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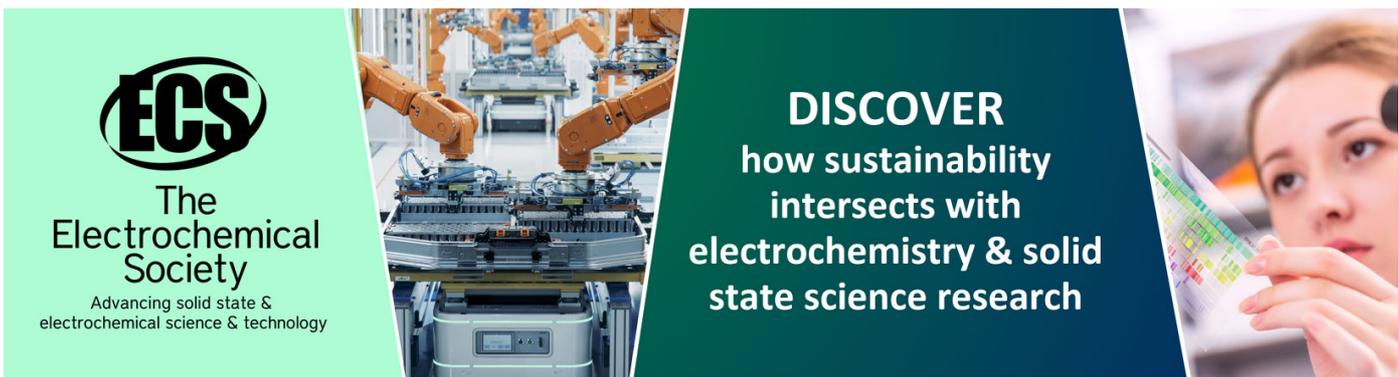
Non-isothermal Dehydration Kinetics of Potassium Citrate Monohydrate

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Non-isothermal Dehydration Kinetics of Potassium Citrate Monohydrate

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Abstract: The dehydration kinetic of potassium citrate monohydrate has been investigated by TG-DTG. The kinetic parameters of activation energy and pre-exponential factor were calculated using the methods of FWO and KAS. The results show that the kinetic parameters calculated by two methods were consistent. Meanwhile, the most probable kinetic function was acquired by means of the Malek method. The thermodynamic functions of the dehydration process are then calculated according to the transition theory, which indicate that the dehydration process of potassium citrate monohydrate is endothermic and non-spontaneous.

1. Introduction

Potassium citrate is a potassium salt of citric acid, which is widely used in several fields^[1-4]. For example, potassium citrate is used in food industry as a food additive to regulate acidity, and used in medicine industry to control kidney stones derived^[5], etc.

There are some recently published work about the dehydration of some other types of compounds^[6]. The kinetic parameters of the dehydration step can be evaluated using non-mechanistic equations, such as, Free-man and Carroll^[7], Flynn-Wall-Ozawa Kissinger-Akahira-Sunose equations, etc. However, the dehydration mechanism can not be obtained by the methods above. However, the dehydration mechanism is significant for controlling the stability of hydrate.

In this paper, the dehydration behavior of potassium citrate monohydrate was investigated by the non-isothermal kinetic method using TG-DTG data. The kinetic parameters of A and E were determined according to the methods of FWO and KAS. Meanwhile, the most probable kinetic function is determined by the Malek method. In addition, the thermodynamic function (ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger) for the dehydration process of potassium citrate monohydrate were determined.

2. Theory

2.1. Non-isothermal kinetic analysis

On the basis of the thermogravimetric curves, the kinetic parameters (E and A) were determined using many methods. The methods of FWO and KAS were generally used to determine E of the dehydration process.



