Thermodynamic models for solution behavior and solid-liquid equilibrium in acetate binary systems from low to very high concentration at 25°C

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In this study we developed new thermodynamic models for solution behavior and solid-liquid equilibrium in eight acetate binary systems from low to very high concentration at 25°C: six systems of the type 1-1 ($X(CH_3COO)$-H_2O with X= (Li, Na, K, Rb, Cs, and Tl)) and two systems of the type 2-1 ($Y(CH_3COO)_2$-H_2O with Y= (Mg, and Ba)). Models were developed on the basis of Pitzer ion interactions approach. To parameterize models for binary systems we used all available experimental osmotic coefficients data (φ) for the whole concentration range of solutions. To develop models, we used different versions of the standard molality-based Pitzer approach. It was established that for all acetate systems under study application of extended approach with 4 parameters (β^0, β^1, β^2 and C^φ) and variation of α_1 and α_2 terms in fundamental Pitzer equations leads to the lowest values of standard model-experiment deviation. The predictions of new developed here models are in excellent agreement with experimental φ data, and with recommendations on the mean activity coefficients ($\gamma_\pm$) from low to very high concentration: up to 23.8 m in $K(CH_3COO)$-H_2O, up to 39.2 m in $Rb(CH_3COO)$-H_2O, and up to 52.2 m in $Cs(CH_3COO)$-H_2O. On the basis of evaluated binary parameters important thermodynamic characteristics (Deliquescence Relative Humidity DRH, thermodynamic solubility products K°_{sp}; standard molar Gibbs free energy of formation, $\Delta_f G^\circ_m$) for 7 acetate solids were determined at 25°C. The calculated DRH and $\Delta_f G^\circ_m$ values were compared with those reported in the literature. The models described in this study are of high importance, especially in development and improvement of technology for production and purification of acetate solutions and solid phases.

Keywords: Computer thermodynamic modeling; Pitzer approach; acetate binary systems; solid-liquid equilibrium

INTRODUCTION

Computer models that predict solution behavior and solid-liquid-gas equilibria close to experimental accuracy have wide applicability. They can simulate the complex changes that occur in nature and can replicate conditions that are difficult or expensive to duplicate in the laboratory. Such models can be powerful predictive and interpretive tools to study the geochemistry of natural waters and mineral deposits, solve environmental problems and optimize industrial processes. However, development of comprehensive models for natural systems, with their complexity and sensitivity, is a very difficult, time consuming and challenging task.

The specific interaction approach for describing electrolyte solutions to high concentration introduced by Pitzer [1, 2] represents a significant advance in physical chemistry that has facilitated the construction of accurate computer thermodynamic models. It was shown that this approach could be expanded to accurately calculate solubilities in complex brines, and to predict the behavior of natural and industrial fluids from very low to very high concentration at standard temperature of 25°C,

and in the temperature range from 0°C to 250°C [2-14]. In this study we developed new not concentration-restricted thermodynamic models for solution behavior and solid-liquid equilibrium in eight acetate binary systems from low to very high concentration at 25°C: six systems of the type 1-1 ($X(CH_3COO)$-H_2O with X= (Li, Na, K, Rb, Cs, and Tl)) and two systems of the type 2-1 ($Y(CH_3COO)_2$-H_2O with Y= (Mg, and Ba)). Models were developed on the basis of Pitzer ion interactions approach [1-14]. The previously developed by Pitzer and Mayorga [2] and by Kim and Frederick [3] Pitzer approach based thermodynamic models for acetate binary systems were tested by comparison with experimental osmotic coefficient data and with recommendations on activity coefficients ($\gamma_\pm$) in binary solutions. The models which give the best agreement with (φ)-, and ($\gamma_\pm$) data from low to high concentration, up to m(sat), were accepted as correct models which can be used for solubility calculations in binary acetate systems.

Acetate is an ingredient used in many products like cosmetics, cleaning supplies, textiles and photographic films.

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Acetate has also historically been used as a coating on magnetic tapes used for early computer storage, and for the plastic sheets used with overhead projectors. The models described in this study are of high importance, especially in development and improvement of technology for production and purification of acetate solutions and solid phases.

