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## Preparation of Peracetic Acid from Acetic Acid and Hydrogen Peroxide: Experimentation and Modeling

ZHAO Xue-bing(赵雪冰)<sup>1</sup>, ZHANG Ting(张婷)<sup>1</sup>, ZHOU Yu-jie(周玉杰)<sup>2</sup>, LIU De-hua(刘德华)<sup>1</sup>

(1. Institute of Applied Chemistry, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China;

2. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China)

**Abstract:** Based on the kinetic equations and equilibrium constants, some mathematic models were developed for calculating peracetic acid (PAA) concentration, equilibrium conversion rate of hydrogen peroxide, etc. The effects of several parameters on PAA synthesis were investigated by experimentation and modeling. The equilibrium constants determined from the forward and reverse rate constants at 293, 303, 313 and 323 K were 2.91, 2.81, 2.72 and 2.63, respectively. The models could predict the values of equilibrium concentration of PAA with average relative deviation of less than 10%. Both of the experimental and model-calculated results demonstrated that temperature and catalyst loading were the most important factors affecting the rate of PAA synthesis, but high temperature led to the decrease of equilibrium concentration of PAA. According to the model, the reaction could achieve equilibrium within 24 h when operated at 303 K with 1%~1.5%( $\omega$ ) sulfuric acid as catalyst. Additionally, when using anhydrous acetic acid and 30% hydrogen peroxide to prepare PAA, the volumetric ratio of the two solutions should be in the range of 1.2~1.5 in order to obtain the highest equilibrium concentration of PAA. This study can serve as a step towards the further optimization of PAA synthesis and some other related investigations.

**Key words:** peracetic acid; hydrogen peroxide; equilibrium constant; modeling

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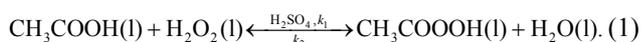
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### 1 INTRODUCTION

Peracetic acid (PAA) is a strong disinfectant with a wide spectrum of antimicrobial activity. It has been widely used in medical and hygiene fields, and disinfection of wastewater<sup>[1]</sup>. Recently, PAA emerges as alternative to conventional chlorine containing chemicals in an effort to develop a more environmentally friendly bleaching process in pulping and paper-making industry<sup>[2]</sup>. It is also an excellent active reagent for epoxidation of unsaturated triglycerides for obtaining low cost plasticizers with good performance from natural and renewable sources<sup>[3]</sup>. PAA pretreatment has been proved to enhance enzymatic digestibility of hybrid polar and sugarcane bagasse without the need of high temperature<sup>[4-6]</sup>.

In conventional preparation of PAA, namely by reaction of acetic acid (AA) and hydrogen peroxide (HP), homogeneous acidic catalysts (e.g. sulfuric acid, SA) are usually used to facilitate the reaction to achieve equilibrium:



This reaction is reversible, which proceeds to an

equilibrium between reactants and products. A few studies show that the concentration of PAA at equilibrium varied with the concentration of HP used and the molar ratio of AA to HP. The loading of sulfuric acid also differed from 1% to 9%( $\omega$ )<sup>[7-10]</sup>.

The concentration equilibrium constant ( $K_C$ ) for this reversible reaction is expressed as:

$$K_C = (C_{\text{PAA}} C_{\text{H}_2\text{O}})_e / (C_{\text{AA}} C_{\text{HP}})_e, \quad (2)$$

where the subscript e denotes the reaction equilibrium. According to Rangarajan et al.<sup>[11]</sup>, the values obtained for  $K_C$  ranged between 0.7 and 5, and depended on the HP concentration, reactants ratio and mineral acid concentration. Musante et al.<sup>[3]</sup> reported the values for chemical equilibrium constant ( $K$ ), determined experimentally by a kinetic study of acid resin-catalyzed liquid-phase reaction at 323, 333 and 343 K, of 1.911, 2.18 and 2.778, respectively. Dul'neva et al.<sup>[10]</sup> estimated that the equilibrium constant at 293, 313 and 333 K was 2.10, 1.46 and 1.07, respectively. It seems that the values of equilibrium constant determined by different researchers scatter obviously. However, all of these constants can not well predict our experimental data. Furthermore, those studies did not suggest any

