Articles

Measurement of the Metastable Zone Width of Phosphoric Acid Hemihydrate in the Presence of Impurity Ions

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The effect of five different impurities, the cations Al^{3+}, Fe^{2+}, and Mg^{2+} and the anions SO_4^{2-} and Cl^-, on the metastable zone width of phosphoric acid hemihydrate has been investigated using a laser method with a linear cooling rate. The metastable zone width was measured as a function of impurity concentration and cooling rate in the seeded system. The influences of impurity ions on the metastable zone width of phosphoric acid hemihydrate take place by different mechanisms. Mg^{2+} has enlargement effects on the metastable zone width, whereas Al^{3+} and Fe^{2+} have both enlargement or suppression effects under different impurity concentrations. Cl^- and SO_4^{2-} have relative weak effects on the metastable zone width.

Introduction

High-purity phosphoric acid is one of the fundamental chemical compounds and is widely used in the chemical, food, and electronic industries. Many impurity ions exist in phosphoric acid such as the cations Fe^{2+}, Al^{3+}, and Na^+ and the anions SO_4^{2-}, NO_3^-, and Cl^-. Several methods, for example, solvent extraction, ion exchange, electro-osmosis, and crystallization, are employed for the purification of phosphoric acid to remove impurities from the acid.[1] Among these technologies, crystallization presents several advantages such as having higher efficiency, being more economic to operate, and being environmentally friendly. At present, the crystallization technique is mainly employed for phosphoric acid purification to high purity, which is mainly applied to the silicon plane tube and integrated circuit production as an acidic cleansing and corrosive agent, in which impurities are strictly limited.

Crystallization processes are the critical steps that determine the quality of the final product.[2] To achieve an appropriate crystallization rate and the highest-purity product, a seeding strategy is generally required in industrial crystallization. Solubility data and the metastable zone width (MZW) are of great technical interest with regard to optimization of the crystallization process and design of the crystallizer. The MZW usually depends on temperature, cooling rate, stirring rate, the presence of impurities, and type of measuring technique. Of these factors, the influence of impurities on the MZW is poorly understood and cannot be clearly predicted to date.[3] It is reported that phosphoric acid hemihydrate has an approximate MZW as wide as 40 °C, and impurities have an important influence on its MZW and crystallization process.[4] However, little data are available in the literature on the MZW of phosphoric acid hemihydrate and the influence of impurities on its MZW.

In this contribution, the MZW for phosphoric acid hemihydrate as a function of impurity concentration and cooling rates in seeded systems were obtained experimentally by the laser method. To examine the reliability of this method, another way, the in-line FBRM (focused beam reflectance measurement) monitoring system, was used to compare the data obtained.

Table 1. Impurity Concentration in the Analytical-Grade Phosphoric Acid

impurities name	impurities concentration ppm
H_2SO_4	0.60
HF	−
Al^{3+}	0.17
Fe^{3+}	0.74

Experiments

Materials. A high-quality analytical grade phosphoric acid solution at 85 wt % concentration was used for measurement of the MZW. The main impurities in this acid are shown in Table 1. The content of Fe^{2+}, Al^{3+}, and SO_4^{2-} in the solution was measured by inductively coupled plasma atomic emission spectrometry (ICP, VISTA-MPX). To avoid introducing anion impurities, fine reductive Fe, Al, and $Mg(OH)_2$ powders were slowly added into a known analytical phosphoric acid solution at the reaction temperature of 60 °C in this study. After the Fe, Al, and $Mg(OH)_2$ powders completely reacted with the acid, a certain amount of phosphoric acid hemihydrate crystals were added into the solution to maintain the acid concentration at 85.0 ± 0.05 %. The exact content of Fe^{2+}, Al^{3+}, and Mg^{2+} in the solution was then analyzed by ICP. With regard to the anions, HCl (37 wt %) and H_2SO_4 (98 wt %) were used. All additives used for the experiments were analytical reagent grade.

Measurements for the Metastable Zone. The laser method was used to measure the metastable zone width. The measurement was based on cooling the saturated solution in the seeded system with a constant cooling rate until homogeneous nucleation took place at the upper limit of the metastable zone. The apparatus for metastable zone width is the same as that described

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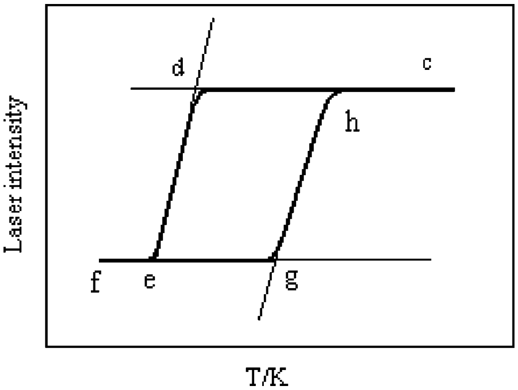

Figure 1. Determination sketch of the MZW of phosphoric acid hemihydrate by means of the laser method.

in the literature.[2] The laser monitoring system, which is composed of a laser generator, a photoelectric transformer, and a light intensity display, was used to detect nucleation and dissolution of crystals. The metastable zone apparatus consisted of a 500 mL cylindrical double-jacketed glass vessel maintained at desired temperatures by circulating water through the outer jacket from a thermostat with a precision of ± 0.01 K.

