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Phase Diagram of Ternary Calcium Acetate—Magnesium Acetate—Water System at 298 K, 313 K and 323 K

Hong-Kun Zhao, Dao-Sen Zhang, Cao Tang, Pan-Ming Jian and Shi-Hai Yuan

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The solubility data of the calcium acetate-magnesium acetate-water system at 298, 313, and 323 K were measured using the Schreinemaker's wet residue method, the corresponding phase diagram for the system were constructed. The solid phase in the system at different temperatures was confirmed by the Schreinemaker's wet residue method, which correspond to $Mg(CH_3COO)_2{\cdot}4H_2O$ and $Ca(CH_3COO)_2{\cdot}2H_2O$. At the studied temperature, no double salt was formed. The crystalline region of $Ca(CH_3COO)_2{\cdot}2H_2O$ is larger than that of $Mg(CH_3COO)_2{\cdot}4H_2O$. The solubility of $Mg(CH_3COO)_2$ increases with the increasing of the temperature, while the solubility of $Ca(CH_3COO)_2$ decreases with the increasing of the temperature.

Keywords ternary system, calcium acetate, magnesium acetate, phase diagram

1. Introduction

Calcium magnesium acetate (CMA) was first identified as a low corrosion, environmental alternative to road salt by the US Federal Highway Administration in the late 1970s. It is a relatively new product in the world market and a chemical with two major large-scale potential applications for solving environmental problems: (a) as the best road deicing salt candidate to replace the corrosive and environmentally unacceptable sodium chloride and calcium chloride currently in use for road and highway deicing and (b) as a control agent for the toxic particulate, SO_x, NO_x, H_2S emissions[1-7] and sulfur,[7] as well as an effective catalyst for the facilitation of coal combustion.

Due to the great importance of CMA, efforts have been made to produce it on a commercial scale.[8-13] A commercial method of making CMA involves formation of the CMA in an aqueous environment in which all the reactants are soluble and in equilibrium with the CMA product, thus resulting in a CMA-containing solid, which is contaminated, in various amounts, with calcium acetate and magnesium acetate. Particularly, Fu Su et al.[12] directly used calcium acetate and magnesium acetate as raw materials reaction with glacial acetic acid to produce calcium magnesium acetate. It is well-known that the preparing process of CMA is based on the phase diagram of the quinary Ca^{2+}, Mg^{2+}, H^+ // CH_3COO^- - H_2O system. Calcium acetate solubilities in water was investigated in 1887 by Krasnicki,[14] in 1902 by Lumsden,[15] in 1934 by Dunn[16] and new solubilities were presented by Saury et al.[17] and Apelblat et al.[18] Magnesium acetate solubilities were reported in 1926 by Rivett,[19] recently by Apelblat.[18,20] The solubilities of magnesium acetate and calcium acetate in water at studied temperatures (298, 313, and 323 K) are presented in Table 1. It can be seen from Table 1 that the reported solubilities of calcium acetate and magnesium acetate did not agree well with each other.

Although the phase diagrams of the subsystems $Mg(CH_3COO)_2$-H_2O and $Ca(CH_3COO)_2$-H_2O have been

Hong-Kun Zhao, Dao-Sen Zhang, Cao Tang, Pan-Ming Jian, and **Shi-Hai Yuan,** College of Chemistry and Chemical Engineering, YangZhou University, Yangzhou, Jiangsu 225002, P. R. China. Contact e-mail: hkzhao@zzu.edu.cn

Table 1 Solubility of calcium acetate/magnesium acetate in water at 298, 313 and 323 K

System	Temperature (K)	Solubility (mass %)	References
Calcium acetate-water	298	25.46	15
		24.83	15
		26.08	16
		24.84	18
		25.57	18
		25.78	this work
	313	24.9	15
		25.03	this work
	323	24.8	15
		24.7	18
		24.51	this work
Magnesium acetate-water	298	38.50	18
		39.62	19
		39.79	this work
	313	41.28	18
		43.26	19
		43.29	this work
	323	42.95	18
		47.05	19
		47.17	this work

Table 2 Solubility Data for $Mg(CH_3COO)_2$ (1)-$Ca(CH_3COO)_2$ (2)-H_2O(3) Systems from 298, 313 and 323 K