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**Biography:** ZHAO Xue-bing(1981-), male, native of Lincang City, Yunnan Province, Ph.D. candidate, major in chemical engineering and technology; LIU De-hua, corresponding author, Tel: 010-62794742, E-mail: dhliu@tsinghua.edu.cn.

mathematic model for computation of  $K_C$  or  $K$ . Janković et al.<sup>[12]</sup> developed an expression of  $K$  for PAA synthesis from AA and HP in an aqueous solution, based on the Van't Hoff and Kirchhoff equation, as follows:

$$K = \exp(12.2324 \ln T - 0.0229913T + 9.704 \times 10^{-6} T^2 + 3045.76/T - 72.8758). \quad (3)$$

Nevertheless, this expression does not well reflect the thermodynamic relationship between  $K$  and  $T$ . Furthermore, so far as we know, no published paper has reported the mathematical models for calculating PAA concentration during the preparation. The objective of this article is to develop some mathematic models for calculating PAA concentration and further investigate the effects of several factors on PAA concentration from experimental results and mathematical modeling, which can serve as a step for further optimization of PAA synthesis and some other related studies.

## 2 EXPERIMENTAL

### 2.1 Materials and Experimentation

All the chemicals used in the experiments, including anhydrous acetic acid, 30% hydrogen peroxide, potassium permanganate, potassium iodide, sodium thiosulfate, sulfuric acid, etc., were analytically pure and purchased locally. Higher concentration of HP was obtained by vacuum distillation of 30% HP. The metallic ions in the reaction system were less than  $0.5 \times 10^{-6}$  g/L. Deioned water was used in the experiments.

Before the reaction, certain volumes of AA and 98% sulfuric acid were put in the 100 mL clean ground-glass stoppered flasks. Then certain volumes of HP solution were added and mixed homogeneously. The system was kept at a constant temperature in a water bath. Samples were taken and quickly analyzed in a certain reaction time.

### 2.2 Analytical Method

The concentrations of PAA and HP were determined in accordance with the Chinese Standard GB/T 19108-2003. The principle is that HP is first titrated with potassium permanganate and then PAA determined iodometrically. Each of the experimental data was the average result of at least duplicate tests.

The average relative deviation ( $A_{RD}$ ) between model-calculated datum and experimental datum was defined by the following expression:

$$A_{RD} = (C_{cal} - \bar{C}_{exp}) / \bar{C}_{exp} \times 100\%, \quad (4)$$

where  $C_{cal}$  and  $\bar{C}_{exp}$  denote the calculated and experimental values of PAA concentration, respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 Mathematical Models for Calculation of PAA Concentration

Based on reaction (1), the observed differential equation for concentration of PAA versus time  $t$  can be expressed as

$$\frac{dC_C}{dt} = k_{1obs} C_A C_B - k_{2obs} C_C C_D, \quad (5)$$

where  $k_{1obs}$  and  $k_{2obs}$  are observed forward and reverse reaction constants respectively, and  $C$  is the concentration of reactants or products in mol/L. The subscripts A, B, C, and D at the right side of the expression denote AA, HP, PAA and water, respectively. It is assumed that the spontaneous decomposition of PAA at a low temperature can be negligible. Based on the mass balance, Eq.(5) can be expressed as

$$\frac{dC_C}{dt} = \lambda C_C^2 - \mu C_C + \varphi, \quad (6)$$

where  $\lambda = k_{1obs} - k_{2obs}$ ,  $\mu = k_{1obs}(C_{A0} + C_{B0}) + k_{2obs} C_{D0}$ ,  $\varphi = k_{1obs} C_{A0} C_{B0}$ . These parameters are not functions of  $C_C$ , with their relation of  $\mu^2 - 4\lambda\varphi \geq 0$ . Thus the analytic solution of Eq.(6) is obtained as

