Hydroxymethylation of Phenol Revisited: A Readjusted Mathematical Model

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ABSTRACT: The hydroxymethylation of phenol in alkaline conditions is the first step in the synthesis of resols, which must be later cured for the production of final articles. A mathematical model for the hydroxymethylation of phenol is presented. It is based on the kinetic mechanism by Freeman and Lewis (*J. Am. Chem. Soc.* **1954**, *76*, 2080−2087) and includes a set of side reactions. Arrhenius expressions for the seven hydroxymethylation kinetic constants at pH 8−10 and temperatures 30−57 °C, and in the absence of methanol, were recalculated from the constants reported by Zavitsas et al. (*J. Polym. Sci., Part A-1: Polym. Chem.* **1968**, *6*, 2541−2559), in order to take into consideration the hydration/dehydration of formaldehyde and other side reactions. The model adequately predicts the measurements in the mentioned publications and in Higuchi et al. (*J. Wood Sci.* **1999**, *45*, 306−312). All of the kinetic parameters were directly or indirectly taken from the literature and were not readjusted to the measurements.

■ INTRODUCTION

Phenol−formaldehyde resins were the first totally synthetic polymers. Commercialized since 1910, they still find wide applications as decorative laminates, wood binders, adhesives, coatings, molded plastics, and aerospace components. Phenol−formaldehyde resins are produced by hydroxymethylation of phenol (P) with formaldehyde (F), followed by a controlled condensation of the phenolic rings. According to the reaction medium and initial F:P ratio, the reaction can lead to resols or novolaks. Resols are obtained in alkaline conditions with initial F:P molar ratios > 1 and are cured by heat. Novolaks are obtained in strong acid media with initial F:P < 1 and are thermoplastics that can be cured by addition of a hardener.

Resols for paper impregnation and production of decorative laminates are typically produced in batch stirred reactors. The initial solutions (of F:P ratios between 1 and 2) are obtained by mixing a (37% in weight) water solution of F (or formaline) with a 91% in weight water solution of P. Then, the pH is adjusted to 9.0 by addition of NaOH, and the temperature is raised from room temperature to 90 °C at 2−3 °C/min and then is maintained at 90 °C for around 2 h. As condensation proceeds, oligomers turn immiscible in water. Finally, water is vacuum-removed, and the base resin is cooled and dissolved in alcohol for storage. Hydroxymethylation reactions are fast at the lower reaction temperatures and mostly take place during the initial heating period. Thus, it is important to investigate the hydroxymethylation of P between 20 and 60 °C.

The NaOH-catalyzed hydroxymethylation of P in the absence of condensation was reviewed by Gardziella et al.[1] and had been previously investigated by Freeman and Lewis,[2] Eapen and Yeddanapalli,[3] Zavitsas et al.,[4] Aldersley and Hope,[5] Higuchi et al.,[6] Conner and Reeves,[7] and Mitsunaga et al.[8,9] All of these articles either explicit or implicity adopt the following irreversible reaction mechanism, originally proposed by Freeman and Lewis:[2]

(1)
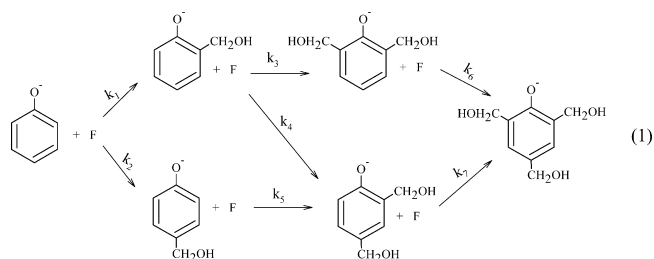
In each reaction step, F reacts with a phenolic species in the ortho or para position. Today, it seems clear that F ($\equiv CH_2O$) is the reactive species in eqs 1.[1] However, this was a matter of discussion 40 years ago, and, for example, Zavitsas et al.[4] assumed that the reacting species was methylene glycol rather than F. Equations 1 stress that, in alkaline conditions, P and its derived species are as phenolate ions. This was explicitly considered by Higuchi et al.,[6] Conner and Reeves,[7] and Mitsunaga et al.,[8,9] but not by Freeman and Lewis,[2] Zavitsas et al.,[4] or Aldersley and Hope,[5] where the nonionic compounds are presented. To simplify notation, we rewrite eqs 1 as follows:
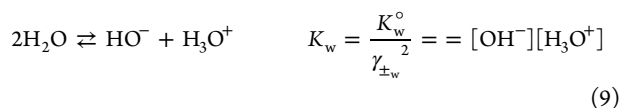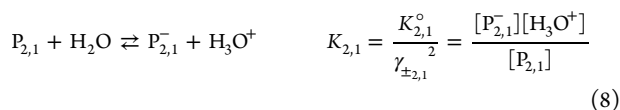

