

Phase Diagram of Ternary Magnesium Acetate-Acetic Acid-Water System at 298.1 and 333.1 K

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In this investigation, the mutual solubilities for the ternary $\text{Mg}(\text{CH}_3\text{COO})_2\text{-CH}_3\text{COOH-H}_2\text{O}$ system were determined at 298.1 and 333.1 K. Two partial isothermal phase diagrams for this ternary system were constructed on the basis of the measured solubilities, one at 298.1 K and the other at 333.1 K. At 298.1 K, two solid phases were formed and confirmed by the Schreinemaker's wet residue method, and the two were identified as $2\text{Mg}(\text{CH}_3\text{COO})_2\cdot 3\text{CH}_3\text{COOH}\cdot 3\text{H}_2\text{O}$ and $\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$. However, only one solid phase, $\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ was formed in the ternary $\text{Mg}(\text{CH}_3\text{COO})_2\text{-CH}_3\text{COOH-H}_2\text{O}$ system at 333.1 K. The solubilities of $\text{Mg}(\text{CH}_3\text{COO})_2$ in water- CH_3COOH solutions increased with increasing temperature.

Keywords acetate acid, magnesium acetate, phase diagram

1. Introduction

Calcium magnesium acetate (CMA) is a chemical with two major large-scale potential applications for solving environmental problems: (a) as the best deicing salt candidate to replace the corrosive and environmentally unacceptable sodium chloride and/or calcium chloride currently in use for road and highway deicing^[1-3] and (b) as a control agent for the toxic particulates, SO_x , NO_x , and H_2S emissions^[4-7] as well as for sulfur.^[8] CMA has the potential for large-scale production^[9] with a commercial method for making CMA involving formation of CMA in an aqueous environment in which all of the reactants are soluble and in equilibrium with the CMA product. The CMA produced in this way may contain calcium acetate and magnesium acetate as contaminants.

It is recognized that the quinary $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-H}^+//\text{CH}_3\text{COO}^-\text{-H}_2\text{O}$ system is relevant to the proposed production process for the large-scale preparation of CMA. The two binary subsystems, $\text{Mg}(\text{CH}_3\text{COO})_2\text{-H}_2\text{O}$ ^[9-11] and $\text{Ca}(\text{CH}_3\text{COO})_2\text{-H}_2\text{O}$,^[18] and the ternary subsystem, $\text{Mg}(\text{CH}_3\text{COO})_2\text{-Ca}(\text{CH}_3\text{COO})_2\text{-H}_2\text{O}$,^[18] have been investigated, but the investigation of this latter ternary system involved only solubility studies and no phase diagram was proposed. The present investigation was undertaken to construct, at least, partial phase diagrams for the $\text{Mg}(\text{CH}_3\text{COO})_2\text{-CH}_3\text{COOH-H}_2\text{O}$ system at 298.1 ± 0.1 K and at 333.1 ± 0.1 K.

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2. Materials and Experimental Method

2.1 Materials

Magnesium acetate tetrahydrate, $\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, >99.5 mass% purity, was supplied by Simopharm Group Chemical Reagent Co. Ltd., China and was used without further purification. Acetic acid, CH_3COOH , >99.5 mass% purity, was supplied by Jilin Ji'an Group Co. Ltd., China. The water for preparing solutions was twice distilled (conductivity <5 mS/cm, the unit on a Siemen's meter). A water bath, thermostatically controlled to ± 0.1 K, was used for equilibrating samples.

2.2 Procedure

Schreinemaker's wet residue method consists of filtering the wet solid residue from an equilibrated saturated aqueous solution and analyzing both the solid residue and the saturated liquid that passed through the filter. This technique was used in the present study. Initial samples were prepared as mixtures of known amounts of magnesium acetate, acetic acid, and water with the relevant amounts being chosen to vary the acetic acid/magnesium acetate ratio from 0 to ~ 1 . All liquid mixtures were stirred in flasks that were surrounded by a constant temperature water bath. Aliquots of the liquid phase were taken at 2 h intervals and analyzed. When the composition of the liquid became constant, this was taken to indicate that equilibration had been attained. The solid and liquid were then separated by filtration.

2.3 Analysis

After separation of the liquid and solid, a portion of the solid was taken and enough water was added for complete dissolution. Aliquots of the liquid containing the solid and of the liquid in equilibrium with the solid were each analyzed for the relative percentages of magnesium acetate and acetic acid. The amount magnesium acetate in an aliquot of defined volume was determined by titrating for Mg with a standardized solution of the chelating agent

EDTA (ethylenediamine tetraacetic acid disodium), and the amount of acetic acid was also determined by titration with basic NaOH to achieve acidic neutrality. Titrations were done at temperatures controlled by the water bath. Each analysis was repeated three times, and the average of the three results was accepted as the desired value.

