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EFFECT OF VARIOUS ADDITIVES ON THE NUCLEATION KINETICS OF POTASSIUM DİHYDROGEN PHOSPHATE

G. Yıldız YÜKSEL* and A. Abdullah CEYHAN**
**Department of Chemical Engineering, Istanbul Technical University, 34469, Maslak, İSTANBUL*
***Department of Chemical Engineering, Selcuk University, 42031, Campus, KONYA*

ABSTRACT: In this study, the effect of K_2HPO_4 and KOH on the nucleation kinetics of potassium di hydrogen phosphate (KDP) was investigated. The polythermal method was used for the measurement of the metastable zone width(MZW) and experiments were carried out at three cooling rates. It was found that, additives not measured with concentration, but they increased the solubility and decreased the MZW of KDP. The MZW was sharply decreased by the addition of additive(s) up to 100 ppm concentration to the aqueous solution of KDP.

Keywords Potassium dihydrogen phosphate, nucleation kinetics, metastable zone width, additives.

Bazı Katkı Maddelerinin Potasyum Dihidroyen Fosfatin Nükleasyon Kinetiği Üzerine Etkileri

ÖZET: Bu çalışmada, potasyum dihidrojen fosfat (KDP)' ın nükleasyon kinetiği üzerine K_2HPO_4 ve KOH katkılarının etkileri incelenmiştir. Metastabil bölge ölçümleri politermal yöntem kullanılarak, üç farklı soğutma hızı için gerçekleştirilmiştir. Çalışma sonucunda, katkı maddelerinin çözelti pH'ı üzerine önemli bir etkilerinin olmadığı, bununla birlikte, KDP'nin çözünürlüğünü artırdıkları ve metastabil bölge genişliğini daralttıkları tespit edilmiştir. Metastabil bölgenin özellikle 100 ppm'e kadar katkı konsantrasyonları için hızla daraldığı bulunmuştur.

Anahtar Kelimeler Potasyum dihidrojen fosfat,nükleasyon kinetiği, metastabil bölge genişliği, katkı maddesi.

INTRODUCTION

In the production of a substance by crystallization , a lot of factors such as supersaturation level, impurities/additives, hydrodynamic conditions affect the nucleation and growth rates, morphology, quality, average particle size and particle size distribution etc(Ulrich and Strege, 2002). Impurities/additives affect the crystallization kinetics by not only with their types but also with their concentrations. Furthermore, the additives show different results when they are exist alone or together with other reagents in the crystallization medium. There are a lot of studies about the effect of impurities/additives on the crystallization of several substances in the literature. These studies were done by using nucleation and/or growth rates measuring methods (Davey, 1981; Nývlt and Ulrich, 1995).

In recent years an appreciable attention is given to grow large potassium dihydrogen phosphate (KDP) single crystals from solution for laser fusion systems. To grow large KDP with faster rates which have high optical quality requires the solution stability (Guohui. et al.2001). KDP has impurities of some metal ions like most of the commercially available chemicals and these impurities affect the solution stability negatively. Chelating agents such as EDTA and sulfosalicylic acid were used to suppress chemical activity of the metal ions present in the KDP solutions. Researchers reported that chelating agents enhance the metastable zone width (MZW) of KDP (Srinivasan et al., 2001; Guohui. et al.2001;

Srinivasan, et al., 2000) Several organic additives such as urea and thiourea (Rajesh, 2002) or inorganic additives such as KCl and borates have also been used in several studies and the effects of these additives on the growth and nucleation kinetics of KDP and/or on the quality of its single crystal were determined (Podder, 2002; Guohui, et.al, 2005; Shangfeng, et.al, 1999). The subject of this paper is to determine the effects of K_2HPO_4 and KOH as additives on the metastable zone width of KDP.