FWO equation:

$$\lg \beta = \ln \left(\frac{AE_\alpha}{RG(\alpha)} \right) - 2.315 - 0.4567 \left(\frac{E_\alpha}{RT} \right) \quad (1)$$

KAS equation:

$$\ln \left(\frac{\beta}{T^2} \right)_\alpha = \ln \left(\frac{AE}{G(\alpha)R} \right) - \frac{E_\alpha}{RT} \quad (2)$$

Malek method

The malek method equation:

$$y(\alpha) = \frac{f(\alpha) \cdot G(\alpha)}{f(0.5) \cdot G(0.5)} \quad (3)$$

and

$$y(\alpha) = \left(\frac{T}{T_{0.5}} \right)^2 \frac{\left(\frac{d\alpha}{dt} \right)}{\left(\frac{d\alpha}{dt} \right)_{0.5}} \quad (4)$$

The calibration curve can be obtained by equation (3), and the experiment curve can be obtained by equation (4). If the two curves can be consistent, the $G(\alpha)$ and $f(\alpha)$ is the most probable kinetic function.

2.2. Thermodynamic function

The thermodynamic function can be estimated by the equation (5) as following:

$$k_{\text{exp}} = \chi K^\ddagger \frac{k_B T}{h} \quad (5)$$

Where k^\ddagger is the equilibrium constant. χ is the transmission coefficient. For the simple reaction, χ is approximately 1 unit? k_B and h are the Boltzmann and Planck constants, respectively. The ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger can be calculated at $T=T_p$ by the equations (6), (7) and (8).

$$\Delta S^\ddagger = R \ln \left(\frac{Ah}{\chi e k_B T_p} \right) \quad (6)$$

$$\Delta H^\ddagger = E^\ddagger - RT_p \quad (7)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T_p \Delta S^\ddagger \quad (8)$$

Where e is the Neper number ($e=2.7183$), T_p is the peak temperature of DTG curve.

3. Experimental apparatus and methods

3.1 Chemicals

Potassium citrate monohydrate was purchased from Tianjin tianzhi chemical Co. Ltd. The purity is above 99.5 %. The material was analyzed by the PXRD, and shows in the Figure 1.

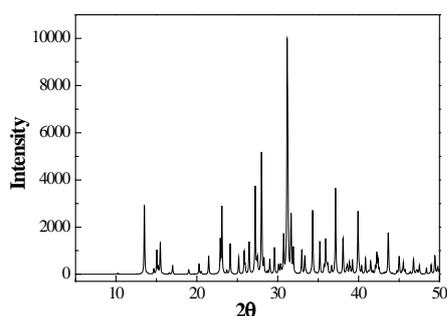


Figure 1. PXRD pattern of potassium citrate monohydrate

3.2. Non-isothermal dehydration kinetic analysis

A thermal gravimetric analyzer was used to investigate the mass loss of water in potassium citrate monohydrate in the course of heating. Potassium citrate monohydrate were heated in an open aluminum pan from 30 to 800 °C at 2 °C/min under a nitrogen purge.

4. Results and discussions

4.1. The dehydration process of potassium citrate monohydrate

The dehydration process of potassium citrate monohydrate was analyzed by TG, and the TG-DTG curves are presented in Figure 2. The result shows that there is one DTG maxima peak at the temperature of 214.6 °C, which show that the dehydration process of potassium citrate monohydrate could be a single-step mechanism. The TG result suggests that mass loss in dehydration process is about 5.78%, almost 1 mol water.

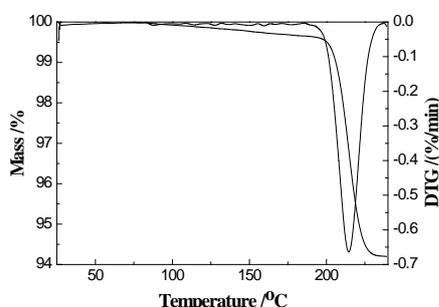


Figure 2. TG-DTG curves of dehydration for potassium citrate monohydrate

The thermal dehydration process may be represented by the following equation:



