Supporting Information

Applying Modified Chemical Equilibrium Constants for Improving Equilibrium Species Distribution and Vapor−Liquid Equilibrium (VLE) Prediction of Formaldehyde Aqueous Solutions

Guizhen Li,[†] *Yansheng Liu,*[†,*] *Yufeng Hu,*[†,*] *Jun Wang,*[‡] *Lehuan Wu,*[†] and *Chunfeng Shi*[§]

[†]College of Chemical Engineering, China University of Petroleum-Beijing, Beijing, 102249, China

[‡]School of Petrochemical Engineering, Changzhou University, Changzhou, 213164, China

[§] Central Research Institute, Wanhua Chemical Group Co., Ltd., Yantai, 264006, China

Table S1. Parameter *B* of K_2 for the Formation of MG_2

338.15 K					383.15 K				
$\tilde{x}_{FA}$ (mol/mol)	K_2	lnK_2	A	B	$\tilde{x}_{FA}$ (mol/mol)	K_2	lnK_2	A	B
0.0605	5.1582	1.6406	0.01449	549.86	0.0605	4.157	1.4248	0.01449	540.36
0.1295	5.4341	1.6927	0.01449	567.48	0.0605	4.059	1.4008	0.01449	531.18
0.2049	5.9652	1.7859	0.01449	599.02	0.1295	4.407	1.4831	0.01449	562.71
0.2779	5.7548	1.7500	0.01449	586.88	0.1295	4.255	1.4481	0.01449	549.27
0.3851	5.6364	1.7293	0.01449	579.85	0.2049	4.856	1.5802	0.01449	599.92
0.446	6.1196	1.8115	0.01449	607.66	0.2779	4.894	1.5880	0.01449	602.88
					0.3851	5.523	1.7089	0.01449	649.23
					0.446	5.423	1.6907	0.01449	642.24
353.15 K					368.15 K				
$\tilde{x}_{FA}$ (mol/mol)	K_2	lnK_2	A	B	$\tilde{x}_{FA}$ (mol/mol)	K_2	lnK_2	A	B
0.0605	4.5752	1.5206	0.01449	531.90	0.0605	4.413	1.4845	0.01449	541.19
0.1295	4.7122	1.5501	0.01449	542.32	0.1295	4.638	1.5344	0.01449	559.55
0.1888	5.3323	1.6738	0.01449	585.98	0.1888	4.652	1.5373	0.01449	560.60
0.2049	5.2930	1.6664	0.01449	583.37	0.2049	4.838	1.5765	0.01449	575.06
0.2132	5.3449	1.6761	0.01449	586.81	0.2131	4.637	1.5341	0.01449	559.44
0.2779	5.3610	1.6791	0.01449	587.87	0.2779	5.118	1.6329	0.01449	595.80
0.291	5.6211	1.7265	0.01449	604.61	0.291	5.028	1.6150	0.01449	589.22
0.3475	5.3426	1.6757	0.01449	586.66	0.3475	5.196	1.6479	0.01449	601.35
0.3851	5.7308	1.7458	0.01449	611.43	0.3851	5.524	1.7091	0.01449	623.89
0.446	5.9067	1.7761	0.01449	622.11	0.446	5.612	1.7248	0.01449	629.67

Table S2. Parameter *B* of K_3 for the Formation of MG_3

338.15 K					383.15 K				
$\tilde{x}_{FA}$ (mol/mol)	K_3	lnK_3	A	B	$\tilde{x}_{FA}$ (mol/mol)	K_3	lnK_3	A	B
0.0605	3.5667	1.2716	-0.1084	466.66	0.0605	4.7004	1.5476	-0.1084	634.51
0.1295	3.5638	1.2708	-0.1084	466.39	0.0605	3.2875	1.1901	-0.1084	497.53
0.2049	4.0860	1.4076	-0.1084	512.63	0.1295	3.1919	1.1606	-0.1084	486.23
0.2779	3.8503	1.3481	-0.1084	492.53	0.1295	2.6174	0.9622	-0.1084	410.19
0.3851	3.8485	1.3477	-0.1084	492.38	0.2049	3.6553	1.2962	-0.1084	538.16
0.446	4.0584	1.4008	-0.1084	510.33	0.2779	3.4913	1.2503	-0.1084	520.57
					0.3851	3.6619	1.2980	-0.1084	538.85
					0.446	3.7768	1.3289	-0.1084	550.69