(2)
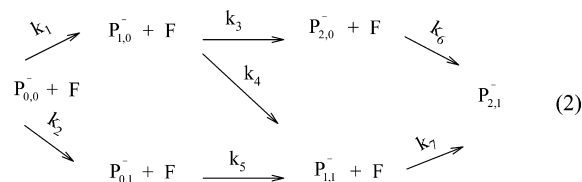
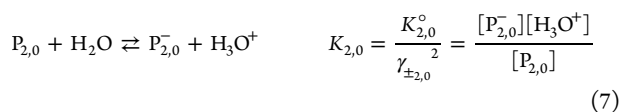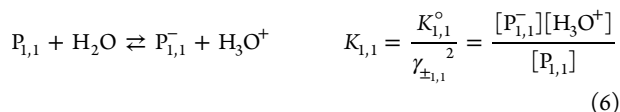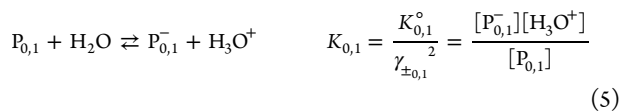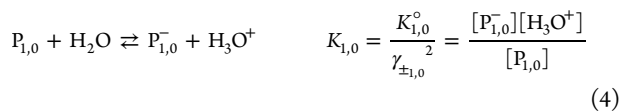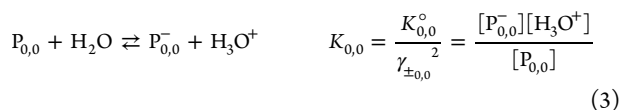where $P_{o,p}^-$ (with o,p = 0,0; 1,0; 0,1; 1,1; 2,0; and 2,1) is an ionic phenolic species containing o-hydroxymethyl groups in the ortho position and p in the para position; and $P_{0,0}^-$ represents the ionized P. The ionization reactions are as follows:

$$P_{0,0} + H_2O \rightleftarrows P_{0,0}^- + H_3O^+ \qquad K_{0,0} = \frac{K_{0,0}^\circ}{\gamma_{\pm_{0,0}}^2} = \frac{[P_{0,0}^-][H_3O^+]}{[P_{0,0}]}$$

(3)

$$P_{1,0} + H_2O \rightleftarrows P_{1,0}^- + H_3O^+ \qquad K_{1,0} = \frac{K_{1,0}^\circ}{\gamma_{\pm_{1,0}}^2} = \frac{[P_{1,0}^-][H_3O^+]}{[P_{1,0}]}$$

(4)

$$P_{0,1} + H_2O \rightleftarrows P_{0,1}^- + H_3O^+ \qquad K_{0,1} = \frac{K_{0,1}^\circ}{\gamma_{\pm_{0,1}}^2} = \frac{[P_{0,1}^-][H_3O^+]}{[P_{0,1}]}$$

(5)

$$P_{1,1} + H_2O \rightleftarrows P_{1,1}^- + H_3O^+ \qquad K_{1,1} = \frac{K_{1,1}^\circ}{\gamma_{\pm_{1,1}}^2} = \frac{[P_{1,1}^-][H_3O^+]}{[P_{1,1}]}$$

(6)

$$P_{2,0} + H_2O \rightleftarrows P_{2,0}^- + H_3O^+ \qquad K_{2,0} = \frac{K_{2,0}^\circ}{\gamma_{\pm_{2,0}}^2} = \frac{[P_{2,0}^-][H_3O^+]}{[P_{2,0}]}$$

