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 $Mg(CH_3COO)_2$ ·4H₂O and Ca(CH₃COO)₂·2H₂O. At the studied temperature, no double salt was formed. The crystalline region of Ca(CH₃COO)₂·2H₂O is larger than that of $Mg(CH_3COO)_2$ ·4H₂O. The solubility of $Mg(CH_3COO)_2$ increases with the increasing of the temperature, while the solubility of Ca(CH₃COO)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, H₂S 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 and magnesium acetate. It is well-known that the preparing process of CMA is based on the phase diagram of the quinary Ca²⁺, Mg²⁺, H⁺ // CH₃COO⁻ - H₂O 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(CH₃COO)₂-H₂O and Ca(CH₃COO)₂-H₂O have been

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

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Section I: Basic and Applied Research

b0v, 10v, 10v, 10v, Equilibrium solid phase 7-298 K. -	Composition of liquid phase (mass %)		Composition (mas	of solid phase ss %)		
r = 298 K 39.79 0 Mg(CH ₂ COO); 39.33 3.31 57.10 1.56 Mg(CH ₂ COO); 39.90 4.71 40.667 22.38 Mg(CH ₂ COO); 35.21 5.85 10.16 65.54 Ca(CH ₂ COO); 35.21 5.85 10.16 65.54 Ca(CH ₂ COO); 29.16 7.61 7.28 66.89 Ca(CH ₂ COO); 26.22 8.61 64.64 67.20 Ca(CH ₂ COO); 27.8 65.89 Ca(CH ₂ COO); 63.13 20.15 27.8 65.89 Ca(CH ₂ COO); 63.1 20.15 2.27 10.16 16.82 3.31 68.92 Ca(CH ₂ COO); 3.1 23.34 1.13 68.16 Ca(CH ₂ COO); 3.1 23.34 1.13 68.16 Ca(CH ₂ COO); 3.1 23.34 1.13 68.16 Ca(CH ₂ COO); 42.31 3.85 39.49 2.5.11 Mg(CH ₂ COO); 42.46 19.19 65.82 Ca(CH ₂ COO); Ca(CH ₂ COO); 42.31	100·w ₁	100·w ₂	100·w ₁	100·w ₂	Equilibrium solid phase	
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43.29 0 Mg(CH_5COO)_2 42.68 2.65 58.26 1.55 Mg(CH_5COO)_2 42.31 3.85 39.49 25.31 Mg(CH_5COO)_2 41.2 4.15 11.91 65.82 Ca(CH_5COO)_2 38.61 4.45 10.44 67.29 Ca(CH_5COO)_2 34.49 5.36 9.32 66.57 Ca(CH_5COO)_2 27.46 7.19 8.24 66.18 Ca(CH_5COO)_2 2.43 10.45 6.63 67.84 Ca(CH_5COO)_2 2.43 10.45 6.63 67.84 Ca(CH_5COO)_2 2.43 10.45 6.63 67.84 Ca(CH_5COO)_2 5.43 13.29 4.95 66.49 Ca(CH_5COO)_2 6.35 19.81 3.11 67.08 Ca(CH_5COO)_2 0 25.03 Ca(CH_5COO)_2 Ca(CH_5COO)_2 Ca(CH_5COO)_2 7 = 323 K - - Mg(CH_5COO)_2 Ca(CH_5COO)_2 47.04 1.41 60.32 0.87 Mg(CH_5COO)_2 Ca(CH_5COO)_2 42.14 3.02 10.56	<i>T</i> = 313 K					