Composition of liquid phase (mass %)		Composition of solid phase (mass %)		
$100 \cdot w_1$	$100 \cdot w_2$	$100 \cdot w_1$	$100 \cdot w_2$	Equilibrium solid phase
T = 298 K				
39.79	0			$Mg(CH_3COO)_2$
39.33	3.31	57.10	1.56	$Mg(CH_3COO)_2$
39.09	4.71	40.67	22.38	$Mg(CH_3COO)_2$+ $Ca(CH_3COO)_2$
36.97	5.22	11.25	66.41	$Ca(CH_3COO)_2$
35.21	5.85	10.16	65.54	$Ca(CH_3COO)_2$
32.15	6.26	8.84	65.32	$Ca(CH_3COO)_2$
29.16	7.61	7.28	66.89	$Ca(CH_3COO)_2$
26.22	8.61	6.46	67.20	$Ca(CH_3COO)_2$
22.18	10.08	5.39	67.56	$Ca(CH_3COO)_2$
17.68	12.49	5.23	66.89	$Ca(CH_3COO)_2$
13.66	14.76	4.55	67.82	$Ca(CH_3COO)_2$
10.16	16.82	3.31	68.92	$Ca(CH_3COO)_2$
6.31	20.15	2.27	67.43	$Ca(CH_3COO)_2$
3.1	23.34	1.13	68.16	$Ca(CH_3COO)_2$
0	25.78			$Ca(CH_3COO)_2$
T = 313 K				
43.29	0			$Mg(CH_3COO)_2$
42.68	2.65	58.26	1.55	$Mg(CH_3COO)_2$
42.31	3.85	39.49	25.31	$Mg(CH_3COO)_2$ + $Ca(CH_3COO)_2$
41.2	4.15	11.91	65.82	$Ca(CH_3COO)_2$
38.61	4.45	10.44	67.29	$Ca(CH_3COO)_2$
34.49	5.36	9.32	66.57	$Ca(CH_3COO)_2$
27.46	7.19	8.24	66.18	$Ca(CH_3COO)_2$
20.43	10.45	6.63	67.84	$Ca(CH_3COO)_2$
15.43	13.29	4.95	66.49	$Ca(CH_3COO)_2$
8.93	17.65	3.47	66.93	$Ca(CH_3COO)_2$
6.35	19.81	3.11	67.08	$Ca(CH_3COO)_2$
2.25	22.77	1.64	67.29	$Ca(CH_3COO)_2$
0	25.03			$Ca(CH_3COO)_2$
T = 323 K				
47.17	0			$Mg(CH_3COO)_2$
47.04	1.41	60.32	0.87	$Mg(CH_3COO)_2$
46.99	2.32	40.61	20.63	$Mg(CH_3COO)_2$ + $Ca(CH_3COO)_2$
44.76	2.74	11.92	66.17	$Ca(CH_3COO)_2$
42.14	3.02	10.56	67.33	$Ca(CH_3COO)_2$
37.49	3.94	9.61	67.42	$Ca(CH_3COO)_2$
31.98	5.23	8.35	67.28	$Ca(CH_3COO)_2$
27.85	6.34	8.39	64.35	$Ca(CH_3COO)_2$
22.79	8.3	6.05	68.16	$Ca(CH_3COO)_2$
17.09	11.44	5.79	66.18	$Ca(CH_3COO)_2$
13.66	13.58	4.57	65.24	$Ca(CH_3COO)_2$
9.85	16.31	3.06	66.84	$Ca(CH_3COO)_2$
5.22	19.24	1.98	67.43	$Ca(CH_3COO)_2$
3.19	21.53	0.85	65.76	$Ca(CH_3COO)_2$
0	24.51			$Ca(CH_3COO)_2$

investigated, no research was reported on the phase diagram of the quinary system and its other subsystems. The study of the quinary system is of great importance above all in association with the choice of optimum preparation conditions of calcium magnesium acetate production. In order to construct the phase diagram of the quinary Ca^{2+}, Mg^{2+}, H^+ // CH_3COO^- H_2O system, the subsystems $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O was measured in this paper. The objective of this research is to investigate and generate the phase diagrams of the $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O system at 298, 313, and 323 K by the Schreinemaker's wet residue method.

The composition of the solid phase $Ca(CH_3COO)_2$ is hitherto not definitively established. The formation of calcium acetate monohydrate,[14] or calcium acetate hemihydrate,[17] or calcium acetate dehydrate[18] is postulated. Another object of the present research is to determine the composition of the solid phase by Schreinemaker's wet residue method.

2. Materials and Experimental Method

2.1 Materials

Magnesium acetate tetrahydrate, $Mg(CH_3COO)_2{\cdot}4H_2O$, >99.5 mass percent, was supplied by Sinopharm Group Chemical Reapent CO., LTD; calcium acetate $Ca(CH_3COO)_2{\cdot}2H_2O$, >99.5 mass per cent, was supplied by Shanghai fine aggregate CO. LTD and used without further purification. The water used to prepare solutions was twice distilled water (conductivity <5 μS/cm).