METHODOLOGY

The models for acetate binary systems have been developed and tested on the basis of Pitzer's semi-empirical equations [1, 2]. Pitzer approach has found extensive use in modeling of the thermodynamic properties of aqueous electrolyte solutions. According to Pitzer theory, electrolytes are completely dissociated and in the solution there are only ions interacting with one another [1, 2]. Two kinds of interactions are observed: (i) specific Coulomb interaction between distant ions of different signs, and (ii) nonspecific short-range interaction between two and three ions. The first kind of interaction is described by an equation of the type of the Debye-Hueckel equations. Short-range interactions in a binary system (MX(aq)) are determined by Pitzer using the binary parameters of ionic interactions $(\beta^{(0)}, \beta^{(1)}), C^\varphi$. The Pitzer's equations are described and widely discussed in the literature [1-14]. Therefore, these equations are not given here. According to the basic Pitzer equations, at constant temperature and pressure, the solution model parameters to be evaluated for mixed ternary system are: 1) pure electrolyte $\beta^{(0)}$, $\beta^{(1)}$, and C^φ for each cation-anion pair; 2) mixing θ for each unlike cation-cation or anion-anion pair; 3) mixing ψ for each triple ion interaction where all ions are not of the same sign [4-14]. Pitzer and Mayorga [2] did not present analysis for any 2-2 (e.g. $MgSO_4$-H_2O) or higher {e.g. 3-2: $Al_2(SO_4)_3$-H_2O} electrolytes. Pitzer and Mayorga modified the original equations for the description of 2-2 binary solutions: parameter $\beta^{(2)}(M,X)$, and an associated α_2 term are added to the original expression. Pitzer presented these parameterizations, assuming that the form of the functions (i.e. 3 or 4 β and C^φ values, as well as the values of the α terms) vary with electrolyte type. For binary electrolyte solutions in which either the cationic or anionic species are univalent (e.g. NaCl, Na_2SO_4, or $MgCl_2$), the standard Pitzer approach uses 3 parameters (i.e. omits the $\beta^{(2)}$ term) and α_1 is equal to 2.0 ([1, 2, 4, 6]). For 2-2 type of electrolytes the model includes the $\beta^{(2)}$ parameter and α_1 equals to 1.4 and α_2 equals to 12 [13].

To describe the high-concentration solution behavior of systems showing a "smooth" maximum on $\gamma\pm$ *vs.* m dependence, and to account for strong association reactions at high molality, Christov and co-authors [5-12, 14] used a very simple modeling technology: introducing into a model a fourth ion interaction parameter from the basic Pitzer theory $\{\beta^{(2)}\}$, and varying the values of α_1 and α_2 terms. According to previous studies of Christov [6-13] an approach with 4 ion interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^φ), and varying α_1 and α_2 values can be used for solutions for which ion association occurs in the high molality region. This approach was used for binary electrolyte systems of different type: 1-1, 2-1, 3-1, 1-2 and 3-2 [5-12,14]. The resulting models reduce the sigma values of fit of experimental activity data, and extend the application range of models for binary systems to the highest molality, close or equal to molality of saturation {m(sat)}, and in case of data availability: up to supersaturation.

RESULTS AND DISCUSSION

In this study we developed new not concentration-restricted thermodynamic models at 25ºC for solution behavior and solid-liquid equilibrium in all acetate binary systems, for which activity data are available: six systems of the type 1-1 (X(CH_3COO)-H_2O with X= (Li, Na, K, Rb, Cs, and Tl)) and two systems of the type 2-1 (Y(CH_3COO)$_2$-H_2O with Y= (Mg, and Ba)). The new models are developed on the basis of Pitzer ion interactions approach. To parameterize models for acetate binary systems we used all available experimental osmotic coefficients data for whole concentration range of solutions, and up to saturation point. The models have been constructed using low molality data from Hamer and Wu [15] and Mikulin [17], and osmotic coefficients data-point at saturation from Mikulin [17]. The low molality osmotic coefficients data presented by Robinson and Stokes [16] are very close to the data given in [17]. To develop the models, we used different versions of standard molality-based Pitzer approach. It was established that for all acetate systems application of extended approach with 4 parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^φ) and variation of α_1 and α_2 terms in fundamental Pitzer equations leads to the lowest values of standard model-experiment e deviation. In Table 1 we compare single electrolyte parameters for the binary acetate systems (Li(CH_3COO)-H_2O, Na(CH_3COO)-H_2O, K(CH_3COO)-H_2O, Rb(CH_3COO)-H_2O, Cs(CH_3COO)-H_2O, Tl(CH_3COO)-H_2O, Mg(CH_3COO)$_2$-H_2O, and Ba(CH_3COO)$_2$-H_2O), evaluated within this study and given in the literature.