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 15.33 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 0 25.03 Ca(CH_3COO)_2 Ca(CH_3COO)_2 Ca(CH_3COO)_2 7 = 323 K 41.1 60.32 0.87 Mg(CH_3COO)_2 + Ca(CH_3COO)_2 44.76 2.74 11.92 66.17 Ca(CH_3COO)_2 Ca(CH_3COO)_2 42.14 3.02 10.56 67.33 Ca(CH_3COO)_2 Ca(CH_3COO)_2 42.14 3.02 10.56 67.33 <	43.29	0			Mg(CH ₃ COO) ₂	
42.31 3.85 39.49 25.31 $Mg(CT_3COO)_2 + Ca(CH_3COO)_2$ 41.2 4.15 11.91 65.82 $Ca(CH_3COO)_2$ 38.61 4.45 10.44 67.29 $Ca(CH_3COO)_2$ 38.61 4.45 10.44 67.29 $Ca(CH_3COO)_2$ 27.46 7.19 8.24 66.18 $Ca(CH_3COO)_2$ 20.43 10.45 6.63 67.84 $Ca(CH_3COO)_2$ 20.43 13.29 4.95 66.49 $Ca(CH_3COO)_2$ 6.35 19.81 3.11 67.08 $Ca(CH_3COO)_2$ 6.35 19.81 3.11 67.08 $Ca(CH_3COO)_2$ 7 2.25 22.77 1.64 67.29 $Ca(CH_3COO)_2$ 7 7 1.64 67.29 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$ 7 7 0 Mg(CH_3COO)_2 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$ 7 9 2.32 40.61 2.06.37 Mg(CH_3COO)_2 + Ca(CH_3COO)_2 41.92 66.17 Ca(CH_3COO)_2 Ca(CH_3COO)_2 $Ca(CH_3COO)_2$ 42.14 3.02<	42.68	2.65	58.26	1.55	Mg(CH ₃ COO) ₂	
41.2 4.15 11.91 65.82 Ca(CH_{COO})_2 38.61 4.45 10.44 67.29 Ca(CH_{COO})_2 34.49 5.36 9.32 66.57 Ca(CH_{COO})_2 27.46 7.19 8.24 66.18 Ca(CH_{3COO})_2 27.43 10.45 6.63 67.84 Ca(CH_{3COO})_2 20.43 10.45 6.63 67.84 Ca(CH_{3COO})_2 8.93 17.65 3.47 66.93 Ca(CH_{3COO})_2 8.93 17.65 3.47 66.93 Ca(CH_{3COO})_2 0 25.03 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 0 25.03 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 7 0 Mg(CH_{3COO})_2 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 47.17 0 Mg(CH_{3COO})_2 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 44.76 2.74 11.92 66.17 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 42.14 3.02 10.56 67.33 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2 Ca(CH_{3COO})_2	42.31	3.85	39.49	25.31	$Mg(CH_3COO)_2 + Ca(CH_3COO)_2$	
38.61 4.45 10.44 67.29 Ca(CH_2CO)_2 34.49 5.36 9.32 66.57 Ca(CH_3CO)_2 27.46 7.19 8.24 66.18 Ca(CH_3CO)_2 20.43 10.45 6.63 67.84 Ca(CH_3CO)_2 20.43 10.45 6.63 67.84 Ca(CH_3CO)_2 8.93 17.65 3.47 66.93 Ca(CH_3CO)_2 6.35 19.81 3.11 67.08 Ca(CH_3CO)_2 0 25.03 Ca(CH_3CO)_2 $Ca(CH_3CO)_2$ $Ca(CH_3CO)_2$ 7 = 323 K T 6.632 0.87 Mg(CH_3CO)_2 47.04 1.41 60.32 0.87 Mg(CH_3CO)_2 44.76 2.74 11.92 66.17 Ca(CH_3CO)_2 44.76 2.74 11.92 66.17 Ca(CH_3CO)_2 37.49 3.94 9.61 67.42 Ca(CH_3CO)_2 27.85 6.34 8.39 64.35 Ca(CH_3CO)_2 27.85 6.34 8.39 64.35 Ca(CH_3CO)_2 27.9	41.2	4.15	11.91	65.82	Ca(CH ₃ COO) ₂	