EXPERIMENTAL

Merck grade dipotassium hydrogen phosphate and potassium hydroxide were used as additives in the experiments. The working solution was prepared from reagent grade KDP (Merck) and distilled water; hence it should be saturated at approximately 308K. This solution was heated up to 313K, filtered using a membrane filter (Millipore, 0.45μm pore size) and kept at 313K as stock solution. Metastable zone width measurements were carried out in this solution and also in solutions prepared from this solution by adding 10, 50, 100, 500 and 1000 ppm K_2HPO_4 and KOH as additives. A 0.5 L jacketed glass nucleation cell with a cover, a cooling thermostatic bath and a magnetic stirrer were used in the experimental set-up. The stirring rate was 410 rpm and 278, 293 and 313 K/h cooling rates were applied in all experiments. Temperature of solutions was measured with a precision of ±0.01 K using a digital thermometer as in our previous study (Yuksel and Ceyhan, 2005). The experimental set-up was given in Fig.1.

The nucleation moment was determined as the temperature at which turbidity was observed. After nucleation, the solution was heated just below the saturation temperature with 313K/h heating rate and kept at this temperature for 2 hours. Then, the solution was heated with 278K/h heating rate. The temperature at which the crystals were disappeared and clear solution was observed was taken as the saturation temperature. To determine the saturation temperature more accurately, the heating was repeated up to just below the first determined saturation temperature, and the procedures were repeated. Experiments were repeated at least twice. The pH values of the solutions were also measured at 311K.

The difference between saturation temperature and nucleation temperature was taken as maximum allowable supercooling ($\Delta T_{max.}$). The maximum allowable supercooling (ΔT_{max}) is related to the cooling rate (-b, K/h) by following equation:

$$\ln \Delta T_{max} = \frac{1-n}{n} \ln\left(\frac{dC^*}{dT}\right) - \frac{1}{n} \ln(K_n) - \frac{1}{n} \ln(-b) \quad (1)$$

According to Eq.2 the dependence of max ΔT on ($-b$) is linear on a logarithmic plot and corresponds to the equation of a straight line

$$Y = A + Bx \quad (2)$$

Where x= ln(-b) ve $Y = \ln(\Delta T_{max})$ (3)

The values of nucleation parameters n and kN are obtained from the fitted constant of the correlation equation.

$$n = \frac{1}{B} \quad (4)$$

$$K_n = (1-n) \ln\left(\frac{dC^*}{dT}\right) - An \quad (5)$$

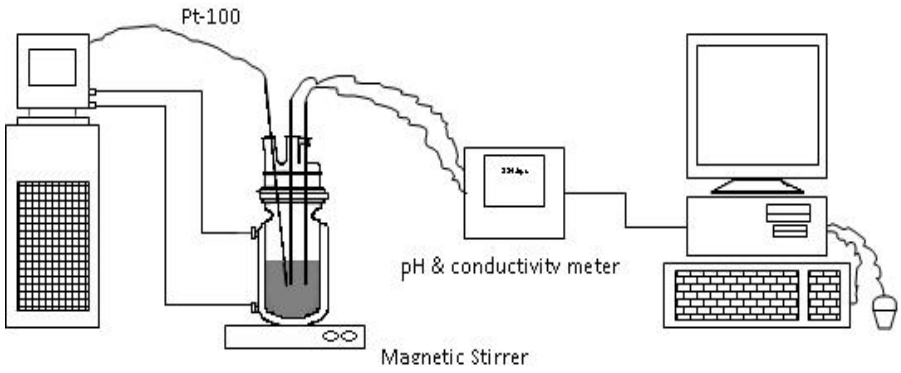

Figure 1. *Experimental setup for metastable zone width measurement.*

RESULTS AND DISCUSSION

Saturation temperature of stock KDP solution was determined as 308.9K. Fig.2 shows the changes in saturation temperatures of the KDP solutions with additive concentrations.
According to this figure, the investigated additives at 10 ppm concentrations increase the solubility of KDP. When the concentrations of additives increase from 10 ppm to 100 ppm, the solubility increased with K_2HPO_4. Increase in the concentrations of this additive from 100 ppm to 1000 ppm causes no clear change in the solubility of KDP. The presence of 10-500 ppm of KOH also affects the solubility as K_2HPO_4 does, but the change of the solubility of KDP is relavitely less. KDP solution containing 1000 ppm KOH has the lowest saturation temperature. In general, both of the additive types and concentrations cause to increase the solubility of KDP.