Table 1. Comparison of single electrolyte parameters for binary acetate systems (Li(CH₃COO) (aq), Na(CH₃COO) (aq), K(CH₃COO) (aq), Cs(CH₃COO) (aq), Rb(CH₃COO) (aq), Tl(CH₃COO) (aq)), Ba(CH₃COO)₂ (aq), Mg(CH₃COO)₂ (aq)), evaluated within this study and given in literature. m (max) = maximum molality (mol.kg⁻¹) of experimental activity data used in model parameterization and validation, σ = standard deviation of fit of osmotic coefficients, n = number of experimental data points

System	Ref. Model /This study	α_1	α_2	$\beta^{(0)}$	$\beta^{(1)}$	C^φ	$\beta^{(2)}$	σ	m (max)/	Activity data (φ) source
Li(CH₃COO) (aq)	K&F[a]	2	-	0.11215	0.20243	-0.00519	-	0.00117	4	[15]
	P&M[b]	2	-	0.1124	0.2483	-0.00525	-	0.001	4	[16]
	This study[c]	2	-1	0.110162	0.252672	-0.00598	0.00068	0.00039	9	[17] (n=24)
Na(CH₃COO) (aq)	K&F[a]	2	-	0.13723	0.34195	-0.00474	-	0.00096	3.5	[15]
	P&M[b]	2	-	0.1426	0.3237	-0,00629	-	0.001	3.5	[16]
	This study[c]	2	1	0.114574	0.173754	-0.00333	0.12613	0.00037	8	[17] (n=24)
K(CH₃COO) (aq)	K&F[a]	2	-	0.15283	0.35513	-0.00432	-	0.00087	3.5	[15]
	P&M[b]	2	-	0.1587	0.3251	-0,00660	-	0.001	3.5	[16]
	This study[c]	2	-1	0.156809	0.327685	-0.00727	0.00046	0.00259	25	[17] (n=41)
Rb(CH₃COO) (aq)	K&F[a]	2	-	0.16296	0.32918	-0.00561	-	0.00062	3.5	[15]
	P&M[b]	2	-	0.1622	0.3353	-0.00551	-	0.001	3.5	[16]
	This study[c]	2.62	0.02	-2.247348	0.264659	0.00215	2.47881	0.00161	40	[17] (n=48)
Cs(CH₃COO) (aq)	K&F[a]	2	-	0.17144	0.32896	-0.00793	-	0.00063	3.5	[15]
	P&M[b]	2	-	0.1628	0.3605	-0.00555	-	0.001	3.5	[16]
	This study[c]	-0.8	1	0.112181	0.000109	-0.00252	0.28736	0.00436	53	[17] (n=47)
Tl(CH₃COO) (aq)	K&F[a]	2	-	0.00878	-0.04105	-0.00153	-	0.00215	6	[15]
	P&M[b]	2	-	0.0082	0.0131	-0.00127	-	0.001	6	[16]
	This study[c]	2	1	0.026702	0.131112	-0.00326	-0.09122	0.00021	6	[17] (n=23)
Mg(CH₃COO)₂ (aq)	K&F[a]	2	-	0.22930	2.04167	-0.01460	-	0.00370	4	[16]
	This study[c]	2	1	0.111212	-0.27943	0.00080	0.71466	0.00251	6	[17] (n=21)
Ba(CH₃COO)₂ (aq)	K&F[a]	2	-	0.28725	2.87507	-0.04539	-	0.00663	3.5	[16]
	This study[c]	2	1	-0.013209	-1.44114	0.00519	1.63477	0.00200	5	[17] (n=18)