(7)

$$P_{2,1} + H_2O \rightleftarrows P_{2,1}^- + H_3O^+ \qquad K_{2,1} = \frac{K_{2,1}^\circ}{\gamma_{\pm_{2,1}}^2} = \frac{[P_{2,1}^-][H_3O^+]}{[P_{2,1}]}$$

(8)

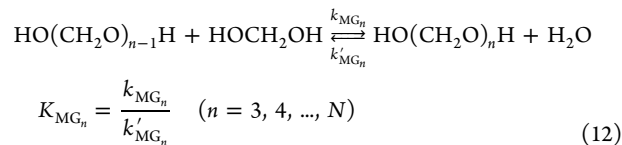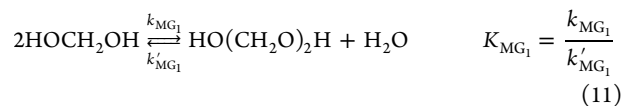$$2H_2O \rightleftarrows HO^- + H_3O^+ \qquad K_w = \frac{K_w^\circ}{\gamma_{\pm_w}^2} = = [OH^-][H_3O^+]$$

(9)

where $(K_{o,p}, K_w)$ are concentration acid dissociation constants; $(K_{o,p}^\circ, K_w^\circ)$ are their thermodynamic counterparts; and $(\gamma_{\pm_{o,p}}, \gamma_{\pm_w})$ are mean activity coefficients. The mean activity coefficients in turn depend on the ionic strength: $\mu = {}^1/_2 \sum_{i=1}^n [i]\delta z_i^2$, where δ is the solution density and $[i]$ is the molar concentration of the ith ionic species of charge z_i. When NaOH is the single added electrolyte and $\delta \approx 1000$ g/L, then $\mu \approx [\text{NaOH}]^0$.

Due to differences in the experimental procedures, reaction conditions, and model assumptions, a variety of hydroxymethylation rate constants under basic conditions have been reported [Freeman and Lewis,[2] Eapen and Yeddanapalli,[3] Zavitsas et al.[4] Aldersley and Hope,[5] Higuchi et al.,[6] Conner and Reeves,[7] and Mitsunaga et al.[8]]. In Conner and Reeves,[7] a table is presented that compares the rate constants of refs 2−6. In Mitsunaga et al.,[8,9] the hydroxymethylation rate constants for P and several phenol derivatives in the presence of dimethyl formamide (DMF) were determined from the consumption of F and each of the phenol derivatives, while the charges were calculated by semiempirical molecular orbital and ab initio methods on the reactive sites of phenol derivatives. Some of the investigated phenol derivatives can be considered as substructures of lignin and tannin.[8,9]
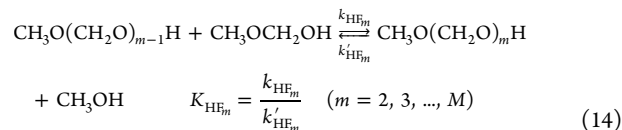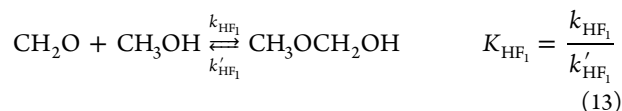
Consider the side reactions that operate in parallel with eqs 1−9. In water solution, F is mainly present as methylene glycol:[10]

$$CH_2O + H_2O \underset{k_d}{\overset{k_h}{\rightleftarrows}} HOCH_2OH \qquad K_{MG} = \frac{k_h}{k_d}$$

(10)
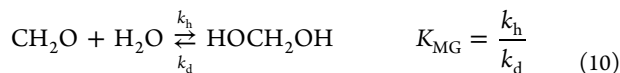
where (k_h, k_d) are respectively the hydration and dehydration rate constants of F and K_{MG} is the equilibrium constant. While k_h depends on the temperature and pH,[11] K_{MG} only depends on the temperature.[12] Methylene glycol partially polymerizes into (the water insoluble) paraformaldehyde or poly(oxymethylene glycol):[10]

$$2HOCH_2OH \underset{k_{MG_1}'}{\overset{k_{MG_1}}{\rightleftarrows}} HO(CH_2O)_2H + H_2O \qquad K_{MG_1} = \frac{k_{MG_1}}{k_{MG_1}'}$$