34.495.369.3266.57Ca(CH_2CO)_227.467.198.2466.18Ca(CH_3COO)_220.4310.456.6367.84Ca(CH_3COO)_215.4313.294.9566.49Ca(CH_3COO)_215.4313.294.9566.49Ca(CH_3COO)_26.3519.813.1167.08Ca(CH_3COO)_26.3519.813.1167.08Ca(CH_3COO)_2025.03Ca(CH_3COO)_2Ca(CH_3COO)_27 = 323 K71.6467.29Ca(CH_3COO)_247.041.4160.320.87Mg(CH_3COO)_2 + Ca(CH_3COO)_246.992.3240.6120.63Mg(CH_3COO)_2 + Ca(CH_3COO)_247.041.4160.320.67Mg(CH_3COO)_2 + Ca(CH_3COO)_247.762.7411.9266.17Ca(CH_3COO)_242.143.0210.5667.33Ca(CH_3COO)_237.493.949.6167.42Ca(CH_3COO)_227.856.348.3964.35Ca(CH_3COO)_227.856.348.3964.35Ca(CH_3COO)_227.856.348.3964.35Ca(CH_3COO)_217.0911.445.7966.18Ca(CH_3COO)_213.6613.584.5765.24Ca(CH_3COO)_29.8516.313.0666.84Ca(CH_3COO)_25.2219.241.9867.43Ca(CH_3COO)_23.1921.530.8565.76Ca(CH_3COO)_23.1921.51 <td< td=""><td>38.61</td><td>4.45</td><td>10.44</td><td>67.29</td><td>Ca(CH₃COO)₂</td></td<>	38.61	4.45	10.44	67.29	Ca(CH ₃ COO) ₂	
27.46 7.19 8.24 66.18 $C_{a}(CH_{3}COO)_{2}$ 20.43 10.45 6.63 67.84 $C_{a}(CH_{3}COO)_{2}$ 15.43 13.29 4.95 66.49 $C_{a}(CH_{3}COO)_{2}$ 8.93 17.65 3.47 66.93 $C_{a}(CH_{3}COO)_{2}$ 6.35 19.81 3.11 67.08 $C_{a}(CH_{3}COO)_{2}$ 2.25 22.77 1.64 67.29 $C_{a}(CH_{3}COO)_{2}$ 0 25.03 Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} 7 = 323 K 47.17 0 Mg(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} 47.04 1.41 60.32 0.87 Mg(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} 44.76 2.74 11.92 66.17 Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} 42.14 3.02 10.56 67.33 Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} 37.49 3.94 9.61 67.42 Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} 27.85 6.34 8.39 64.35 Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2} Ca(CH_{3}COO)_{2}	34.49	5.36	9.32	66.57	Ca(CH ₃ COO) ₂	
20.4310.456.6367.84Ca(CH_3COO)_215.4313.294.9566.49Ca(CH_3COO)_28.9317.653.4766.93Ca(CH_3COO)_26.3519.813.1167.08Ca(CH_3COO)_22.2522.771.6467.29Ca(CH_3COO)_2025.03Ca(CH_3COO)_2Ca(CH_3COO)_2 $T = 323$ KTMg(CH_3COO)_2Ca(CH_3COO)_247.041.4160.320.87Mg(CH_3COO)_246.992.3240.612.063Mg(CH_3COO)_244.762.7411.9266.17Ca(CH_3COO)_242.143.0210.5667.33Ca(CH_3COO)_231.985.238.3567.28Ca(CH_3COO)_222.798.36.0568.16Ca(CH_3COO)_217.0911.445.7966.18Ca(CH_3COO)_213.6613.584.5765.24Ca(CH_3COO)_213.6613.584.5765.24Ca(CH_3COO)_25.2219.241.9867.43Ca(CH_3COO)_25.1921.530.8565.76Ca(CH_3COO)_23.1921.530.8565.76Ca(CH_3COO)_2024.5157.6657.66Ca(CH_3COO)_2	27.46	7.19	8.24	66.18	Ca(CH ₃ COO) ₂	