2.2 Procedure

The Schreinemaker's wet residue method was used during experiments. A known mass of $Mg(CH_3COO)_2{\cdot}4H_2O$ and $Ca(CH_3COO)_2{\cdot}2H_2O$ were dissolved in distilled water, and the saturated solution was transferred to a conical flask. The conical flask was stoppered and placed in a thermostat at a certain temperature. After 6-24 h, a sample of the liquid phase was analyzed, and this was repeated several hours later. If the two analyses gave identical results, it was assumed that equilibrium had been reached. Generally, it took about 23 h to be equilibrium. After the equilibrium was accomplished, the solid and the liquid phase were separated and analyzed.

2.3 Analysis

Weighed samples of saturated solutions of magnesium acetate and calcium acetate were titrated complexometrically with EDTA (solutions were prepared using $C_{10}H_{14}N_2O_8Na_2{\cdot}2H_2O$). Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis. In these studies, X-ray diffraction was also employed to determine whether the solid phase is pure or compound.

3. Results and Discussion

The measured solubility data of the ternary systems $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O at 298, 313, and 323 K are shown in Table 2. The isothermal phase diagrams of the systems were given in Fig 1, 2, 3, respectively.

It is shown in Fig. 1-3 that no double salt was presented in the system $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O at a temperature of 298-323 K. The results of chemical analysis, X-ray power diffusion indicated that one solid phase is $Mg(CH_3COO)_2{\cdot}4H_2O$, and the other is $Ca(CH_3COO)_2{\cdot}2H_2O$. In the phase diagram as shown in Fig. 1-3, E_1, E_2, and E_3 are cosaturated point, which indicates a solution saturated with $Mg(CH_3COO)_2{\cdot}4H_2O$ and $Ca(CH_3COO)_2{\cdot}2H_2O$. The regions in the diagram are denoted as follows: I, unsaturated solution; II, region corresponding to the coexistence of $Ca(CH_3COO)_2{\cdot}2H_2O$ and the saturated solution where D_1, D_2, and D_3 are the percentage concentration of

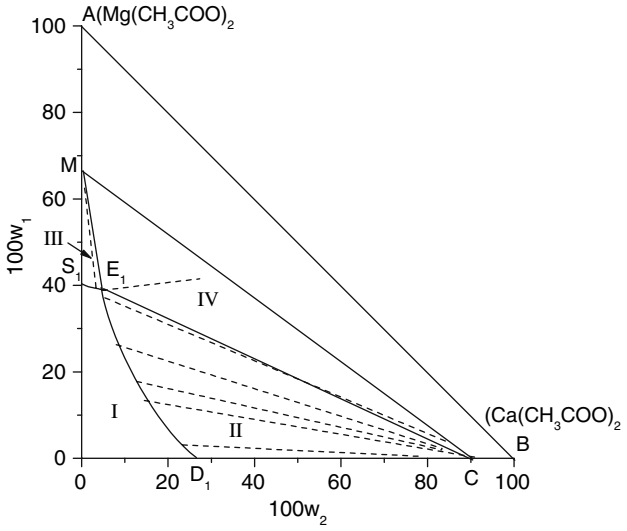

Fig. 1 Measured solubility and isothermal phase diagram of the ternary $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O system at 298: S_1, solubility of $Mg(CH_3COO)_2$ in water at 298 K; D_1, solubility of $Ca(CH_3COO)_2$ in water at 298 K; E_1, cosaturated point; M, $Mg(CH_3COO)_2{\cdot}4H_2O$; C, $Ca(CH_3COO)_2{\cdot}2H_2O$

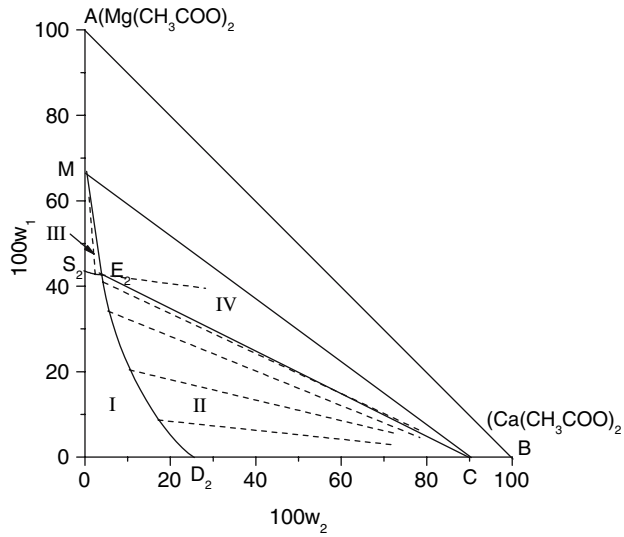

Fig. 2 Phase diagram of the ternary $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O system at 313 K: S_2, solubility of $Mg(CH_3COO)_2$ in water at 313 K; D_2, solubility of $Ca(CH_3COO)_2$ in water at 313 K; E_2, cosaturated point