(11)

$$HO(CH_2O)_{n-1}H + HOCH_2OH \underset{k_{MG_n}'}{\overset{k_{MG_n}}{\rightleftarrows}} HO(CH_2O)_nH + H_2O$$

$$K_{MG_n} = \frac{k_{MG_n}}{k_{MG_n}'} \quad (n = 3, 4, ..., N)$$

(12)

Methanol is a typical impurity of F, since F is produced by oxidization of methanol. Also, between 5 and 15% of methanol is sometimes intentionally added into formaline, to promote generation of poly(oxymethylene glycol) hemiformals (hemiformals are preferred to poly(oxymethylene glycols) because they are more water-soluble):

$$CH_2O + CH_3OH \underset{k_{HF_1}'}{\overset{k_{HF_1}}{\rightleftarrows}} CH_3OCH_2OH \qquad K_{HF_1} = \frac{k_{HF_1}}{k_{HF_1}'}$$

(13)

$$CH_3O(CH_2O)_{m-1}H + CH_3OCH_2OH \underset{k_{HF_m}'}{\overset{k_{HF_m}}{\rightleftarrows}} CH_3O(CH_2O)_mH$$

$$+ CH_3OH \qquad K_{HF_m} = \frac{k_{HF_m}}{k_{HF_m}'} \quad (m = 2, 3, ..., M)$$

(14)

At pH > 10, F undergoes the Cannizzaro reaction, with generation of methanol and formate ion:[10]

$$2CH_2O + OH^- \underset{k_c'}{\overset{k_c}{\rightleftarrows}} CH_3OH + HCOO^-$$

(15)
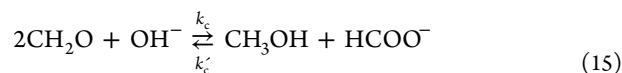
Methylene glycol also produces hemiformals by reaction with hydroxyl groups from (a) any of the hydroxymethylated phenols obtained through eqs 1 and 2 (eq 16) and (b) P (eq 17):[13]

(16)

(17)
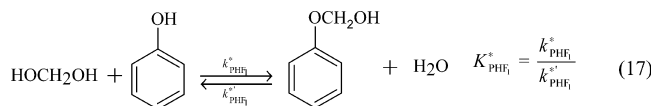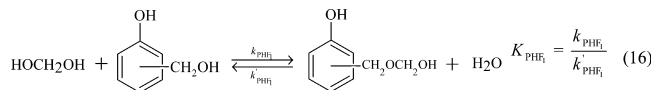
Finally, these hemiformals can also polymerize as follows:

$(l = 2, 3, ..., L)$ (18)

$(q = 2, 3, ..., Q)$ (19)
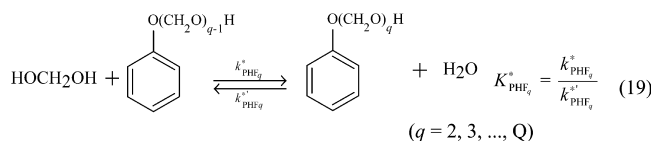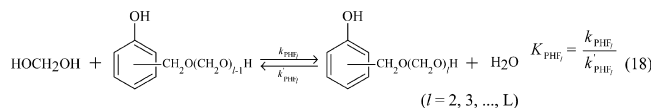
When F is consumed through eqs 1 and 2, all of the initial polymeric species eventually revert into F.[10] In alkaline conditions, the production of hemiformals from P (eqs 17 and 19) has not been detected,[4,14,15] and for this reason eqs 17 and 19 will not be further considered.