In the presence of additives, any detectable change was not observed on the pH's of solutions, it was recorded as 4.7 at 311K.

The effects of K_2HPO_4 and KOH additives on the MZW of KDP in terms of ΔT_{max} are shown, graphically for 5, 20 and 40K/h cooling rates in Fig. 3 and 4, respectively.
It can be seen from these figures that additives in the investigated concentration range cause a decrease on the MZW of KDP. The decrease is very sharp up to 100 ppm for all two additives. When the concentrations of KOH rised from 100 ppm up to 500 and 1000 ppm, there is not any detectable effect on the MZW. On the other hand, there is a noticeable increase in the MZW in the presence of 1000 ppm KOH.

A sharp increase and then decrease in the MZW is observed when the K_2HPO_4 concentration is increase from 100 ppm up to 500 ppm and 1000 ppm, respectively. Similar observation was also seen in the investigation of effect of $NaBO_2$ on the MZW of $NaBO_3.4H_2O$ (Titiz, et. al,1992). The same experiments were carried out using a new KDP solution containing K_2HPO_4 once again to check the correctness of the findings and same results were obtained.

To calculate of nucleation rate parameters from Eq.1 which gives relation between maximum allowable supercooling and cooling rate, log ΔT_{max}-logb graphics were drawn for KOH and K_2HPO_4 additives at different concentrations. The variation of maximum allowable undercooling with cooling rate are presented graphically in Figs.5 and 6.

The experimental data were treated using Eq. 1. The nucleation rate orders (n) and rate constants (K_n) were determined from the slops and intercepts of straight lines, respectively. dC*/dT term was determined as $3{,}896.10^{-3}$ kg KDP/kgH_2O (Linke, 1995). The result of measurements of the metastable zone width of potassium hydrogen phosphate in the presence of KOH and K_2HPO_4 are summarized in Table.1.

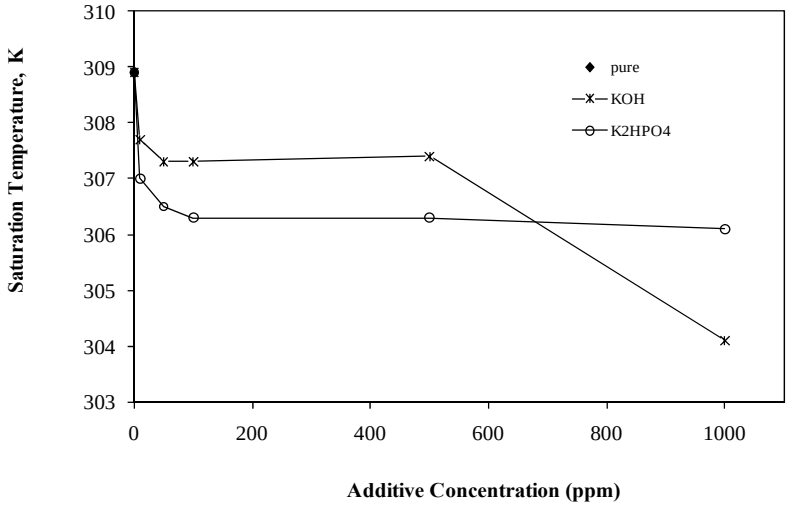

Figure 2. *The changes in saturation temperatures of the KDP solutions with additive concentrations.*