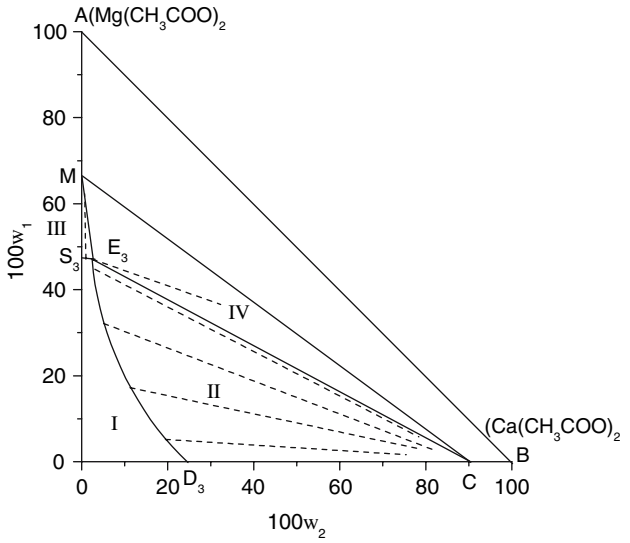

Fig. 3 Phase diagram of the ternary $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O system at 323 K: S_3, solubility of $Mg(CH_3COO)_2$ in water at 323 K; D_3, solubility of $Ca(CH_3COO)_2$ in water at 323 K; E_3, cosaturated point

saturated solution at a certain temperature; III, region corresponding to the coexistence of $Mg(CH_3COO)_2{\cdot}4H_2O$ and the saturated solution where S_1, S_2, and S_3 are the percentage concentration of saturated solution at a certain temperature; IV, region corresponding to the coexistence of $Mg(CH_3COO)_2{\cdot}4H_2O$, $Ca(CH_3COO)_2{\cdot}2H_2O$ and the saturated solution. E_1S_1, E_2S_2, and E_3S_3 are a single saturation curve corresponding to the solid phase $Mg(CH_3COO)_2{\cdot}4H_2O$, and E_1D_1, E_2D_2, and E_3D_3 are a single-saturation curve corresponding to the solid phase $Ca(CH_3COO)_2{\cdot}2H_2O$.

Figures 1-3 further illustrate that, within the region E_1S_1, E_2S_2, and E_3S_3, linking the component points of the liquid phase and the moist solid phase and extended, the point of intersection of these tie lines are approximately the solid phase component for the compound $Mg(CH_3COO)_2{\cdot}4H_2O$ in the wet basis. Similarly, within the region E_1D_1, E_2D_2, and E_3D_3, linking the component points of the liquid phase and the moist solid phase and extended, the point of intersection of these tie lines are approximately the solid phase component for the compound $Ca(CH_3COO)_2{\cdot}2H_2O$. That is to say, the solid phase formed in the ternary $Mg(CH_3COO)_2$-$Ca(CH_3COO)_2$-H_2O system are $Mg(CH_3COO)_2{\cdot}4H_2O$ and $Ca(CH_3COO)_2{\cdot}2H_2O$ at a temperature of 298-323 K, the crystalline region of $Ca(CH_3COO)_2{\cdot}2H_2O$ is larger than that of $Mg(CH_3COO)_2{\cdot}4H_2O$. It can also be found in Fig. 1-3 that the solubility of $Mg(CH_3COO)_2$ increases with the increasing of the temperature, while the solubility of $Ca(CH_3COO)_2$ decreases with the increasing of the temperature.

In this paper the solubilities of calcium acetate and magnesium acetate at investigated temperatures are reconsidered and given in Table 1. Table 1 shows that the results of calcium acetate agree well with the literatures[15, 18] and the result of magnesium acetate accords with the literature.[19]

The compositions of the solid phase were confirmed by Schreinemaker's wet residue method. Results show that composition of the solid phase $Ca(CH_3COO)_2$ is calcium acetate dehydrate, $Ca(CH_3COO)_2{\cdot}2H_2O$, which agrees with the reported by Apelblat.[19] The other solid phase is $Mg(CH_3COO)_2{\cdot}4H_2O$.

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