The aim of this work is to develop a global mathematical model based on the kinetic scheme of eqs 2−16 and 18, for simulating the evolution of reagents and products along nonisothermal hydroxymethylations of P at pH 8−10, at temperatures between 30 and 57 °C, and in the absence of methanol. Arrhenius expressions for the hydroxymethylations of eqs 2 were recalculated from the values reported in Zavitsas et al.,[4]

Table 1. Experimental Conditions and Measured Variables in the Three Base Publications

	Freeman and Lewis[2]					Zavitsas et al.[4]				Higuchi et al.[6]			
	expt 1	expt 2	expt 3	expt 4	expt 5	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
						Experimental Conditions							
T (°C)	30	30	30	30	30	30	30	57	57	20	20	30	40
pH	a	a	a	a	a	8.5	8.3	8.1	8.3	a	a	a	a
$[\text{NaOH}]^0$ (mol/L)	1.81	1.60	1.17	1.20	0.800	0.0314	0.0937	0.0125	0.0962	1	0.5	0.5	0.5
$[\text{H}_2\text{O}]^0$ (mol/L)	32.2	35.6	41.1	40.4	45.3	46.9	20.9	47.2	20.8	45	45	45	45
$[\text{F}_T]^0$ (mol/L)	5.94	3.20	2.13	1.30	0.950	2.12	9.19	2.03	9.46	3.0	3.0	3.0	3.0
$[\text{P}_{0,0_T}]^0$ (mol/L)	1.81	–	–	–	–	1.00	4.71	0.958	4.68	1.0	1.0	1.0	1.0
$[\text{P}_{1,0_T}]^0$ (mol/L)	–	1.61	–	–	–	–	–	–	–	–	–	–	–
$[\text{P}_{0,1_T}]^0$ (mol/L)	–	–	1.20	–	–	–	–	–	–	–	–	–	–
$[\text{P}_{2,0_T}]^0$ (mol/L)	–	–	–	1.21	–	–	–	–	–	–	–	–	–
$[\text{P}_{1,1_T}]^0$ (mol/L)	–	–	–	–	0.801	–	–	–	–	–	–	–	–
$[\text{F}]^0/[\text{P}_{o,p}]^0$	3.29	1.98	1.78	1.07	1.19	2.11	1.95	2.12	2.02	3.0	3.0	3.0	3.0
$[\text{NaOH}]^0/[\text{P}_{o,p}]^0$	1.00	0.992	0.978	0.991	1.00	0.0313	0.0199	0.0130	0.0205	1	0.5	0.5	0.5
						Measured Variables							
formaldehyde	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0b}$	$[\text{F}_T]^{0c}$	$[\text{F}_T]^{0c}$	$[\text{F}_T]^{0c}$	$[\text{F}_T]^{0c}$
phenolic species	$[\text{P}_{0,0_T}]^d$	$[\text{P}_{1,0_T}]^d$	$[\text{P}_{0,1_T}]^d$	$[\text{P}_{2,0_T}]^d$	$[\text{P}_{1,1_T}]^d$	$[\text{P}_{0,0_T}]^e$	$[\text{P}_{0,0_T}]^e$	$[\text{P}_{0,0_T}]^e$	$[\text{P}_{0,0_T}]^e$	$[\text{P}_{0,0_T}]^f$	$[\text{P}_{0,0_T}]^f$	$[\text{P}_{0,0_T}]^f$	$[\text{P}_{0,0_T}]^f$
	$[\text{P}_{1,0_T}]^d$	$[\text{P}_{1,1_T}]^d$	$[\text{P}_{1,1_T}]^d$	$[\text{P}_{2,1_T}]^d$	$[\text{P}_{2,1_T}]^d$	$[\text{P}_{1,0_T}]^e$	$[\text{P}_{1,0_T}]^e$	$[\text{P}_{1,0_T}]^e$	$[\text{P}_{1,0_T}]^e$	$[\text{P}_{1,0_T}]^f$	$[\text{P}_{1,0_T}]^f$	$[\text{P}_{1,0_T}]^f$	$[\text{P}_{1,0_T}]^f$
	$[\text{P}_{0,1_T}]^d$	$[\text{P}_{2,0_T}]^d$	$[\text{P}_{2,1_T}]^d$			$[\text{P}_{0,1_T}]^e$	$[\text{P}_{0,1_T}]^e$	$[\text{P}_{0,1_T}]^e$	$[\text{P}_{0,1_T}]^e$	$[\text{P}_{0,1_T}]^f$	$[\text{P}_{0,1_T}]^f$	$[\text{P}_{0,1_T}]^f$	$[\text{P}_{0,1_T}]^f$
	$[\text{P}_{1,1_T}]^d$	$[\text{P}_{2,1_T}]^d$				$[\text{P}_{1,1_T}]^e$	$[\text{P}_{1,1_T}]^e$	$[\text{P}_{1,1_T}]^e$	$[\text{P}_{1,1_T}]^e$	$[\text{P}_{1,1_T}]^f$	$[\text{P}_{1,1_T}]^f$	$[\text{P}_{1,1_T}]^f$	$[\text{P}_{1,1_T}]^f$
	$[\text{P}_{2,0_T}]^d$					$[\text{P}_{2,0_T}]^e$	$[\text{P}_{2,0_T}]^e$	$[\text{P}_{2,0_T}]^e$	$[\text{P}_{2,0_T}]^e$	$[\text{P}_{2,0_T}]^f$	$[\text{P}_{2,0_T}]^f$	$[\text{P}_{2,0_T}]^f$	$[\text{P}_{2,0_T}]^f$
	$[\text{P}_{2,1_T}]^d$					$[\text{P}_{2,1_T}]^e$	$[\text{P}_{2,1_T}]^e$	$[\text{P}_{2,1_T}]^e$	$[\text{P}_{2,1_T}]^e$	$[\text{P}_{2,1_T}]^f$	$[\text{P}_{2,1_T}]^f$	$[\text{P}_{2,1_T}]^f$	$[\text{P}_{2,1_T}]^f$