$$\ln \frac{C_C - 0.5\mu/\lambda + a}{C_C - 0.5\mu/\lambda - a} = -2\lambda at + \text{Const}, \quad (7)$$

where  $a = \sqrt{\mu^2 / (4\lambda^2) - \varphi / \lambda}$  and Const are the integral constants. When  $t=0$  and  $C_C=0$ , thus Const can be determined by the following expression:

$$\text{Const} = \ln \frac{-0.5\mu/\lambda + a}{-0.5\mu/\lambda - a}. \quad (8)$$

Therefore, the concentration of PAA at time  $t$  can be calculated as:

$$C_C = \frac{ab + a}{b - 1} + \frac{\mu}{2\lambda}, \quad (9)$$

where  $b = \exp\{-2\lambda at + \ln[(-0.5\mu/\lambda + a)/(-0.5\mu/\lambda - a)]\}$ . As  $t \rightarrow +\infty$  and  $C_C \rightarrow C_{Ce}$ , the equilibrium concentration of PAA ( $C_{Ce}$ ) can be estimated by the following expression:

$$C_{Ce} = \lim_{t \rightarrow +\infty} \left( \frac{ab + a}{b - 1} + \frac{\mu}{2\lambda} \right) = -a + \frac{\mu}{2\lambda}. \quad (10)$$

To be more intuitive, this equation can be written as the following expression based on  $K_C$ :

$$C_{Cc} = \frac{K_C C_{A0} + K_C C_{B0} + C_{D0}}{2(K_C - 1)} - \frac{\sqrt{(K_C C_{A0} + K_C C_{B0} + C_{D0})^2 - 4K_C C_{A0} C_{B0} (K_C - 1)}}{2(K_C - 1)}. \quad (11)$$

Corresponding equilibrium conversion ratio of HP ( $X_e$ ) is

$$X_e = \frac{K_C C_{A0} + K_C C_{B0} + C_{D0}}{2C_{B0} (K_C - 1)} - \frac{\sqrt{(K_C C_{A0} + K_C C_{B0} + C_{D0})^2 - 4K_C C_{A0} C_{B0} (K_C - 1)}}{2C_{B0} (K_C - 1)}. \quad (12)$$

At the equilibrium, the concentrations of reactants and products can be related by the following equation:

$$\frac{C_{Cc} C_{Dc}}{C_{Ac} C_{Bc}} = \frac{k_{1obs}}{k_{2obs}} = K_C. \quad (13)$$

Thus, the expressions for  $k_{1obs}$  and  $k_{2obs}$  are obtained as follows<sup>[13]</sup>:

$$k_{1obs} = 6.83 \times 10^8 [H^+] \exp\left(-\frac{57846.15}{RT}\right), \quad (14)$$

$$k_{2obs} = 6.73 \times 10^8 [H^+] \exp\left(-\frac{60407.78}{RT}\right). \quad (15)$$

An expression for temperature dependence (in degree of Kelvin) of  $K_C$  for PAA synthesis thus is obtained as:

$$K_C = 1.015 \exp\left(\frac{2561.63}{RT}\right). \quad (16)$$

This equation is much simpler than Eq.(3). Furthermore, it contains obvious thermodynamic significance for estimation of the standard molar formation Gibbs energy of PAA. Generally, chemical equilibrium constant ( $K$ ) can be calculated from standard Gibbs energy change of molar reaction,  $\Delta_r G_m^0$ , by the following equation:

$$K = \exp\left(-\frac{\Delta_r G_m^0}{RT}\right). \quad (17)$$

On the other hand,  $K$  can also be calculated by the following expression:

$$K = \frac{a_{PAA} a_{H_2O}}{a_{AA} a_{HP}} = \frac{\gamma_{PAA} \gamma_{H_2O}}{\gamma_{AA} \gamma_{HP}} K_C. \quad (18)$$