Measurement procedures were similar to that described by Rauls except with minor modifications.[5] The same counts of seeds were introduced at the beginning of each run. The crystallizer was kept at a temperature, and the agitation speed was at 200 rpm. The variation of the laser intensity and temperature during the cooling of the saturated solution (480 g) with a constant cooling rate was analyzed to find exactly the nucleation temperature. After several seed crystals were added, there was no obvious change in the intensity of the laser beam penetrating the vessel. The intensity of the laser beam was kept constant after an equilibrium was obtained as shown in point c of Figure 1. Then the temperature was cooled down uniformly. A change in the relation between the laser intensity data and the nucleation temperature occurs during cooling. As nucleation starts, the intensity of the laser beam penetrating the vessel dramatically dropped to the minimum, as shown by point e of Figure 1. A typical measurement of the nucleation temperature of a saturated solution can be found at point d in Figure 1. The temperature in the measurement was recorded. Thereafter, the solution was heated at the same rate. As dissolution starts, the intensity of the laser beam penetrating the vessel increased to the maximum as shown in point g of Figure 1. A typical measurement of the equilibrium temperature in the presence of an impurity can be established at point g in Figure 1. The response of the laser intensity during this cycle can be used to determine the nucleation and equilibrium temperature. The MZW would be obtained by calculating the difference between the equilibrium temperature (T^*) and the nucleation temperature (T_n) as expressed in eq 1. The same MZW measurements were performed three times. The uncertainty in the MZW values is estimated to be within 4.0 %. An in-line FBRM monitoring probe (Lasentec D600L FBRM) was used to verify the MZW of analytical-grade phosphoric acid solution at 85 wt % concentration. The procedures of the in-line FBRM measurement were similar with the laser method. The difference is that the FBRM takes the number of crystal nuclei as the response.

$$\Delta T_{\max} = T^* - T_n \tag{1}$$

Results and Discussion

The solubility of phosphoric acid hemihydrate has been reported in the literature[6] and is shown in Figure 2. From Figure 2, it can be seen that the solubility has a remarkable dependence on temperature. In industry, more than 85 % concentration of phosphoric acid hemihydrate is needed to reduce energy consumption during crystallization.

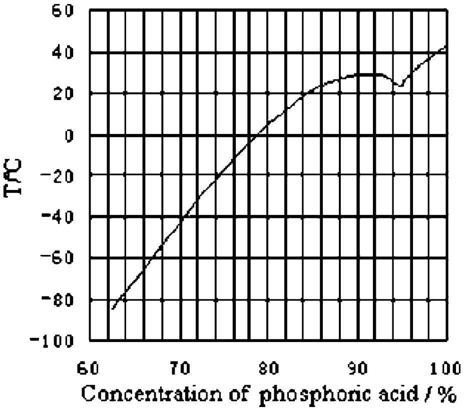

Figure 2. Solubility of phosphoric acid hemihydrate.

Table 2. MZW Measurement for 85 wt % Phosphoric Acid Hemihydrate

	$\Delta T_{\max}$/K	
cooling rates/K·h^{-1}	laser method	FBRM method
0.2	1.40	1.60
0.4	1.80	1.95
1.0	2.10	2.20
2.0	2.20	2.40

Table 3. MZW Measurement for 85 wt % Phosphoric Acid Hemihydrate in the Presence of Mg^{2+}, Al^{3+}, and Fe^{2+}

	$\Delta T_{\max}$/K					
C_{im}	0.4	1.0	2.0	0.4	1.0	2.0
ppm	K·h^{-1}	K·h^{-1}	K·h^{-1}	K·h^{-1}	K·h^{-1}	K·h^{-1}
		Mg^{2+}			Al^{3+}	
50	1.70	2.61	3.14	2.65	2.67	2.69
100	1.95	2.65	3.29	3.50	3.90	4.20
500	2.15	2.95	3.50	2.85	2.89	3.26
2000	4.04	4.90	6.10	6.85	7.25	7.90
5000	5.40	7.32	9.87	9.10	10.1	11.6
			Fe^{2+}			
50	2.30	2.40	2.41			
100	3.09	3.55	3.63			
500	2.46	2.82	3.06			
2000	3.60	4.05	5.29			
5000	5.10	5.60	8.09			

To assess the applicability of the laser method to determine the MZW of phosphoric acid hemihydrate, the FBRM probe was used to compare data by measuring the MZW of analytical grade phosphoric acid solution at 85 wt % concentration. The results obtained by the two methods are listed in Table 2. As can be seen from Table 2, the MZW increases with increasing cooling rates, and there is a systematic difference of 0.1 to 0.2 °C in the MZW. These differences come from the sensitivity of the sensor.