[a] Not reported. [b] Measured by the hydroxylamine chlorohydrate method.[10] [c] Measured by a modified hydroxylamine chlorohydrate method.[16] [d] Measured by quantitative paper chromatography. [e] Measured by an acetylation—gas—liquid chromatography (GLC) method.[14] [f] Measured by HPLC.

Table 2. Reaction Mechanisms and Model Parameters in the Three Base Publications

	Freeman and Lewis[2]					Zavitsas et al.[4]				Higuchi et al.[6]			
	expt 1	expt 2	expt 3	expt 4	expt 5	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
main hydroxymethyl. reacn: eqs 1, 2			adopted				adopted				adopted		
$k_1 \times 10^{-5}$ (L mol^{-1} s^{-1})	1.05	–	–	–	–	3.87	8.35	51.0	146	0.635	0.635	1.96	5.63
$k_2 \times 10^{-5}$ (L mol^{-1} s^{-1})	0.620	–	–	–	–	2.75	4.79	33.9	78	0.492	0.492	1.43	3.88
$k_3 \times 10^{-5}$ (L mol^{-1} s^{-1})	–	0.870	–	–	–	4.82	8.48	49.5	135	0.628	0.628	1.83	4.98
$k_4 \times 10^{-5}$ (L mol^{-1} s^{-1})	–	0.730	–	–	–	3.49	7.76	36.0	102	0.939	0.939	3.28	10.6
$k_5 \times 10^{-5}$ (L mol^{-1} s^{-1})	–	–	0.750	–	–	4.15	7.68	55.8	135	0.545	0.545	1.79	5.48
$k_6 \times 10^{-5}$ (L mol^{-1} s^{-1})	–	–	–	4.17	–	10.3	15.5	108	213	1.55	1.55	4.63	12.9
$k_7 \times 10^{-5}$ (L mol^{-1} s^{-1})	–	–	–	–	0.910	2.46	6.19	26.5	84.3	0.452	0.452	1.72	6.01
acid dissocn reacn: eqs 3–8			neglected				adopted				adopted		
$pK_{0,0}{}^a$			–			9.80^b	9.80^b	9.52^b	9.52^b	10.0^c	10.0^c	10.0^c	10.0^c
$pK_{1,0}{}^a$			–			9.77^b	9.77^b	9.46^b	9.46^b	9.84^c	9.84^c	9.84^c	9.84^c
$pK_{0,1}{}^a$			–			9.68^b	9.68^b	9.41^b	9.41^b	9.73^c	9.73^c	9.73^c	9.73^c
$pK_{2,0}{}^a$			–			9.63^b	9.63^b	9.34^b	9.34^b	9.69^c	9.69^c	9.69^c	9.69^c
$pK_{1,1}{}^a$			–			9.50^b	9.50^b	9.23^b	9.23^b	9.70^c	9.70^c	9.70^c	9.70^c
$pK_{2,1}{}^a$			–			9.39^b	9.39^b	9.13^b	9.13^b	9.45^c	9.45^c	9.45^c	9.45^c
self-ionization of water: eq 9			neglected				neglected				adopted with $K_w = 1 \times 10^{-14}$		
hydration/dehydration of F: eq 10			neglected				neglected				neglected		
poly(oxymethylene glycol) formation: eqs 11, 12			neglected				adopted with $n = 3^d$				neglected		
						$Q_1 = \{[\text{OH}(\text{CH}_2\text{O})_3\text{H}][\text{H}_2\text{O}]^2\}/\{[\text{OHCH}_2\text{OH}]_3\} = 45^e$							
hemiformals formation: eqs 13, 14			neglected				neglected				neglected		
Cannizzaro reacn: eq 15			neglected				neglected				neglected		
hemiformals formation: eqs 16, 18			neglected				adopted with $l = 2^d$				neglected		
						$K_{\text{PHF}_2}\{[\text{-CH}_2\text{O}(\text{CH}_2\text{O})_2\text{H}][\text{H}_2\text{O}]^2\}/\{[\text{-CH}_2\text{OH}][\text{HCH}_2\text{OH}]^2\} = 4^e$							