Approximately,  $(\gamma_{PAA} \gamma_{H_2O})/(\gamma_{AA} \gamma_{HP}) \approx 1$ , so the following equation can be obtained:

$$K \approx K_C \approx \exp\left(\frac{2561.63}{RT}\right). \quad (19)$$

Thus the  $\Delta_r G_m^0$  estimated by Eqs.(17) and (18) for the

forward reaction is  $-2.56$  kJ/mol approximately. Furthermore,  $\Delta_r G_m^0$  can be calculated from

$$\Delta_r G_m^0 = \sum \Delta_f G_m^0, \quad (20)$$

where  $\Delta_f G_m^0$  is the standard molar formation Gibbs energy of reactants or products. The  $\Delta_f G_m^0$  values of  $CH_3COOH(l)$ ,  $H_2O_2(l)$  and  $H_2O(l)$  can be obtained from a reference handbook<sup>[14]</sup> as  $-390.2$ ,  $-120.42$  and  $-237.14$  kJ/mol, respectively. Therefore, the  $\Delta_f G_m^0$  of PAA(l) estimated by Eq.(17) is about  $-276$  kJ/mol. Since  $\Delta_f G_m^0$  for PAA is not available in the handbook, this value can be used in some approximate calculations.

It can also be known from Eq.(16) that  $K_C$  is the single parameter function of temperature.  $H^+$  has no effect on  $K_C$ . This conclusion is in accordance with the conventional characteristic of catalyst, that is, the catalyst can not change the chemical equilibrium. However, according to Sawaki et al.<sup>[15]</sup>, the equilibrium constant increased with loading of sulfuric acid. Their explanation for this phenomenon was the elimination of free water from the reaction system by protonation. However, such explanation could be acceptable only on the condition that water was regarded as a strong base. A more acceptable explanation to the phenomenon can be summarized in two aspects: firstly, increasing SA loading can reduce the spontaneous decomposition rate of PAA<sup>[2,16]</sup>; secondly, SA can also react with HP, forming peroxymonosulfuric acid, which makes the observed total concentration of PAA increase when the peracid is measured as PAA in the experiment. Therefore, SA played the role of a catalyst, and a reactant as well, when its loading was excessive.

### 3.2 Effect of Temperature on PAA Concentration

Temperature affects the forward and reverse reaction constants, which further impacts the synthesis rate of PAA, equilibrium concentration of PAA and the time when the reaction achieves equilibrium. The experimental and calculated time profiles of PAA concentration are shown in Fig.1. It can be seen that the model [Eq.(9)] can well predict the PAA concentration at different temperatures. Both the experimental and calculated results show that increasing temperature accelerated the synthesis of PAA. However, it is known from Eq.(16) that increasing temperature leads to the decrease of  $K_C$ , resulting in the decrease of PAA concentration at equilibrium state. The calculated values of  $K_C$  at 293, 303, 313 and 323 K are 2.91, 2.81, 2.72 and 2.63, respectively. Therefore, for higher equilibrium PAA concentration, the reaction should be operated at

relatively low temperature, for example, at room temperature, but it takes longer reaction time.

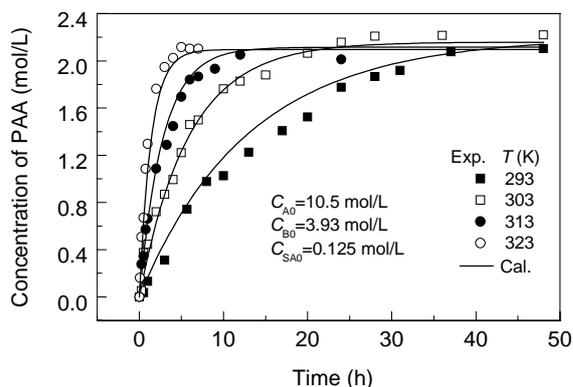


Fig.1 Experimental and calculated time profiles of PAA concentrations at different temperatures

Table 1 shows the comparison of experimental and calculated values of equilibrium PAA concentration at 293 and 313 K. The calculated data based on the equilibrium constants from Janković et al.<sup>[12]</sup> and this work could well fit the experimental data. The  $A_{RD}$  values were less than 10% in this work. Furthermore, it is obvious that the expression for computation of equilibrium constant in this work is much easier than that by Janković's.