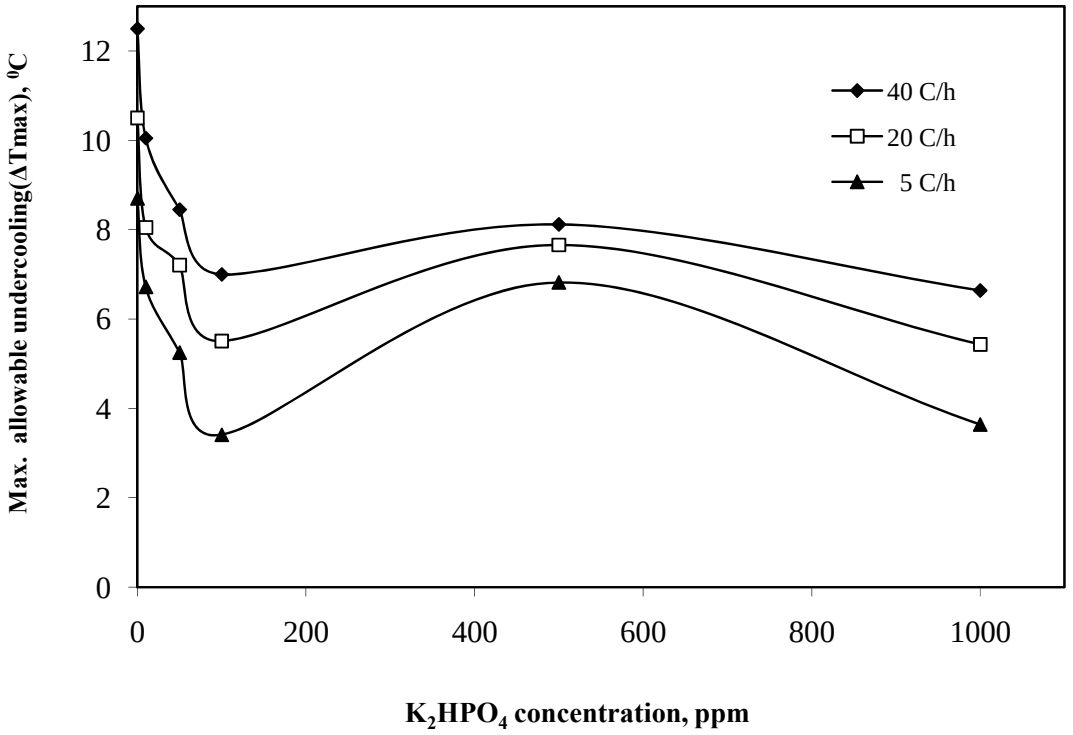

Figure 3. *Metastable zone width change of KDP solutions versus K_2HPO_4 concentration.*