In many instances, small amounts of impurities have dramatic effects on crystal growth, morphology, and nucleation.[3] In this paper, the influence of the cations Al^{3+}, Fe^{2+}, and Mg^{2+} and the anions SO_4^{2-} and Cl^{-} on the MZW of 85 % $H_3PO_4 \cdot 0.5H_2O$ solution saturated at 21.3 °C at different cooling rates was investigated. The metastable zone widths for different impurity concentrations and cooling rates are listed in Table 3 and Table 4. These results show that the MZW of phosphoric acid hemihydrate increases with the cooling rates for all the experimental conditions explored. From Table 3 and Table 4,

Table 4. MZW Measurement for 85 wt % Phosphoric Acid Hemihydrate in the Presence of SO_4^{2-} and Cl^-

	ΔT_{max}/K					
C_{im}	0.4	1.0	2.0	0.4	1.0	2.0
ppm	$K\cdot h^{-1}$	$K\cdot h^{-1}$	$K\cdot h^{-1}$	$K\cdot h^{-1}$	$K\cdot h^{-1}$	$K\cdot h^{-1}$
	SO_4^{2-}			Cl^-		
50	2.47	2.72	2.72	2.29	2.37	2.36
500	2.25	2.45	2.56	2.34	2.41	2.39
5000	2.52	2.56	2.75	2.48	2.52	2.61
10000	2.60	2.66	2.75	2.52	2.56	2.63
20000	2.39	2.46	2.53	2.55	2.59	2.68

the MZW of phosphoric acid hemihydrate increases with an increasing concentration of Mg^{2+} ions. However, the case is different with regard to Al^{3+} and Fe^{2+}. The MZW of phosphoric acid hemihydrate increases up to an ion concentration of 100 ppm Al^{3+} and Fe^{2+}. By addition of more than 100 ppm Al^{3+} and Fe^{2+}, the MZW of phosphoric acid hemihydrate decreases until approximately an ion concentration of 500 ppm and then subsequently increases. It is clear that the MZW has a remarkable dependence on the concentration of impurity ions.

Compared with Al^{3+}, Fe^{2+}, and Mg^{2+}, the effect of SO_4^{2-} and Cl^- on the MZW is obviously weaker. The MZW of phosphoric acid hemihydrate decreases to an ion concentration of 500 ppm SO_4^{2-}. Thereafter, the MZW of phosphoric acid hemihydrate increases with an increase in the SO_4^{2-} ion concentration. The MZW of phosphoric acid hemihydrate increases up to an ion concentration of 10 000 ppm SO_4^{2-} ion. After an addition of 20 000 ppm SO_4^{2-} ion, the MZW of phosphoric acid hemihydrate decreases. Compared with the SO_4^{2-} ion, the effect of Cl^- on the MZW is simple. The MZW of phosphoric acid hemihydrate increases up to an ion concentration of 5000 ppm Cl^-. Thereafter, there is a slight rise in the MZW until an ion concentration of 20 000 ppm Cl^-.

This type of tendency is not common. Titiz-Sargut and Ulrich[3] investigated the influence of Cr^{3+} ions on the MZW of seeded potassium alum solution. Sayan and Ulrich[7] have investigated the influence of Cu^{2+} and Mg^{2+} ions on the MZW of ammonium sulfate. The effect is different from the results obtained in this paper. The influence on the MZW can take place by different mechanisms. It is generally believed that the enlargement effect of impurities on the MZW can be explained on the basis of the adsorption of impurity molecules on the surface of subcritical embryos in the solution. These impurities suppress the growth of embryos to larger than critical size and induce the enlargement of the MZW. In addition, it is possible that impurities can increase the formation of clustering in the solution, which induces promotion of nucleation and tends to narrow the MZW. Although it is difficult to give general explanations of the phenomenon of nucleation suppression or enhancement by the use of impurities, the concentration of impurities investigated is very effective on the enlargement or suppression of the MZW of phosphoric acid hemihydrate, especially Mg^{2+}, Al^{3+}, and Fe^{2+}. Therefore, the relationship between the MZW and impurities must be known and the concentration of impurities in solution should be controlled to obtain crystal products with desired properties.

Conclusions

The laser method can be used to determine the MZW of phosphoric acid hemihydrate. Results obtained show that the MZW of phosphoric acid hemihydrate increases with the cooling rate for all the experimental conditions explored, and the influences of the cations Al^{3+}, Fe^{3+}, and Mg^{2+} on the MZW of phosphoric acid hemihydrate are far more remarkable than the anions SO_4^{2-} and Cl^-. The influences of impurity ions on the MZW of phosphoric acid hemihydrate can take place by different mechanisms. Mg^{2+} has enlargement effects on the MZW of phosphoric acid hemihydrate, whereas Al^{3+} and Fe^{2+} have both enlargement and suppression effects under different impurity concentrations. Cl^- and SO_4^{2-} have relative weak effects on the MZW of phosphoric acid hemihydrate. These data are of great interest for the design and operation of industrial crystallization processes for phosphoric acid hemihydrate.

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