[a]Kim, Frederlck (1988) [3]; [b] Pitzer, Mayorga (1973) [2]; [c]Accepted model

On Fig. 1 we compare model calculated (lines) osmotic coefficients (φ) of Li(CH₃COO), Na(CH₃COO), K(CH₃COO), Rb(CH₃COO), Cs(CH₃COO), Tl(CH₃COO), Mg(CH₃COO)₂, and Ba(CH₃COO)₂ in binary solutions Li(CH₃COO)-H₂O, Na(CH₃COO)-H₂O, K(CH₃COO)-H₂O, Rb(CH₃COO)- H₂O, Cs(CH₃COO)-H₂O, Tl(CH₃COO)-H₂O, Mg(CH₃COO)₂-H₂O and Ba(CH₃COO)₂-H₂O against molality at T = 25ºC with recommendations in literature (symbols). The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data (φ) in

binary solutions from low to extremely high concentration (up to 23.8 m in K(CH$_3$COO)-H$_2$O, up to 39.2 m in Rb(CH$_3$COO)-H$_2$O, and up to 52.2 m in Cs(CH$_3$COO)-H$_2$O). As it is shown on Fig. 1 for acetate systems, the new models developed in this study are in pure agreement at high concentration with the standard approach 3-parameters low molality models of Pitzer and Mayorga [2] and of Kim and Frederick [3].
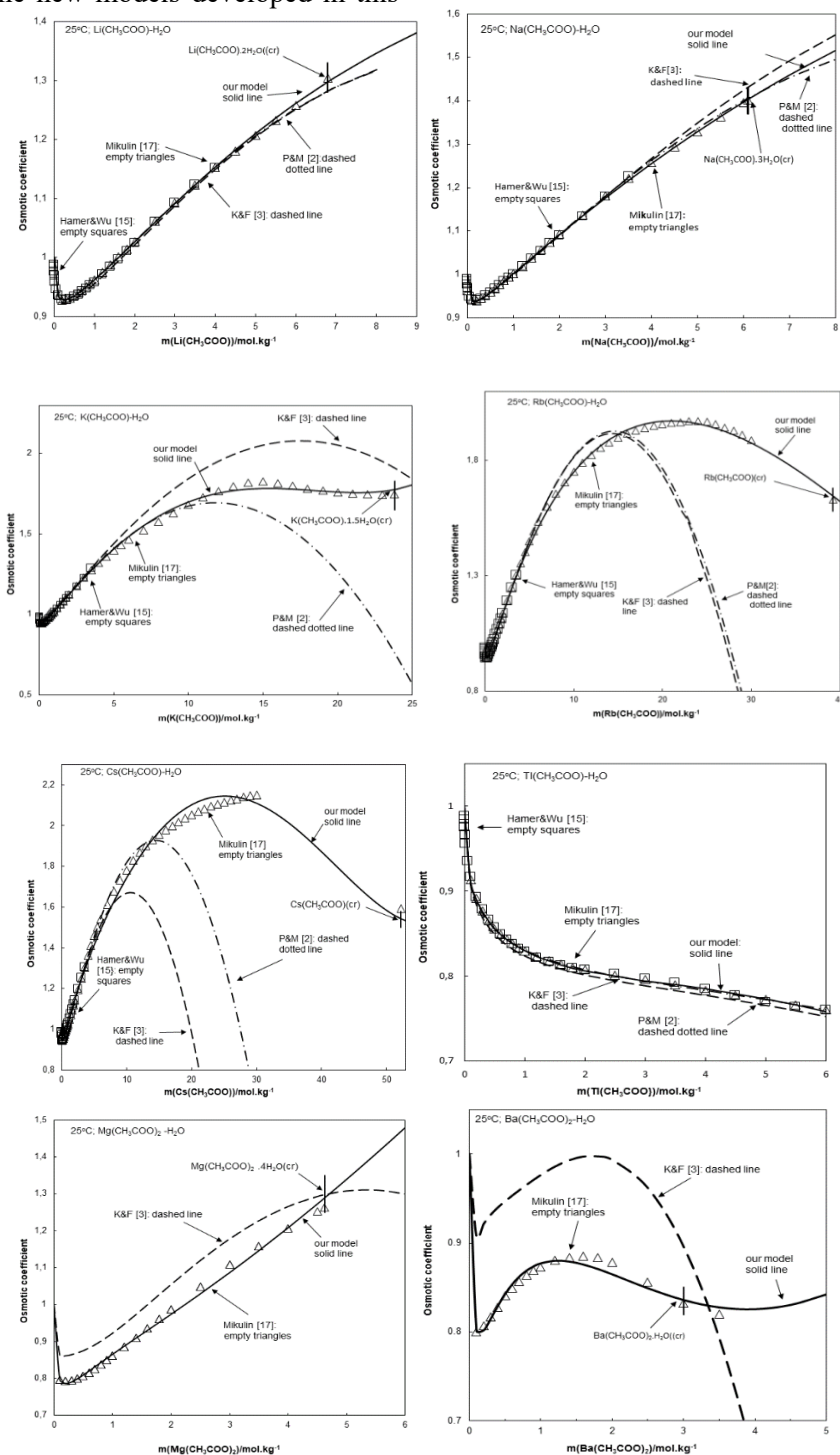