15.4313.294.95 66.49 $Ca(CH_3COO)_2$ 8.9317.653.47 66.93 $Ca(CH_3COO)_2$ 6.3519.813.11 67.08 $Ca(CH_3COO)_2$ 2.2522.771.64 67.29 $Ca(CH_3COO)_2$ 025.03 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$ $T = 323$ K T T $G(CH_3COO)_2$ 47.170 $Mg(CH_3COO)_2$ $Ca(CH_3COO)_2$ 46.992.3240.6120.63 $Mg(CH_3COO)_2 + Ca(CH_3COO)_2$ 44.762.7411.92 66.17 $Ca(CH_3COO)_2$ 42.143.0210.56 67.33 $Ca(CH_3COO)_2$ 37.493.949.61 67.42 $Ca(CH_3COO)_2$ 31.985.238.35 67.28 $Ca(CH_3COO)_2$ 27.85 6.34 8.39 64.35 $Ca(CH_3COO)_2$ 17.0911.44 5.79 66.18 $Ca(CH_3COO)_2$ 13.6613.58 4.57 65.24 $Ca(CH_3COO)_2$ 9.8516.313.06 66.84 $Ca(CH_3COO)_2$ 5.2219.241.98 67.43 $Ca(CH_3COO)_2$ 3.1921.530.85 65.76 $Ca(CH_3COO)_2$ 024.51 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$	20.43	10.45	6.63	67.84	Ca(CH ₃ COO) 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 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$ $T = 323 \text{ K}$ T $Mg(CH_3COO)_2$ $Ca(CH_3COO)_2$ 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 $Ca(CH_3COO)_2 + Ca(CH_3COO)_2$ 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 $Ca(CH_3COO)_2$ 27.9 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 $Ca(CH_3COO)_2$ 9.85 16.31 3.06 66.84 $Ca(CH_3COO)_2$ 5.22 19.24 1.98 67.43 $Ca(CH_3COO)_2$ 0 24.51 0.85 65.76 $Ca(CH_3COO)_2$	15.43	13.29	4.95	66.49	Ca(CH ₃ COO) ₂	
6.3519.813.1167.08 $Ca(CH_3COO)_2$ 2.2522.771.6467.29 $Ca(CH_3COO)_2$ 025.03 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$ $T = 323$ K $T = 323$ K $Ca(CH_3COO)_2$ 47.170Mg(CH_3COO)_246.992.3240.6120.632.7411.9266.17 $Ca(CH_3COO)_2$ 42.143.0210.5667.33 $Ca(CH_3COO)_2$ 31.985.238.3567.28 $Ca(CH_3COO)_2$ 27.856.348.3964.35 $Ca(CH_3COO)_2$ 27.98.36.0568.16 $Ca(CH_3COO)_2$ 13.6613.584.5765.24 $Ca(CH_3COO)_2$ 13.6613.584.5765.24 $Ca(CH_3COO)_2$ 9.8516.313.0666.84 $Ca(CH_3COO)_2$ 5.2219.241.9867.43 $Ca(CH_3COO)_2$ 024.51 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$	8.93	17.65	3.47	66.93	Ca(CH ₃ COO) ₂	