3. Results and Discussion

Terminal solubilities (liquidus lines) of solutions $\text{Mg}(\text{CH}_3\text{COO})_2$ and CH_3COOH in water were measured for 17 samples at 298.1 ± 0.1 K and nine samples at 333.1 ± 0.1 K. The analyses of both equilibrium solid and liquid phase compositions are shown in Table 1 where 100 w_1 represents the mass percentage of magnesium acetate and 100 w_2 represents the mass percentage of acetic acid. On the basis of these data, proposed partial ternary diagrams for the magnesium acetate-acetic acid-water system are shown for 298.1 K in Fig. 1 and for 333.1 K in Fig. 2. Saturation

curves (liquidus) are designated by the lines S_1C_1 and C_1T_1 in Fig. 1 at 298.1 K and by line S_2T_2 in Fig. 2 at 333.1 K. In Fig. 1, the line S_1C_1 represents the contour for first precipitation of the solid phase, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, from saturated liquid solutions while line C_1T_1 represents the contour of first precipitation of the solid phase, $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$, from saturated liquid solutions with acetic acid contents of ~ 40 mass% or greater. For an isothermal diagram at fixed pressure, the point C_1 is an invariant point at which coprecipitation of both $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ will occur and represents the point at which both phases simultaneously reach saturation in the liquid. In Fig. 2 it may be noted that saturation of the liquid with $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ is never reached within the composition range that was investigated. The line S_2T_2 represents the saturation contour for $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and the nature of the contour is such as to imply that $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ may no longer be a stable phase in the diagram at 333.1 K.

Table 1 Solubility data for $\text{Mg}(\text{CH}_3\text{COO})_2$ (1) - CH_3COOH (2) - H_2O (3) systems at 298.1 K and 333.1 K

Composition of liquid phase, mass%		Composition of liquid phase, mass%		Equilibrium solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
<i>T</i> = 298.1 K				
39.76	0	61.43	0	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
39.74	5.88	60.15	2.21	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
39.5	11.73	56.87	4.98	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
38.66	15.07	57.83	4.54	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
37.95	18.49	58.23	4.91	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
37.27	21.73	57.65	4.84	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
36.15	25.64	57.92	4.96	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
35.59	29.81	58.46	4.98	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
34.19	33.12	58.07	5.05	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
33.07	36.81	58.33	5.09	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
32.08	38.63	58.61	5.13	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
31.27	41.17	49.83	29.42	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} + 2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$
33.06	41.71	51.71	36.84	$2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$
34.76	42.66	51.92	36.91	$2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$
35.99	44.33	51.24	36.97	$2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$
37.27	47.38	51.62	38.19	$2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$
37.81	51.58	51.78	38.65	$2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$
<i>T</i> = 333.1 K				
55.21	0	60.26	0	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
56.84	4.09	61.94	2.41	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
57.69	7.96	61.95	3.68	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
57.25	11.01	60.68	3.67	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
56.41	13.98	60.69	7.96	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
55.53	16.96	61.03	9.65	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
54.54	20.38	60.62	9.38	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
53.01	22.47	60.48	9.95	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
51.27	25.93	60.57	10.13	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$

w_1 , mass fraction of $\text{Mg}(\text{CH}_3\text{COO})_2$; w_2 , mass fraction of CH_3COOH