Fig. 1. Comparison of model calculated (lines) osmotic coefficients (φ) of Li(CH$_3$COO), Na(CH$_3$COO), K(CH$_3$COO), Rb(CH$_3$COO), Cs(CH$_3$COO), Tl(CH$_3$COO), Mg(CH$_3$COO)$_2$, and Ba(CH$_3$COO)$_2$ in binary solutions Li(CH$_3$COO)-H$_2$O, Na(CH$_3$COO)-H$_2$O, K(CH$_3$COO)-H$_2$O, Rb(CH$_3$COO)-H$_2$O, Cs(CH$_3$COO)-H$_2$O, Tl(CH$_3$COO)-H$_2$O, Mg(CH$_3$COO)$_2$-H$_2$O and Ba(CH$_3$COO)$_2$-H$_2$O against molality at T = 298.15 K with recommendations in literature (symbols). Heavy solid lines represent the predictions of the developed in this study and accepted models. Dashed lines, and dashed dotted lines represent the predictions of the reference models of Kim and Frederick [3], and of Pitzer and Mayorga [2], respectively. The experimental data are taken from Mikulin [17] (empty triangles), and Hammer and Wu [15] (empty squares). The vertical lines denote the molality of stable crystallization of solid acetate phases {from Mikulin [17]}.

Table 2. Comparison between model calculated and recommended values of the Deliquescence Relative Humidity [DRH (%) = a_w^s × 100; where a_w^s is activity of water at saturation], of the logarithm of the thermodynamic solubility product (K^o_{sp}), and standard molar Gibbs energy of formation, $\Delta_f G^o_m$, of acetate solid phases crystallizing from saturated binary solutions at T = 25°C; m^s= molality of saturation (mol.kg^{-1}).

Salt composition	m^s		$\ln K^o_{sp}$	DRH(%)		$\Delta_f G^o_m$ /(kJ.mol^{-1})		
	Exp[17]	Calc.	Calc.	Calc.	From [17]	Calc.^{a}	From [18]	From [17]
Li(CH$_3$COO).2H$_2$O(cr)	6.79	6.79	3.4669	72.81	72.70	-1128.28	-	- 1135.16
Na(CH$_3$COO).3H$_2$O(cr)	6.1	6.1	3.4977	73.46	73.5	-1333.93	-1328.6	- 1340.34
K(CH$_3$COO).1.5H$_2$O(cr)	23.8	23.8	7.7059	21.84	22.5	-989.17	-	- 997.26
Rb(CH$_3$COO)(cr)	39.2	39.2	11.9479	9.77	≈ 10	- 623.67	-	- 622.12
Cs(CH$_3$COO)(cr)	52.2	52.2	13.0764	5.48	≈ 5	-628.916	-	-
Mg(CH$_3$COO)$_2$.4H$_2$O(cr)	4.62	4.62	2.5138	72.47	72.9	-2135.71	-	- 2149.40
Ba(CH$_3$COO)$_2$.H$_2$O(cr)	3.0	3.0	0.6006	87.33	87.4	-1535.03	-	- 1546.82

$^a\Delta_f G^o_m$ values for solid phases are calculated using chemical potential values of solution components given in Wagman *et al.* [18].