**Table 1 Comparison of experimentally determined and calculated values of PAA concentration at equilibrium state using different values of equilibrium constant**

Parameter	Experimental data <sup>1)</sup>		Calculated data					
	293 K	313 K	Ref.[3]		Ref.[12]		This work	
	293 K	313 K	293 K	313 K	293 K	313 K	293 K	313 K
$K$			0.97	1.53	3.0	2.46	2.91	2.72
$C_{PAA}$ (mol/L)	2.39±0.01	2.28±0.01	1.27	1.72	2.19	2.02	2.17	2.11
$A_{RD}$ (%)	—	—	-46.9	-32.6	-8.37	-11.4	-9.21	-7.46

Note: 1) The initial concentrations of reagents were  $C_{A0}$ =10.5 mol/L,  $C_{B0}$ =3.93 mol/L, and  $C_{D0}$ =17.52 mol/L.

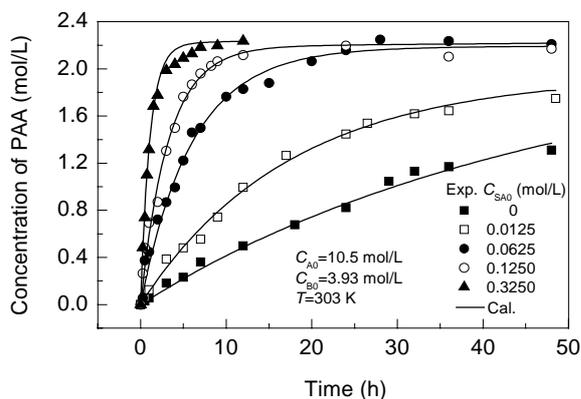


Fig.2 Experimental and calculated time profiles of PAA concentration with different loadings of sulfuric acid as catalyst<sup>[13]</sup>

Table 2 shows the values of  $t_e$  (h) estimated by Eq.(21) when the initial concentration of sulfuric acid

### 3.3 Effect of Sulfuric Acid on PAA Concentration

The synthesis of PAA from AA and HP is an acid-catalyzed process, because the reaction follows a protonation-promoted pathway<sup>[13]</sup>. The experimental and model-based calculation results indicate that the reaction was obviously facilitated to achieve equilibrium by addition of SA, as shown in Fig.2. However, as chemical equilibrium is a dynamic process, theoretically, infinitely long time is needed for the reaction achieving equilibrium. In practical preparation of PAA, we can not, even need not, wait until the reaction achieves the theoretical equilibrium. Supposing that the actual concentration of PAA at time  $t_e$  was 99.5% of that under theoretical equilibrium state, we could consider that the reaction at time  $t_e$  had achieved equilibrium, and  $t_e$  was the time for the reaction achieving equilibrium (under the condition that the initial time for the reaction was  $t=0$ ). Based on Eqs.(9) and (10), thus  $t_e$  can be estimated as:

$$t_e = -\frac{1}{2\lambda a} \left( \ln \frac{0.005a - 0.0025\mu/\lambda}{-0.0025\mu/\lambda - 1.995a} - \ln \frac{-0.5\mu/\lambda + a}{-0.5\mu/\lambda - a} \right). \quad (21)$$

In the system,  $H^+$  mainly comes from two parts, dissociation of sulfuric acid and AA. The concentration of  $H^+$  was calculated based on our previous work<sup>[13]</sup>.