2.2522.771.6467.29Ca(CH_3COO)_2025.03Ca(CH_3COO)_2 $T = 323 \text{ K}$ TMg(CH_3COO)_247.170Mg(CH_3COO)_247.041.4160.320.8747.62.7411.9266.1747.62.7411.9266.1742.143.0210.5667.3337.493.949.6167.2831.985.238.3567.2822.798.36.0568.1622.798.36.0566.18Ca(CH_3COO)_213.6613.584.5765.24Ca(CH_3COO)_213.6516.313.0666.84Ca(CH_3COO)_25.2219.241.9867.43Ca(CH_3COO)_26.18Ca(CH_3COO)_26.19Ca(CH_3COO)_213.6067.4313.1921.5314.110.8515.2119.2414.2119.815.2219.2415.230.8516.310.08516.310.08515.2219.2415.230.8516.310.8516.310.8515.2219.2415.230.8516.310.8516.310.8517.2219.2417.330.8516.310.8517.340.8517.350.8516.310.8517.350.85 <td>6.35</td> <td>19.81</td> <td>3.11</td> <td>67.08</td> <td>Ca(CH₃COO)₂</td>	6.35	19.81	3.11	67.08	Ca(CH ₃ COO) ₂	
025.03 $Ca(CH_3COO)_2$ $T = 323 \text{ K}$ $Mg(CH_3COO)_2$ 47.17 0 $Mg(CH_3COO)_2$ 47.04 1.41 60.32 0.87 46.99 2.32 40.61 20.63 47.66 2.74 11.92 66.17 21.14 3.02 10.56 67.33 21.14 3.02 10.56 67.33 21.98 5.23 8.35 67.28 21.98 5.23 8.35 67.28 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 68.16 22.79 8.3 6.05 62.24 22.79 8.3	2.25	22.77	1.64	67.29	Ca(CH ₃ COO) ₂	
T = 323 K 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 13.66 13.58 4.57 65.24 Ca(CH_3COO)_2 9.85 16.31 3.06 66.84 Ca(CH_3COO)_2 9.85 16.31 3.06 66.84 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 0 24.51 .985 62.76 Ca(CH_3COO)_2	0	25.03			$Ca(CH_3COO)_2$	
47.17 0Mg(CH_3COO)_2 47.04 1.4160.320.87Mg(CH_3COO)_2 46.99 2.3240.6120.63Mg(CH_3COO)_2 + Ca(CH_3COO)_2 44.76 2.7411.9266.17Ca(CH_3COO)_2 42.14 3.0210.5667.33Ca(CH_3COO)_2 37.49 3.949.6167.42Ca(CH_3COO)_2 31.98 5.238.3567.28Ca(CH_3COO)_2 22.79 8.36.0568.16Ca(CH_3COO)_2 21.79 8.36.0566.18Ca(CH_3COO)_2 13.66 13.584.5765.24Ca(CH_3COO)_2 13.66 13.584.5765.24Ca(CH_3COO)_2 5.22 19.241.9867.43Ca(CH_3COO)_2 3.19 21.530.8565.76Ca(CH_3COO)_2	T = 323 K					
47.041.4160.320.87 $Mg(CH_3COO)_2$ 46.992.3240.6120.63 $Mg(CH_3COO)_2 + Ca(CH_3COO)_2$ 44.762.7411.9266.17 $Ca(CH_3COO)_2$ 42.143.0210.5667.33 $Ca(CH_3COO)_2$ 37.493.949.6167.42 $Ca(CH_3COO)_2$ 31.985.238.3567.28 $Ca(CH_3COO)_2$ 27.856.348.3964.35 $Ca(CH_3COO)_2$ 27.98.36.0568.16 $Ca(CH_3COO)_2$ 17.0911.445.7966.18 $Ca(CH_3COO)_2$ 13.6613.584.5765.24 $Ca(CH_3COO)_2$ 9.8516.313.0666.84 $Ca(CH_3COO)_2$ 5.2219.241.9867.43 $Ca(CH_3COO)_2$ 3.1921.530.8565.76 $Ca(CH_3COO)_2$	47.17	0			Mg(CH ₃ COO) ₂	