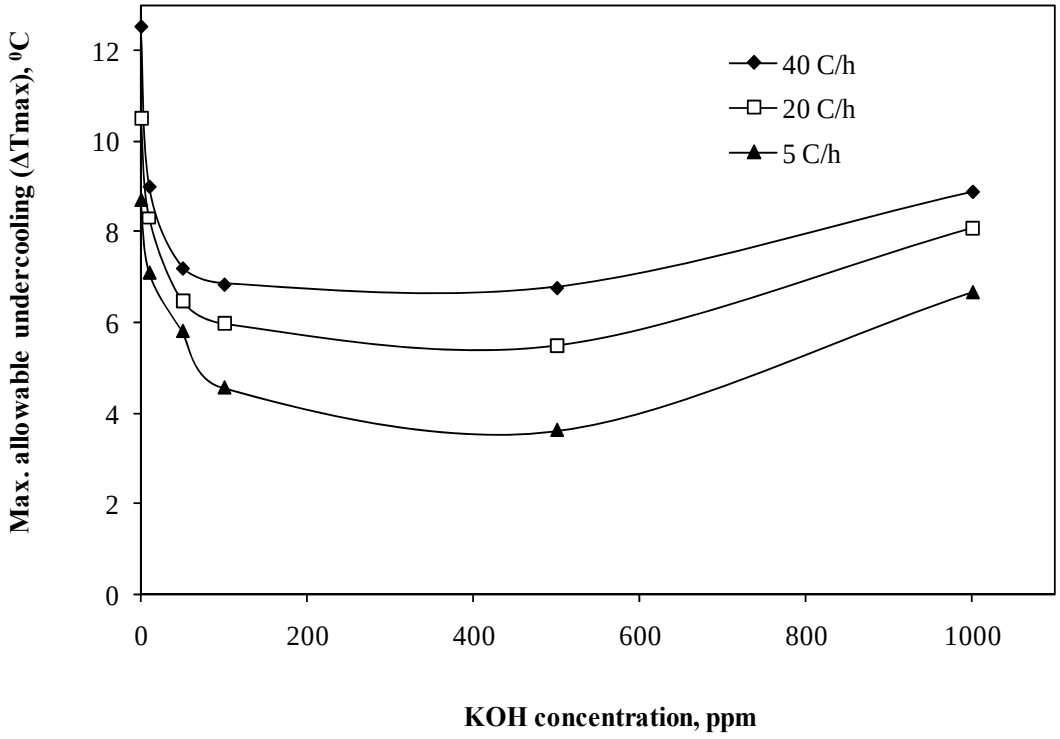

Figure 4. *Metastable zone width change of KDP solutions versus KOH concentration.*

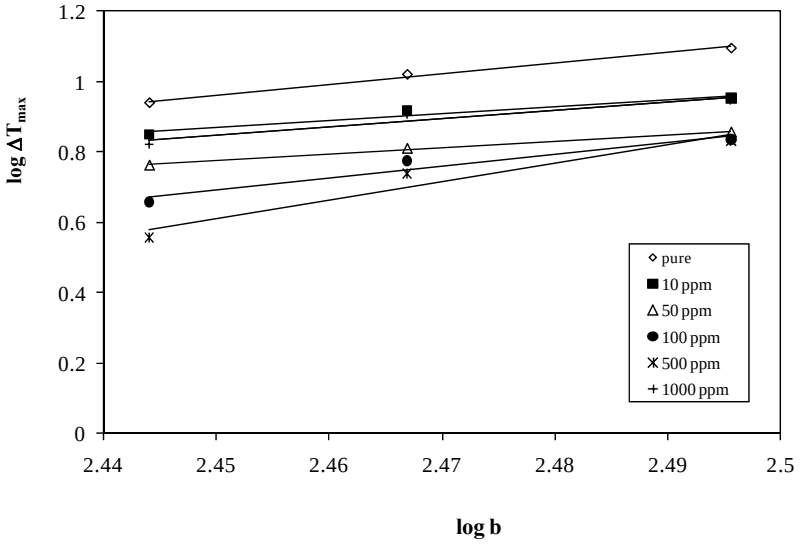

Figure 5. *The variation of maximum allowable undercooling with cooling rate in the presence of KOH.*