( $C_{SA0}$ ) and reaction temperature were different. It is clear that  $t_e$  was reduced obviously by addition of SA or increase of reaction temperature. When  $C_{SA0}$  was increased by one-fold at a certain temperature, corresponding time for the reaction achieving equilibrium was reduced by a half. 0.125 mol/L (about 1.1%,  $\omega$ ) sulfuric acid was enough for the reaction

**Table 2 The values of  $t_e$  estimated by Eq.(21) with different  $C_{SA0}$  at various temperatures (h)**

$C_{SA0}$ (mol/L)	$T$ (K)			
	293	303	313	323
0.0000	4978.6	2237.3	1057.7	523.8
0.0125	358.5	161.1	76.2	37.7
0.0625	71.7	32.2	15.2	7.5
0.1250	35.8	16.1	7.6	3.8
0.3125	14.3	6.4	3.0	1.5

Note: The initial concentrations of reactants were  $C_{A0}$ =10.5 mol/L,  $C_{B0}$ =3.93 mol/L,  $C_{C0}$ =0 mol/L, and  $C_{D0}$ =17.3 mol/L.

achieving equilibrium within 24 h. These conclusions were in accordance with the present experimental results (see Figs.1 and 2).

### 3.4 Effect of HP Strength on PAA Concentration at Equilibrium

It is evident that any reduction in the final water content of the system will increase the equilibrium concentration of PAA, and thus the use of high strength HP is advantageous. Fig.3 gives the comparison of the experimental and calculated values of  $C_{Ce}$  when the strength of  $H_2O_2$  was varied in the range of 0.2~1.2 g/mL.  $A_{RD}$  value was less than 9% in this work.  $A_{RD}$  of less than 6% was obtained when the strength of HP was lower than 0.8 g/mL. Both of the experimental and calculated data show that increasing the HP strength enhanced the equilibrium concentration of PAA, due to the reduction of water concentration in the system. The data calculated by Eqs.(10) or (11) were also compared with the experimental values of equilibrium concentration of PAA from some references, as shown in Table 3. It is found that our model can well predict the values of PAA concentration. Therefore, it is convenient to estimate the equilibrium concentration of PAA by the model and adjust it by easily changing the HP strength in the practical preparation of PAA. On the other hand, the comparison indicates that the equilibrium constant determined in this work was sufficiently accurate for estimation of equilibrium concentration of PAA, which further proved the sufficient accuracy of rate constants for the forward and reverse reactions in our previous work.

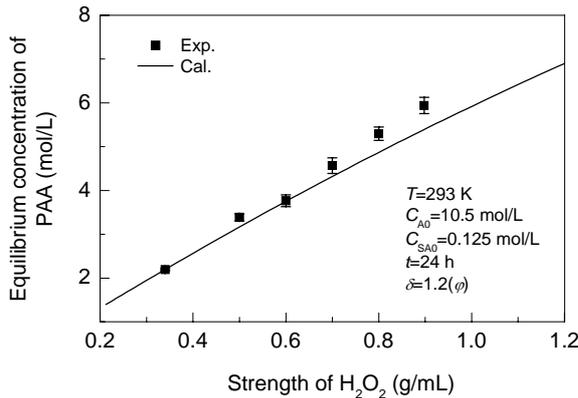


Fig.3 Estimation of equilibrium concentration of PAA prepared from different strengths of HP

### 3.5 Effect of Volumetric Ratio of AA solution to HP solution on PAA Concentration

It is known from Eq.(1) that the equilibrium conversion ratio of HP will increase with the initial amount of AA used. However, the volume of the system

**Table 3 Comparison of equilibrium PAA concentrations calculated by the present model with corresponding experimental values from some references**