[a] $pK_{o,p} = -\log K_{o,p}$. [b] $pK_{o,p}$ with $\mu = 0.1$. [c] $pK_{o,p}$ at 25 °C with $\mu = 0.1$. [d] See F_T measurements in Table 3. [e] See adopted mathematical equations for poly(oxymethylene glycols) and hemiformals in Table 3.

**Table 3. Model Equations in the Three Base Publications and in This Work (See Equations in the Appendix)**

mass balances presented in:	Freeman and Lewis[2]	Zavitsas et al.[4]	Higuchi et al.[6]	this work
eqs A.1–A6 for hydroxymethylphenol	adopted	adopted with $m[F_T]$ instead of $[F]$[a]	adopted	adopted
eqs A.32 for acid dissocn reacn:	neglected	adopted with	adopted	adopted

$$\frac{[P_{1,0}^-]}{[P_{0,0}^-]} = \frac{K_{1,0}([P_{1,0_T}] - [P_{1,0}^-])}{K_{0,0}([P_{0,0_T}] - [P_{0,0}^-])} \qquad \frac{[P_{2,0}^-]}{[P_{1,1}^-]} = \frac{K_{2,0}([P_{2,0_T}] - [P_{2,0}^-])}{K_{1,1}([P_{1,1_T}] - [P_{1,1}^-])}$$

$$\frac{[P_{0,1}^-]}{[P_{1,0}^-]} = \frac{K_{0,1}([P_{0,1_T}] - [P_{0,1}^-])}{K_{1,0}([P_{1,0_T}] - [P_{1,0}^-])} \qquad \frac{[P_{2,1}^-]}{[P_{2,0}^-]} = \frac{K_{2,1}([P_{2,1_T}] - [P_{2,1}^-])}{K_{2,0}([P_{2,0_T}] - [P_{2,0}^-])}$$

$$\frac{[P_{1,1}^-]}{[P_{0,1}^-]} = \frac{K_{1,1}([P_{1,1_T}] - [P_{1,1}^-])}{K_{0,1}([P_{0,1_T}] - [P_{0,1}^-])}$$

mass balances presented in:	Freeman and Lewis[2]	Zavitsas et al.[4]	Higuchi et al.[6]	this work
eqs A.32 for self-ionization of water:	neglected	neglected	adopted	adopted
eq A.9 for charge balance	neglected	adopted with	adopted	adopted

$$[NaOH]^0 = \sum_{o=0}^{2}\sum_{p=0}^{1}[P_{o,p}^-]$$

mass balances presented in:	Freeman and Lewis[2]	Zavitsas et al.[4]	Higuchi et al.[6]	this work
eq A.10 for hydration/dehydr. of F	neglected	neglected	neglected	adopted
eqs A.11 and A.12 for poly(oxymethylene glycol) species	neglected	adopted with	neglected	adopted