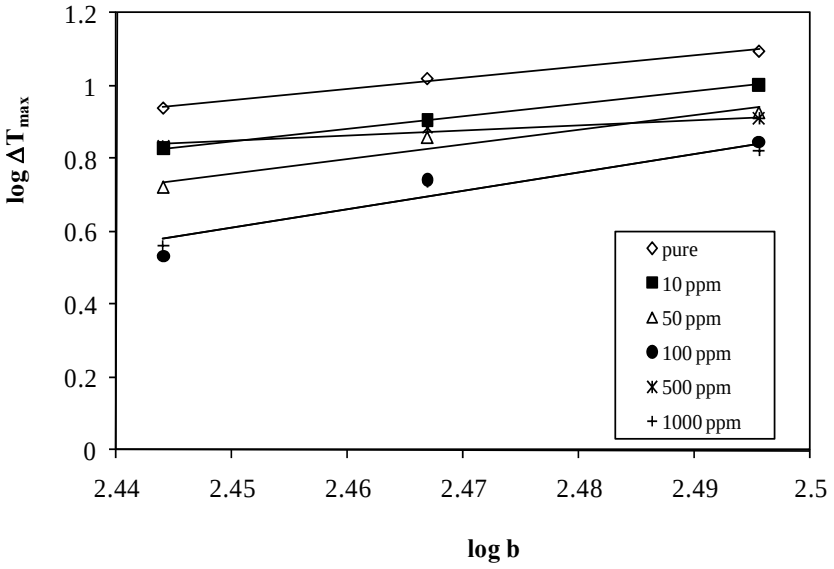

Figure 6. *The variation of maximum allowable undercooling with cooling rate in the presence of K_2HPO_4.*

Table 1. *Nucleation rate orders (n) and rate constants (Kn, $kg_{salt}^{1-n}.kg_{water}^{n-1}.h^{-1}$) of KDP in the presence and absence of additives.*

Additive type	Additive concentration (ppm)											
	0		10		50		100		500		1000	
	n	K_N	n	K_N	n	K_N	n	K_N	n	K_N	n	K_N
Pure	0,329	3,29	-	-	-	-	-	-	--	-	-	-
KOH	-	-	0,508	6,64	0,551	8,72	0,295	3,53	0,295	3,53	0,419	4,95
K_2HPO_4	-	-	0,295	3,17	0,253	2,87	0,168	2,21	0,691	12,88	0,2	2,52

As it can be seen from Table 1, the changes in nucleation rate order and rate constant as the result of types and concentrations of the used additives are exactly similar. While 500 ppm KOH, 100 and 1000 ppm K_2HPO_4 reduce n and K_n ; 50 ppm KOH and 500 ppm K_2HPO_4 drastically increase these values.

CONCLUSIONS

This study can be concluded as follows:

- K_2HPO_4 and KOH in the concentrations of 10-1000 ppm increase the solubility of KDP.
- They have not any effect on the pH.
- These additives cause to decrease of the MZW.

REFERENCES

Davey, R. J., 1981. The role of additives in precipitation processes, 8th Symposium on Industrial Crystallization, Budapest, Hungary, September 28-30.

Guohui, L., et.al., 2004. Rapid growth of KDP crystal with new additive, J. Crystal Growth, 269, 443.

Guohui, L., et.al., 2005. Study on the growth and characterization of KDP-type crystals, J. Crystal Growth, 274, 555.

Linke, W. F. and Seidell, A., 1995. Solubilities of Inorganic and Metalorganic Compounds, American Chemical Society, Washington DC.

Nývlt, J. and Ulrich, J., 1995. Admixtures in Crystallization, 1st ed., VCH Publisher, New York.

Podder, J., 2002. The study of impurities effect on the growth and nucleation kinetics of potassium dihydrogen phosphate, J. Crystal Growth 237-239, 70.

Rajesh, N.P., et.al., 2002. Optical and microhardness studies of KDP crystals grown from aqueous solutions with organic additives, Materials Letters, 52, 326.

Shangfeng, Y., et.al., 1999. Rapid growth of KH_2PO_4 crystals in aqueous solution with additives, J. Crystal Growth, 197, 383.

Srinivasan, et.al., 2000. A novel method to enhance metastable zone width for crystal growth from solution, Crystal Research and Technology, 35, 291.

Srinivasan, K. et.al., 2001. A contemporary method to enhance the metastable zone width for crystal growth from solution, Materials Science and Engineering B 84, 233.

Titiz, S. et.al., 1992. Turkish VIIIth National Symp. on Chemistry and Chemical Engineering, Chemistry'92, 7-11 September 1992, Istanbul, Turkiye.

Ulrich, J. and Strege, C., 2002. Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers, J. Crystal Growth, 237-239, 2130.

Yuksel, G. Y. and Ceyhan, A. A., 2005. Metastable zone width of KDP in the presence of H_3PO_4 and HCl, BIWIC 2005, 7th-9th September 2005, Halle-Wittenberg, Germany.