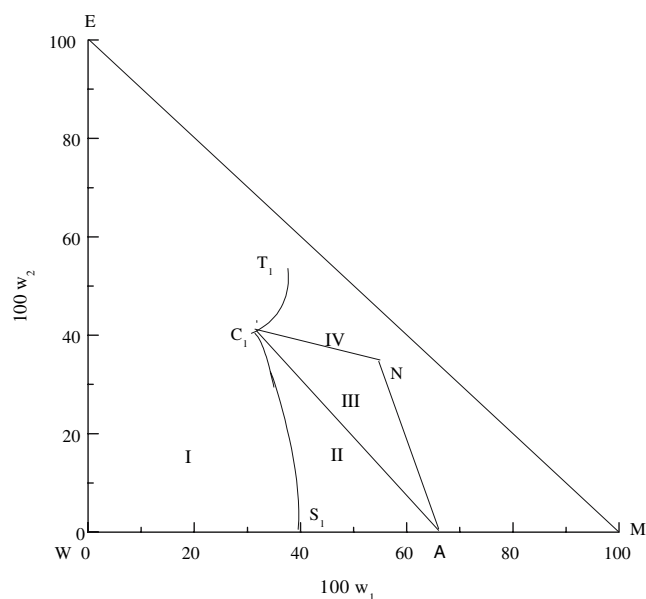


Fig. 1 Isothermal phase diagram of the ternary $\text{Mg}(\text{CH}_3\text{COO})_2$ (1) - CH_3COOH (2) - H_2O (3) system at 298.1 K: S_1 , solubility of $\text{Mg}(\text{CH}_3\text{COO})_2$ in water at 298.1 K; C_1 , cosaturated point; A , $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$; W , H_2O ; M , $\text{Mg}(\text{CH}_3\text{COO})_2$; E , CH_3COOH ; N , $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$; T_1 , experimental data; I, unsaturated region; II, crystalline region of solid $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$; III, crystalline region of solids $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$; IV, crystalline region of solid $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$

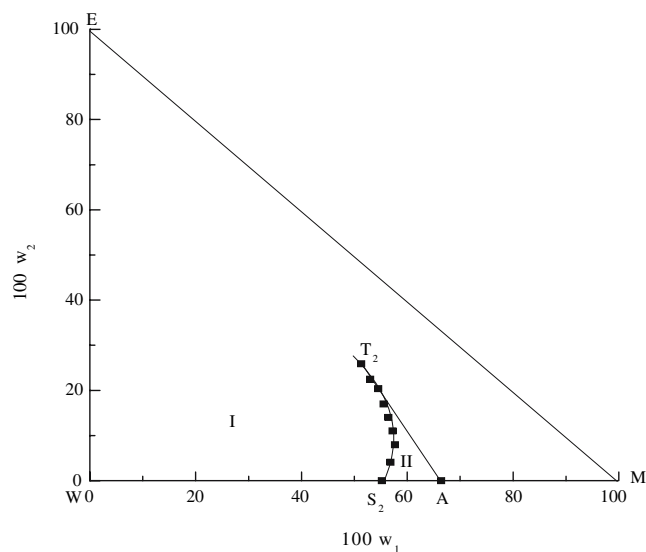


Fig. 2 Isothermal phase diagram of the ternary $\text{Mg}(\text{CH}_3\text{COO})_2$ (1) - CH_3COOH (2) - H_2O (3) system at 333.1 K: S_2 , solubility of $\text{Mg}(\text{CH}_3\text{COO})_2$ in water at 333.1 K; T_2 , experimental data; W , E , M , I and II have the same meaning as described in Fig. 1

In both figures, the corner W is pure water, M is $\text{Mg}(\text{CH}_3\text{COO})_2$, A is $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and E is CH_3COOH . In Fig. 1 the point N is the solid phase

$2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ plotted at the stoichiometric composition of 54.8 mass% $\text{Mg}(\text{CH}_3\text{COO})_2$, 34.7 mass% CH_3COOH , and 10.5 mass% water.

In Fig. 1, region I is a single-phase liquid, region II is $\text{Liq} + \text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, region III is a three-phase region of $\text{Liq} + \text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} + 2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$, and region IV is $\text{Liq} + 2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O} + 2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$. In Fig. 2, regions III and IV are no longer observed and the saturation curve has moved to $\text{Mg}(\text{CH}_3\text{COO})_2$ concentrations well above 50 mass%. The portion of the diagram with magnesium acetate concentrations greater than 66.2 mass% $\text{Mg}(\text{CH}_3\text{COO})_2$, so the $\text{Mg}(\text{CH}_3\text{COO})_2$ -rich portion of the system remains unknown.

4. Conclusions

The results of the present work have resulted in partial isothermal phase diagrams for the magnesium acetate-acetic acid-water ternary system for the temperatures 298.1 and 333.1 K. Two intermediate phases, $\text{Mg}(\text{CH}_3\text{COO})_2$ and $2\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$, were observed in the system at 298.1 K while only $\text{Mg}(\text{CH}_3\text{COO})_2$ was observed at 333.1 K.

The 35 °C difference in temperature between the two diagrams showed a significant increase in the solubility of $\text{Mg}(\text{CH}_3\text{COO})_2$ in water-acetic acid liquid solutions. These solubility data and phase diagrams may provide a guide and serve as a basis for the precipitation of calcium magnesium acetate.