4.2 Kinetic studies

4.2.1. Determination of the most probable kinetic function of the dehydration process for potassium citrate monohydrate. The Malek method was widely used to obtain the most probable kinetic function. According to 21 frequently used kinetic functions in both differential and integral forms^[6], the calibration and experiment curve of dehydration process for potassium citrate monohydrate can be obtained using equations (3) and (4). The results show that the calibration curve is consistent with the experiment curve when the Malek method was carried out by No.18 as the most probable kinetic function (Figure 3). So the kinetic function No.18, Reaction order (n=2), is the most probable kinetic function for the dehydration process of potassium citrate monohydrate, and the kinetic function is

$$f(\alpha) = (1-\alpha)^2 \text{ and } G(\alpha) = (1-\alpha)^{-1} - 1.$$

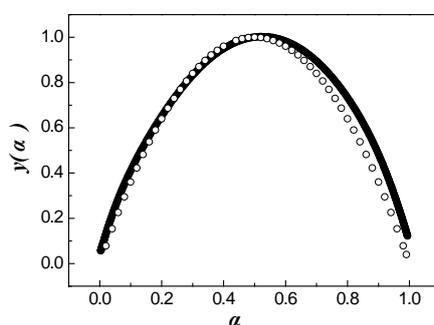


Figure 3. The experiment and calibration curves of dehydration for potassium citrate monohydrate ●: experiment curve; ○ calibration curve.

4.2.2. Calculation of the kinetic parameters by isoconversional method. The isoconversional method was widely used to determine the basic data of T and α , which were collected from the TG curve of the dehydration step for potassium citrate monohydrate at various heating rate are listed in Table 1. The plots of $\lg\beta$ versus $1/T$ (FWO) and $\ln(\beta/T^2)$ vs $1/T$ at different α can be obtained by least-square method by the equations (1) and (2), respectively (Figure 4 and Figure 5). The E and A can be obtained from the slopes and intercept of the straight lines in the α range from 0.2 to 0.8, and list in Table 2. As shown in Table 3, the E and A values calculated from two methods show a consistency. The calculated E and A values change with the different of α . However, the relative error of the E from the methods FWO and KAS is lower than 10%, which indicated that the dehydration process of potassium citrate monohydrate could be a single-step mechanism. This result is agree with the result of DTG analysis.

4.2.3. Determination of the thermodynamic functions. According to equations (6), (7) and (8), the ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger values can be calculated. The values of ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger from FWO are 112.5 J/K.mol, -125.3 kJ/mol and 176.1 kJ/mol, while those from KAS are 110.0 J/K.mol, -136.6 kJ/mol and 179.3 kJ/mol, respectively. The ΔS^\ddagger value means that the dehydration step is a “slow” stage. The positive ΔH^\ddagger and ΔG^\ddagger values mean that they are related to the introduction of heat and they are non-spontaneous process.

Table 1. The temperature at various isoconversion at different heating rate for dehydration process of potassium citrate

α	Temperature at different heating rate ($\beta/\text{K}\cdot\text{min}^{-1}$)/K			
	$\beta=2$	$\beta=5$	$\beta=10$	$\beta=15$
0.2	207.1	222.13	235.61	241.39
0.3	209.79	225.28	238.13	244.08
0.4	211.87	227.59	239.96	246.23
0.5	213.69	229.72	241.83	247.87
0.6	215.45	231.78	243.43	249.69
0.7	217.29	233.89	245.22	251.45
0.8	219.43	236.29	247.15	253.99

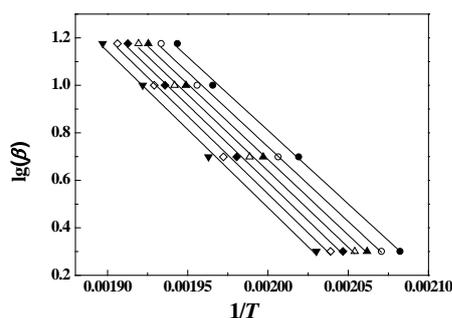


Figure 4. FWO plots of dehydration process for potassium citrate monohydrate. ●: $\alpha=0.2$; ○: $\alpha=0.3$; ▲: $\alpha=0.4$; △: $\alpha=0.5$; ◆: $\alpha=0.6$; ◇: $\alpha=0.7$; ▼: $\alpha=0.8$.