353.15 K					368.15 K				
$\tilde{x}_{FA}$ (mol/mol)	K_3	lnK_3	A	B	$\tilde{x}_{FA}$ (mol/mol)	K_3	lnK_3	A	B
0.0605	3.3936	1.2219	-0.1084	469.80	0.0605	2.5186	0.9237	-0.1084	379.97
0.1295	3.1980	1.1625	-0.1084	448.83	0.1295	3.3011	1.1943	-0.1084	479.57
0.1888	3.4641	1.2425	-0.1084	477.06	0.1888	3.3935	1.2219	-0.1084	489.73
0.2049	3.8269	1.3421	-0.1084	512.23	0.2049	3.4006	1.2239	-0.1084	490.50
0.2132	3.7749	1.3284	-0.1084	507.40	0.2132	3.5471	1.2661	-0.1084	506.03
0.2779	3.8353	1.3443	-0.1084	513.01	0.2779	3.7646	1.3256	-0.1084	527.95

0.291	3.8662	1.3523	-0.1084	515.84	0.291	3.7060	1.3100	-0.1084	522.17
0.3475	3.7228	1.3145	-0.1084	502.49	0.3475	3.7736	1.3280	-0.1084	528.82
0.3851	3.8819	1.3563	-0.1084	517.27	0.3851	3.7905	1.3325	-0.1084	530.47
0.446	3.9609	1.3765	-0.1084	524.38	0.446	3.8473	1.3474	-0.1084	535.95

Table S3. Vapor Pressure (kPa) of Pure Components ($\ln P^S = A + B/(T + C)$, the Unit of T is K)

Components	A	B	C	ref for P_i^S
Formaldehyde	14.4625	-2204.13	-30.15	Reid et al.[S1]
Water	16.2886	-3816.44	-46.13	Reid et al.[S1]
Methylene glycol	19.5527	-6189.19	-9.15	Albert et al.[S2]

Table S4. Division of Components in UNIFAC Groups

Group number	1	2	3	4	5
Component/Group	H_2O	$HOCH_2OH$	CH_2O	CH_2	OH
Water	1				
Formaldehyde			1		
Methylene glycol		1			
Poly(oxymethylene) glycols			*i*-1	1	2

Table S5. The Size and Surface Parameters of the UNIFAC Groups

Group	H_2O	$HOCH_2OH$	CH_2O	CH_2	OH
R	0.9200	2.6744	0.9183	0.6744	1.0000
Q	1.400	2.940	0.780	0.540	1.200

Calculation of species distribution in chemical equilibrium of formaldehyde aqueous solutions

Basic assumptions of the species distribution model in chemical equilibrium of formaldehyde aqueous solutions:

1) The reactions in the formaldehyde aqueous solutions are shown as reactions S1 and S2.

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH \tag{S1}$$

$$HOCH_2OH + HO\left(CH_2O\right)_{i-1}H \rightleftharpoons HO\left(CH_2O\right)_i H + H_2O, i \geq 2 \tag{S2}$$

2) The liquid phase is a mixture of water (W), (very little molecular) formaldehyde (FA), methylene glycol (MG), and a large variety of poly(oxymethylene) glycols (MG_i, $i \geq 2$).

3) The chemical equilibrium constants are defined by

$$K_1^L = \frac{x_{MG}}{x_{FA} \cdot x_W} \tag{S3}$$

$$K_2 = \frac{x_{MG_2} \cdot x_W}{x_{MG} \cdot x_{MG}} \tag{S4}$$

$$K_i = \frac{x_{MG_i} \cdot x_W}{x_{MG_{i-1}} \cdot x_{MG}}, i \geq 3 \tag{S5}$$

And the constants have the relations

$$K_3 = K_4 = \cdots = K_n = K \tag{S6}$$

Based on the basic assumptions, the true composition of formaldehyde and MG_i ($i > 1$) is an expression of the true compositions of MG and water and chemical equilibrium constants.

$$x_{FA} = \frac{x_{MG}}{K_1 \cdot x_W} \tag{S7}$$

$$x_{MG_i} = \frac{K_2 \cdot K^{(i-2)} \cdot x_{MG}{}^{i}}{x_W{}^{(i-1)}} = \frac{K_2 \cdot x_{MG}}{K} \cdot m^{i-1}, i \geq 2 \tag{S8}$$

In the eq S8,

$$m = \frac{K \cdot x_{MG}}{x_W}.$$

Mass balance equations are

$$\tilde{x}_{FA} = \frac{x_{FA} + x_{MG} + \sum_{i=2}^{n} i \cdot x_{MG_i}}{1 + x_{MG} + \sum_{i=2}^{n} i \cdot x_{MG_i}} \tag{S9}$$

$$x_{FA} + x_W + x_{MG} + \sum_{i=2}^{n} x_{MG_i} = 1 \tag{S10}$$

Equation S8 is converted to

$$\sum_{i=2}^{n} x_{MG_i} = \frac{K_2 \cdot x_{MG}}{K} \sum_{i=2}^{n} m^{i-1} = \frac{K_2 \cdot x_{MG}}{K} \cdot \frac{m - m^n}{1 - m} \tag{S11}$$

$$\sum_{i=2}^{n} i \cdot x_{MG_i} = \frac{K_2 \cdot x_{MG}}{K} \sum_{i=2}^{n} i \cdot m^{i-1} = t \tag{S12}$$

