients ($D_{M2+/Mn(CH3COO)2.4H2O} < 0.06$).

Open shell ions (Cu^{2+}, Ni^{2+}, Co^{2+}) generally co-crystallize with $Mn(CH_3COO)_2 \cdot 4H_2O$ to a greater degree than closed shell ones (Mg^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+} Sr^{2+}).

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