Strength of HP used (% , $\omega$ )	Molar ratio of AA to HP	$C_{PAA,Exp.}$ (mol/L)	$C_{PAA,Cal.}$ (mol/L)	$A_{RD}$ (%)
27	4.05	1.82 <sup>1)</sup>	1.83	0.51
27	1.35	1.63 <sup>1)</sup>	1.76	7.99
50	1.01	1.63 <sup>2)</sup>	1.59	2.38
50	2.00	3.27 <sup>2)</sup>	3.56	8.66
50	4.00	2.64 <sup>2)</sup>	2.71	2.49
50	6.66	1.95 <sup>2)</sup>	1.95	0.11
50	10.00	1.42 <sup>2)</sup>	1.43	1.16
64.8	1.25	5.13 <sup>3)</sup>	4.81	-6.24
90	1.50	6.52 <sup>2)</sup>	6.27	-3.91

Note: The average density of liquid mixture was calculated by the following expression:  $\rho_m = [\sum_i (x_i/\rho_i)]^{-1}$ , where  $x_i$  and  $\rho_i$  are the mass fraction and density of species  $i$ , respectively.

1) Ref.[17]; 2) Ref.[8]; 3) This work at 303 K.

will also increase, which will change the equilibrium concentration of PAA. Therefore, the highest equilibrium concentration of PAA will be obtained under the optimum volumetric ratio of AA solution to HP solution ( $\delta$ ). On the other hand, it is more convenient to prepare PAA by directly mixing certain volumes of AA and HP solutions. Thus a mathematical model expressed with  $\delta$  will be more useful for practical preparation of PAA. Using  $V_A$ ,  $\rho_A$  and  $m_A$  to denote the volume (mL), density (g/mL) and concentration ( $\omega$ ) of AA solution at room temperature, and  $V_B$ ,  $\rho_B$  and  $m_B$  to denote the volume (mL), density (g/mL) and concentration ( $\omega$ ) of HP solution at room temperature, respectively, the initial concentrations (mol/L) of reactants in the reaction system can be expressed as the following formulae:

$$C_{A0} = \frac{1000V_A\rho_A m_A}{60(V_A + V_B)} = \frac{16.67\delta\rho_A m_A}{1 + \delta}, \quad (22)$$

$$C_{B0} = \frac{29.39\rho_B m_B}{1 + \delta}, \quad (23)$$

$$C_{D0} = \frac{55.56\delta\rho_A(1 - m_A) + 55.56\rho_B(1 - m_B)}{1 + \delta}. \quad (24)$$

Thus, Eq.(11) can be expressed as

$$C_{Ce} = \frac{P - Q}{2(K_C - 1)}, \quad (25)$$

where

$$P = (16.67\delta K_C \rho_A m_A + 29.39 K_C \rho_B m_B) / (1 + \delta) + [55.56\delta\rho_A(1 - m_A) + 55.56\rho_B(1 - m_B)] / (1 + \delta), \quad (26)$$

$$Q = \sqrt{P^2 - 1959.7 K_C (K_C - 1) \delta \rho_A \rho_B m_A m_B} / (1 + \delta)^2. \quad (27)$$

The solution of the following equation will be the

optimum value of  $\delta$ , and corresponding  $C_{Ce}$  will be the highest.

$$\frac{dC_{Ce}}{d\delta} = \frac{1}{2(K_C - 1)} \left( \frac{dP}{d\delta} - \frac{dQ}{d\delta} \right) = 0. \quad (28)$$

In practical applications of PAA, such as bleaching and disinfection processes, the concentration of PAA is often less than 2 mol/L, which can be prepared from anhydrous AA and 30%( $\omega$ ) HP. In this work, the density of anhydrous AA and 30%( $\omega$ ) HP at 298 K were 1.05 and 1.114 g/mL, respectively. Therefore, according to Eq.(28), when anhydrous AA and 30%( $\omega$ ) HP were used to prepare PAA, the calculated optimum value of  $\delta$  was obtained as 1.20, compared with the experimentally determined value of 1.50. The calculated and experimental values of  $C_{Ce}$  and  $X_e$  at several  $\delta$  values are shown in Fig.4. When  $\delta$  was 1.2~1.5, the values of  $C_{Ce}$  calculated by the model were 2.204~2.175 (mol/L), compared with the experimental data of (2.21±0.045) mol/L at  $\delta=1.5$ . The result indicates that the model had sufficient accuracy for estimation of PAA concentration. At the optimum  $\delta$  (1.5), the experimental and calculated  $X_e$  values were 55.3% and 54.4%, respectively. Further increasing  $\delta$  could enhance  $X_e$ , but the  $C_{Ce}$  was conversely decreased because of solution dilution by the additional acetic acid.