Eq S12 + (-m)*(eq S12), eq S13 is obtained,

$$\frac{K_2 \cdot x_{MG}}{K} \left(m + \frac{m - m^n}{1 - m} - n \cdot m^n \right) = t(1 - m) \tag{S13}$$

Thus,

$$t = \sum_{i=2}^{n} i \cdot x_{MG_i} = \frac{K_2 \cdot x_{MG}}{K} \left[\frac{m}{1 - m} + \frac{m - m^n}{(1 - m)^2} - \frac{n \cdot m^n}{1 - m} \right] \tag{S14}$$

Combine eqs S7, S9-S11, and S14, and then obtain binary nonlinear functions of the true compositions of MG and W.

$$\tilde{x}_{FA} = \frac{\dfrac{m}{K_1 \cdot K} + x_{MG} + \dfrac{K_2 \cdot x_{MG}}{K}\left[\dfrac{m}{1-m} + \dfrac{m-m^n}{(1-m)^2} - \dfrac{n \cdot m^n}{1-m}\right]}{1 + x_{MG} + \dfrac{K_2 \cdot x_{MG}}{K}\left[\dfrac{m}{1-m} + \dfrac{m-m^n}{(1-m)^2} - \dfrac{n \cdot m^n}{1-m}\right]} \tag{S15}$$

$$1 = \frac{m}{K_1 \cdot K} + \frac{K \cdot x_{MG}}{m} + x_{MG} + \frac{K_2 \cdot x_{MG}}{K} \cdot \frac{m-m^n}{1-m} \tag{S16}$$

Because $m < 1$, $m^n \to 0$ when $n \to \infty$, eqs S15 and S16 are simplified to

$$\tilde{x}_{FA} = \frac{\dfrac{m}{K_1 \cdot K} + x_{MG} + \dfrac{K_2 \cdot x_{MG}}{K}\left[\dfrac{m}{1-m} + \dfrac{m}{(1-m)^2}\right]}{1 + x_{MG} + \dfrac{K_2 \cdot x_{MG}}{K}\left[\dfrac{m}{1-m} + \dfrac{m}{(1-m)^2}\right]} \tag{S17}$$

$$1 = \frac{m}{K_1 \cdot K} + \frac{K \cdot x_{MG}}{m} + x_{MG} + \frac{K_2 \cdot x_{MG}}{K} \cdot \frac{m}{1-m} \tag{S18}$$

By the substitution method, eqs S17 and S18 are converted to a quartic equation of m.

$$c_4 \cdot m^4 + c_3 \cdot m^3 + c_2 \cdot m^2 + c_1 \cdot m + c_0 = 0 \tag{S19}$$

In the eq S19,

$c_0 = -K \cdot \tilde{x}_{FA}$;

$c_1 = c + \tilde{x}_{FA} \cdot (2K - 1) + \dfrac{K}{a}$;

$c_2 = c \cdot (2b - 2 - 1/a) + \tilde{x}_{FA} \cdot (2 - K - b) + \left(\dfrac{1}{a} - \dfrac{2K}{a}\right)$;

$c_3 = c \cdot \left(1 - b - \dfrac{2b}{a} + \dfrac{2}{a}\right) + \tilde{x}_{FA} \cdot (b - 1) + \left(\dfrac{K}{a} + \dfrac{b}{a} - \dfrac{2}{a}\right)$;

$c_4 = c \cdot \left(\dfrac{b}{a} - \dfrac{1}{a}\right) + \left(\dfrac{1}{a} - \dfrac{b}{a}\right)$;

$a = K_1 \cdot K$;

$b = \dfrac{K_2}{K}$;

$c = 1 - \tilde{x}_{FA}$。

Due to the conversion above, the species distribution in chemical equilibrium of the formaldehyde + water system is easily calculated by the use of MATLAB, which greatly simplifies the calculation process and therefore avoid using the complex algorithm of MATLAB.

REFERENCES

(S1)Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd Edition; McGraw-Hill: New York, 1977.

(S2)Albert, M.; Coto Garcia, B.; Kreiter, C.; Maurer, G. Vapor liquid and chemical equilibria of formaldehyde water mixtures. *AIChE J.* **1999,** *45,* 2024–2033.