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References

1. R.H. Richard and V.B. Mark, Environmental Evaluation of Calcium Magnesium Acetate for Highway Deicing Applications, *Resour. Conserv. Recy.*, 1992, 7(1-3), p 213-237, (in English)
2. F. Wenge and P.M. Alexander, Two-Stage Fermentation Process for the Production of Calcium Magnesium Acetate and Propionate Road Deicers, *Enzyme Microb. Tech.*, 2005, 36(7), p 953-959, (in English)
3. O. Peterson, Chemical Effects on Cement Mortar of Calcium Magnesium Acetate as a Deicing Agent, *Cement Concrete Res.*, 1996, 26(4), p 637-639, (in English)
4. W. Nimmo, A.A. Patsias, E. Hampartsoumian, B.M. Gibbs, and P.T. Williams, Simultaneous Reduction of NO_x and SO_2 Emissions from Coal Combustion by Calcium Magnesium Acetate, *Fuel*, 2004, 83(2), p 149-155, (in English)

5. W. Nimmo, A.A. Patsias, E. Hampartsoumian, B.M. Gibbs, M. Fairweather, and P.T. Williams, Calcium Magnesium Acetate and Urea Advanced Reburning for NO Control with Simultaneous SO₂ Reduction, *Fuel*, 2004, **83**(9), p 1143-1150, (in English)
6. A. Ajay, S. Judi, and A.L. Yiannis, Combustion and SO₂-NO_x Emissions of Bituminous Coal Particles Treated with Calcium Magnesium Acetate, *Fuel*, 1995, **74**(4), p 495-506, (in English)
7. F. Garcia-Labiano, L.F. de Diego, and V. Fierro, Utilization of Calcium Acetate and Calcium Magnesium Acetate for H₂S Removal in Coal Gas Cleaning at High Temperatures, *Energ. Fuel*, 1999, **13**(2), p 440-448, (in English)
8. A. Ohtsuka and K. Asami, In-bed Sulfur Removal During the Fluidised Bed Combustion of Coal Impregnated with Calcium Magnesium Acetate, *Resour. Conserv. Recycl.*, 1992, **7**(1), p 69-82, (in English)
9. B.A. Gancy, Process of Making Calcium Acetate Deicing Agents, U.S. patent 4,426,308, Jan 17, 1984 (in English)
10. B.A. Gancy, Process of Making Calcium Acetate Deicing Agents and Product, U.S. patent 4,444,672, April 24, 1984 (in English)
11. B.A. Gancy, Nonpolluting Salts and Method of Making Same, U.S. patent 4,511,485, April 16, 1985 (in English)
12. B.A. Gancy, Continuous Process for the Manufacture of Calcium Magnesium Acetate Deicer, U.S. patent 4,606,836, April 19, 1986 (in English)
13. S. Fu and C. Hercules, Process for Manufacturing Crystalline Calcium Magnesium Acetate, U.S. patent 5,430,185, July 4, 1995 (in English)
14. D.D. Dionysiou, M. Tsianou, and G.D. Botsaris, Investigation of the Conditions for the Production of Calcium Magnesium Acetate (CMA) Road Deicer in an Extractive Crystallization Process, *Cryst. Res. Technol.*, 2000, **35**(9), p 1035-1049, (in English)
15. A. Apelblat and E. Manzurola, Solubilities of Magnesium, Calcium, Barium, Cobalt, Nickel, Copper, and Zinc Acetates in Water from $T = (278.15 \text{ to } 348.15) \text{ K}$, *J. Chem. Thermodyn.*, 1999, **31**(10), p 1347-1357, (in English)
16. A.C.D. Rivett, The Constitution of Magnesium Acetate Solutions, *J. Chem. Soc.*, 1926, **105**(5), p 1063-1070, (in English)
17. A. Apelblat, Solubilities of Organic Salts of Magnesium, Calcium, and Iron in Water, *J. Chem. Thermodyn.*, 1993, **25**(12), p 1443-1445, (in English)
18. H.K. Zhao, D.S. Zhang, C. Tang, P.M. Jian, and S.H. Yuan, Phase Diagram of Ternary Calcium Acetate-Magnesium Acetate-Water System at 298.1 K, 313 K and 323 K, *J. Phase Equilib. Diff.*, 2007, **28**(2), p 167-171, (in English)
19. H. Schott, A Mathematical Extrapolation for the Method of Wet Residues, *J. Chem. Eng. Data*, 1961, **6**(3), p 324-324, (in English)