46.992.3240.6120.63 $Mg(CH_3COO)_2 + Ca(CH_3COO)_2$ 44.762.7411.9266.17 $Ca(CH_3COO)_2$ 42.143.0210.5667.33 $Ca(CH_3COO)_2$ 37.493.949.6167.42 $Ca(CH_3COO)_2$ 31.985.238.3567.28 $Ca(CH_3COO)_2$ 27.856.348.3964.35 $Ca(CH_3COO)_2$ 27.98.36.0568.16 $Ca(CH_3COO)_2$ 17.0911.445.7966.18 $Ca(CH_3COO)_2$ 13.6613.584.5765.24 $Ca(CH_3COO)_2$ 9.8516.313.0666.84 $Ca(CH_3COO)_2$ 5.2219.241.9867.43 $Ca(CH_3COO)_2$ 024.510.8565.76 $Ca(CH_3COO)_2$	47.04	1.41	60.32	0.87	Mg(CH ₃ COO) 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 -24.51 -24.51 -24.51	46.99	2.32	40.61	20.63	$Mg(CH_{2}COO)_{2} + Ca(CH_{2}COO)_{2}$	
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 $Ca(CH_3COO)_2$	44.76	2.74	11.92	66.17	$Ca(CH_{2}COO)_{2}$	
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 -24.51 -24.51	42.14	3.02	10.56	67.33	$Ca(CH_3COO)_2$	
31.98 5.23 8.35 67.28 Ca(CH ₃ COO) ₂ 27.85 6.34 8.39 64.35 Ca(CH ₃ COO) ₂ 22.79 8.3 6.05 68.16 Ca(CH ₃ COO) ₂ 17.09 11.44 5.79 66.18 Ca(CH ₃ COO) ₂ 13.66 13.58 4.57 65.24 Ca(CH ₃ COO) ₂ 9.85 16.31 3.06 66.84 Ca(CH ₃ COO) ₂ 5.22 19.24 1.98 67.43 Ca(CH ₃ COO) ₂ 3.19 21.53 0.85 65.76 Ca(CH ₃ COO) ₂	37 49	3 94	9.61	67.42	$Ca(CH_2COO)_2$	
27.85 6.34 8.39 64.35 Ca(CH ₃ COO) ₂ 22.79 8.3 6.05 68.16 Ca(CH ₃ COO) ₂ 17.09 11.44 5.79 66.18 Ca(CH ₃ COO) ₂ 13.66 13.58 4.57 65.24 Ca(CH ₃ COO) ₂ 9.85 16.31 3.06 66.84 Ca(CH ₃ COO) ₂ 5.22 19.24 1.98 67.43 Ca(CH ₃ COO) ₂ 3.19 21.53 0.85 65.76 Ca(CH ₃ COO) ₂	31.98	5.23	8 35	67.28	$Ca(CH_2COO)_2$	
21.00 0.01 0.05 0.02	27.85	6 34	8 39	64 35	$Ca(CH_2COO)_2$	
17.09 11.44 5.79 66.18 Ca(CH ₃ COO) ₂ 13.66 13.58 4.57 65.24 Ca(CH ₃ COO) ₂ 9.85 16.31 3.06 66.84 Ca(CH ₃ COO) ₂ 5.22 19.24 1.98 67.43 Ca(CH ₃ COO) ₂ 3.19 21.53 0.85 65.76 Ca(CH ₃ COO) ₂	22.79	83	6.05	68.16	$Ca(CH_2COO)_2$	
13.66 13.58 4.57 65.24 Ca(CH ₃ COO) ₂ 9.85 16.31 3.06 66.84 Ca(CH ₃ COO) ₂ 5.22 19.24 1.98 67.43 Ca(CH ₃ COO) ₂ 3.19 21.53 0.85 65.76 Ca(CH ₃ COO) ₂ 0 24.51	17.09	11 44	5 79	66 18	$Ca(CH_2COO)_2$	
1.57 1.57 0.127 $Ca(CH_3COO)_2$ 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 $Ca(CH_3COO)_2$	13.66	13 58	4 57	65 24	$Ca(CH_2COO)_2$	
1.02 10.01 1.00 00.07 $Ca(CH_3COO)_2$ 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 $Ca(CH_3COO)_2$ $Ca(CH_3COO)_2$	9.85	16 31	3.06	66 84	Ca(CH ₂ COO) ₂	
1.22 1.23 1.25 0.115 $Ca(CH_3COO)_2$ 3.19 21.53 0.85 65.76 $Ca(CH_3COO)_2$ 0 24.51 $Ca(CH_4COO)_2$	5.22	19 24	1 98	67.43	Ca(CH ₂ COO) ₂	
0 24.51 Co(CH_COO)_	3 19	21.53	0.85	65 76	$Ca(CH_2COO)_2$	
	0	24.53	0.00	00.10	$C_{2}(CH_{2}COO)_{2}$	