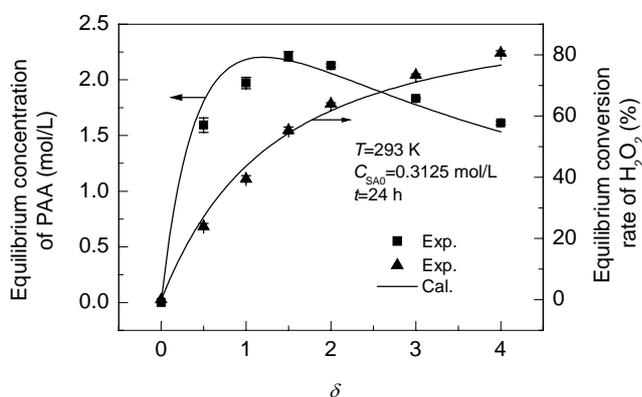


Fig.4 Comparison of experimentally determined values and calculated values of equilibrium concentration of PAA at several  $\delta$  values

## 4 CONCLUSIONS

The equilibrium constants determined from the forward and reverse rate constants of reaction for synthesis of PAA in this work at 293, 303, 313 and 323 K were 2.91, 2.81, 2.72, and 2.63, respectively. The standard molar formation Gibbs energy of PAA estimated from equilibrium constant was -276 kJ/mol approximately. Several models for calculation of equilibrium concentration of PAA based on equilibrium

constant were developed. The models could predict the values of PAA concentration with less than 10% of  $A_{RD}$ . They would make contributions to the prediction of equilibrium concentration of PAA in its practical preparation.

Both of the experimental and calculated results demonstrated that temperature and catalyst loading were the most important factors affecting the rate of PAA synthesis. However, higher temperature led to the decrease of equilibrium concentration of PAA. According to the present model, the reaction can achieve equilibrium within 24 h when operated at 303 K with 1%~1.5%( $\omega$ ) sulfuric acid as catalyst. Additionally, when anhydrous AA and 30%( $\omega$ ) HP were used to prepare PAA, the volumetric ratio of the two solutions at room temperature should be in the range of 1.2~1.5, in order to obtain the highest concentration of PAA. This study can serve as a step towards the further optimization of PAA synthesis and some other related investigations.

## NOMENCLATURE:

$a$	Activity
$A_{RD}$	Average relative deviation (%)
A, B, C, D	Names of components
$C_X$	Concentration of species X (mol/L)
$C_{X0}$	Initial concentration of species X (mol/L)
$C_{Xe}$	Equilibrium concentration of species X (mol/L)
$k_{1obs}$	Observed rate constant of peracetic acid synthesis [L/(mol-h)]
$k_{2obs}$	Observed rate constant of peracetic acid hydrolysis [L/(mol-h)]
$K$	Thermodynamic equilibrium constant
$K_C$	Concentration equilibrium constant
$R$	Universal gas constant [J/(mol-K)]
$t_e$	The needed time for which the reaction reaches equilibrium (h)
$T$	Temperature (K)
$X_e$	Equilibrium conversion ratio of hydrogen peroxide (%)
$\Delta_f G_m^0$	Standard molar formation Gibbs energy (kJ/mol)
$\Delta_r G_m^0$	Standard Gibbs energy change of molar reaction (kJ/mol)
$\delta$	Volumetric ratio of acetic acid to hydrogen peroxide solution
$\gamma$	Activity coefficient

## Subscript:

0	Initial state
e	Equilibrium state

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