On the basis of binary parameters evaluated in this study we determined water activity (a_w) and Deliquescence Relative Humidity (DRH (%)) of solid phases crystallizing from saturated binary solutions. According to Lach *et al.* [5] and Donchev *et al.* [14]:

$$\text{DRH (\%)} = a_w \text{(sat)} \times 100 \qquad (1)$$

where a_w (sat) is activity of water at saturation. The results of DRH calculations are given in Table 2. The DRH predictions of new and accepted models are in excellent agreement with the experimental data determined using isopiestic method, and given in [17]. According to model calculations, the solid-liquid phase change of Cs(CH$_3$COO)(cr) occurs at extremely low relative humidity of environment. As a next step, using the accepted new developed parameterizations, and experimentally determined molalities (m(sat)) of the saturated binary solutions [17] we calculated the logarithm of the thermodynamic solubility product (ln K^o_{sp}) of acetate solid phases crystallizing from saturated binary solutions at 25°C. The calculation approach is the same as in [5-14]. Therefore, for Na(CH3COO.3H$_2$O)(s):

$$K^o sp \, (\text{Na(CH3COO.3H}_2\text{O)(s)}) = \gamma_{(\pm)} \text{(sat)}^2.\text{m(sat)}^2 \, a_w^5 \qquad (2)$$

Then, the calculated K^{o}sp values can be directly used to calculate standard chemical potential ($\Delta_f G^o_m$) of acetate solids [5]. K^{o}sp *vs.* standard chemical potential:

$$\text{RTln } K^o sp \, (\text{Na(CH3COO.3H}_2\text{O)(s)}) = \Delta_f G^o_m \, (\text{Na(CH3COO.3H}_2\text{O)(s)} - \Delta_f G^o_m (\text{Na}^+) - \Delta_f G^o_m (\text{CH3COO}^-) - 3\Delta_f G^o_m (\text{H}_2\text{O}) \qquad (3)$$

In Table 2 we compare model calculated and recommended values of the Deliquescence Relative Humidity (DRH), of the logarithm of the thermodynamic solubility product (ln K$^o_{sp}$), and standard molar Gibbs energy of formation, $\Delta_f G^o_m$, of acetate solid phases crystallizing from saturated binary solutions at T = 25°C.

The calculated $\Delta_f G^o_m$ for Na(CH$_3$COO).3H$_2$O(cr) lies between the recommended values of Wagman *et al.* [18] and Mikulin [17]. For all other acetate solids $\Delta_f G^o_m$ values are given only in [17]. A good agreement is obtained for Rb(CH$_3$COO)(cr). The pure agreement for other acetate solids is mainly due to the different values for chemical potential values of solution components used in this study and in [17] (see Eq. (3)). Here we calculate $\Delta_f G^o_m$ values for solid acetate phases using chemical potential values of solution components given in Wagman *et al.* [18].

CONCLUSIONS

In this study we developed new not concentration restricted thermodynamic models for solution behavior and solid-liquid equilibrium in binary solutions Li(CH$_3$COO)-H$_2$O, Na(CH$_3$COO)-H$_2$O, K(CH$_3$COO)-H$_2$O, Rb(CH$_3$COO)-H$_2$O, Cs(CH$_3$COO)-H$_2$O, Tl(CH$_3$COO)-H$_2$O, Mg(CH$_3$COO)$_2$-H$_2$O and Ba(CH$_3$COO)$_2$-H$_2$O at T = 25°C. The new models were developed on the basis of Pitzer ion interactions approach. To develop the models, we

used different versions of standard molality-based Pitzer approach. The models which give the best agreement with (φ)-, and ($\gamma_\pm$) data from low to high concentration, up to m(sat), were accepted as correct models which can be used for solubility calculations in binary systems and determination of thermodynamic characteristics of acetate solid phases. It was established that for all acetate systems under study application of extended approach with 4 parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^φ) and variation of α_1 and α_2 terms in fundamental Pitzer equations leads to the lowest values of standard model-experiment deviation. The predictions of new developed here models are in excellent agreement with experimental osmotic coefficients data (φ) in binary solutions from low to extremely high concentration (up to 52.2 m in $Cs(CH_3COO)-H_2O$). On the basis of evaluated binary parameters important thermodynamic characteristics (Deliquescence Relative Humidity DRH, thermodynamic solubility products K°_{sp}; standard molar Gibbs free energy of formation, $\Delta_f G^\circ_m$) for 7 acetate solids were determined at 25°C. The calculated DRH and $\Delta_f G^\circ_m$ values are compared with those reported in the literature.

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