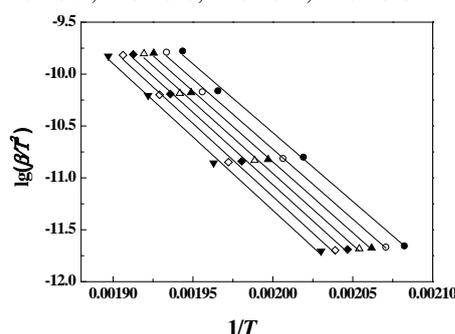


Figure 5. KAS plots of dehydration process for potassium citrate monohydrate. ●: $\alpha=0.2$; ○: $\alpha=0.3$; ▲: $\alpha=0.4$; △: $\alpha=0.5$; ◆: $\alpha=0.6$; ◇: $\alpha=0.7$; ▼: $\alpha=0.8$.

5. Conclusion

Dehydration Kinetics of Potassium Citrate Monohydrate was investigated by non-isothermal method based on the TG data. It is found that potassium citrate monohydrate exhibits one dehydration step:



Based on the data of TG at heating rate of 2 K/min, the most probable kinetic function was obtained using Malek method, the result shows that the kinetic function No.18, Reaction order ($n=2$), is the most probable kinetic function for dehydration process of potassium citrate monohydrate and the kinetic function is $f(\alpha)=(1-\alpha)^2$ and $G(\alpha)=(1-\alpha)^{-1}-1$. The calculated values of E and A using FWO and KAS methods are 116.73 kJ/mol, $8.2 \times 10^6 \text{ s}^{-1}$ and 114.21 kJ/mol, $2.1 \times 10^6 \text{ s}^{-1}$.

On the basis of E , A and the most probable kinetic function, the thermodynamic function (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) was calculated. The values of ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger are 112.5 J/K.mol, -125.3 kJ/mol, 176.1 kJ/mol (from FWO), and 110.0 J/K.mol, -136.6 kJ/mol, 179.3 kJ/mol (from KAS), respectively. The results show that the dehydration process of potassium citrate monohydrate is an endothermic and non-spontaneous process.

Table 2. The E and R^2 caculated by the methods of FWO and KAS for the dehydration process of potassium citrate monohydrate

α	FWO				
	Slope	$E/(kJ/mol)$	Intercept	A/S^{-1}	R^2
0.2	-6187.96	112.65	13.18	9.9×10^5	0.9971
0.3	-6286.08	114.43	13.31	1.9×10^6	0.9979
0.4	-6357.98	115.74	13.40	3.2×10^6	0.9985
0.5	-6430.36	117.06	13.50	5.2×10^6	0.9974
0.6	-6488.14	118.11	13.57	8.3×10^6	0.9970
0.7	-6554.46	119.32	13.65	1.4×10^7	0.9957
0.8	-6580.29	119.79	13.65	2.4×10^7	0.9956
AV.		116.73		8.2×10^6	
α	KAS				
	Slope	$E/(kJ/mol)$	Intercept	A/S^{-1}	R^2
0.2	-13254.71	110.20	15.94	1.6×10^5	0.9967
0.3	-13475.40	112.03	16.23	3.5×10^5	0.9976
0.4	-13636.83	113.37	16.44	6.6×10^5	0.9983
0.5	-13800.08	114.73	16.64	1.2×10^6	0.9970
0.6	-13929.67	115.81	16.79	2.1×10^6	0.9966
0.7	-14078.85	117.05	16.98	3.9×10^6	0.9952
0.8	-14133.78	117,50	16.95	6.5×10^6	0.9951
AV.		114.21		2.1×10^6	

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