Table 2 Solubility Data for Mg(CH₃COO)₂ (1)-Ca(CH₃COO)₂ (2)-H₂O(3) Systems from 298, 313 and 323 K

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^- H₂O system, the subsystems Mg(CH₃COO)₂-Ca(CH₃COO)₂-H₂O was measured in this paper. The objective of this research is to investigate and generate the phase diagrams of the Mg(CH₃COO)₂-Ca(CH₃COO)₂-H₂O 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(CH₃COO)₂·4H₂O, >99.5 mass percent, was supplied by Sinopharm Group Chemical Reapent CO., LTD; calcium acetate Ca(CH₃ COO)₂·2H₂O, >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 μ S/cm).

2.2 Procedure

The Schreinemaker's wet residue method was used during experiments. A known mass of $Mg(CH_3COO)_2$ · $4H_2O$ and $Ca(CH_3COO)_2$ · $2H_2O$ 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



Fig. 1 Measured solubility and isothermal phase diagram of the ternary $Mg(CH_3COO)_2$ -Ca $(CH_3COO)_2$ -H₂O system at 298: S₁, solubility of $Mg(CH_3COO)_2$ in water at 298 K; D₁, solubility of Ca $(CH_3COO)_2$ in water at 298 K; E₁, cosaturated point; M, $Mg(CH_3COO)_2$ ·2H₂O; C, Ca $(CH_3COO)_2$ ·2H₂O

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 $C_{10}H_{14}N_2O_8$ Na₂·2H₂O). 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(CH₃COO)_2-H₂O 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(CH₃COO)₂-Ca(CH₃COO)₂-H₂O at a temperature of 298-323 K. The results of chemical analysis, X-ray power diffusion indicated that one solid phase is Mg(CH₃COO)₂·4H₂O, and the other is Ca(CH₃COO)₂· 2H₂O. In the phase diagram as shown in Fig. 1-3, E₁, E₂, and E₃ are cosaturated point, which indicates a solution saturated with Mg(CH₃COO)₂·4H₂O and Ca(CH₃COO)₂· 2H₂O. The regions in the diagram are denoted as follows: I, unsaturated solution; II, region corresponding to the coexistence of Ca(CH₃COO)₂·2H₂O and the saturated solution where D₁, D₂, and D₃ are the percentage concentration of



Fig. 2 Phase diagram of the ternary $Mg(CH_3COO)_2$ -Ca(CH₃ COO)₂-H₂O system at 313 K: S₂, solubility of $Mg(CH_3COO)_2$ in water at 313 K; D₂, solubility of Ca(CH₃COO)₂ in water at 313 K; E₂, cosaturated point



Fig. 3 Phase diagram of the ternary $Mg(CH_3COO)_2$ -Ca(CH₃ COO)₂-H₂O system at 323 K: S₃, solubility of $Mg(CH_3COO)_2$ in water at 323 K; D₃, solubility of Ca(CH₃COO)₂ in water at 323 K; E₃, cosaturated point

saturated solution at a certain temperature; III, region corresponding to the coexistence of Mg(CH₃COO)₂·4H₂O and the saturated solution where S₁, S₂, and S₃ are the percentage concentration of saturated solution at a certain temperature; IV, region corresponding to the coexistence of Mg(CH₃COO)₂·4H₂O, Ca(CH₃COO)₂·2H₂O and the saturated solution. E₁S₁, E₂S₂, and E₃S₃ are a single saturation curve corresponding to the solid phase Mg(CH₃COO)₂· 4H₂O, and E₁D₁, E₂D₂, and E₃D₃ are a single-saturation curve corresponding to the solid phase Ca(CH₃COO)₂· 2H₂O.

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(CH₃COO)₂·4H₂O 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(CH₃COO)₂·2H₂O. That is to say, the solid phase formed in the ter-Mg(CH₃COO)₂-Ca(CH₃COO)₂-H₂O system nary are Mg(CH₃COO)₂·4H₂O and Ca(CH₃COO)₂·2H₂O at a temperature of 298-323 K, the crystalline region of Ca(CH₃ COO_{2} ·2H₂O is larger than that of Mg(CH₃COO)₂·4H₂O. It can also be found in Fig. 1-3 that the solubility of Mg(CH₃COO)₂ increases with the increasing of the temperature, while the solubility of Ca(CH₃COO)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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