$$3Q_1 K_{PHF_2}[F_T]^5 m'^5 + (3Q_1 + K_{PHF_2})[F_T]^3[H_2O]m'^3 + K_{PHF_2}(2[F_T]^0 - 3[F_T])[F_T]^2[H_2O]^2 m'^2 + [F_T][H_2O]^4(m' - 1) = 0$$

mass balances presented in:	Freeman and Lewis[2]	Zavitsas et al.[4]	Higuchi et al.[6]	this work
eqs A.20–A.24 for hemiformals	neglected	neglected	neglected	adopted
eq A.25 for water	neglected	adopted with	adopted	adopted

$$[H_2O] = [H_2O]^0 - m'[F_T] - \tfrac{1}{3}(1-m')[F_T]$$

mass balances presented in:	Freeman and Lewis[2]	Zavitsas et al.[4]	Higuchi et al.[6]	this work
eq A.26 for F	adopted	adopted with $m[F_T]$ instead of $[F]$[a]	adopted	adopted
measurement equations:				
eq A.29 for $[F_T]$	$[F_T] = [F]$	$[F_T] = [F] + [HOCH_2OH] + 3[HO(CH_2O)_3H] + 2[-CH_2O(CH_2O)_2H]$	$[F_T] = [F]$	$[F_T] = [F] + [HOCH_2OH] + \sum_{n=2}^{6} n[HO(CH_2O)_nH]$
eq A.30 for $[P_{o,p_T}]$	$[P_{o,p_T}] = [P_{o,p}^-]$	adopted	$[P_{o,p_T}] = [P_{o,p}] + [P_{o,p}^-]$	adopted

[a]Methylene glycol is the reactive species; and the following relationship was imposed: $[HOCH_2OH] = m'[F_T]$, with $m' = 0.83, 0.26, 0.84, 0.25$ for Exps. 1, 2, 3 and 4, respectively.

to take into consideration that the true reactive species are CH_2O and the various phenolate ions. Then, the model was verified against the experimental measurements by Freeman and Lewis,[2] Zavitsas et al.,[4] and Higuchi et al.[6] The experiments of refs 3 and 7−9) could not be simulated because measurements are not reported. Similarly, the experiments of ref 5 were not simulated because methanol was included in the reaction recipe.

■ REVIEW OF FREEMAN AND LEWIS,[2] ZAVITSAS ET AL.,[4] AND HIGUCHI ET AL.[6]

Consider the investigations by Freeman and Lewis,[2] Zavitsas et al.,[4] and Higuchi et al.[6] on NaOH-catalyzed hydroxymethylation of P between 20 and 57 °C. Table 1 compares their experimental conditions and measured variables; Table 2 lists the kinetic parameters and adopted reaction schemes, and Table 3 compares their model equations with a general mathematical model that is presented in the Appendix. Finally, Figures 1−3 present the concentration measurements of
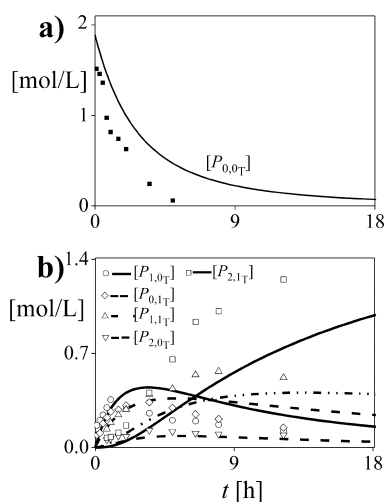
Figure 1. Experiment 1 by Freeman and Lewis:[2] measurements (in symbols) and simulation results (in curves), as calculated in this work with the corresponding model equations and parameters of Tables 3 and 2. Time evolutions of total phenol (a) and total hydroxymethylphenols (b).

reagents and products (in symbols, as obtained by digitization of the original article figures), together with simulation results calculated in this work employing the models and model parameters of the base publications. The following is noted in Table 1.

(1) The initial reagent is always phenol, except for expts 2−5 of Freeman and Lewis,[2] where the pure intermediate phenolic derivatives $P_{1,0}$, $P_{0,1}$, $P_{2,0}$, and $P_{1,1}$ were tested as initial reagents.

(2) All of the initial $F:P_{o,p}$ ratios ranged between 1 and 3, while the initial $NaOH:P_{o,p}$ ratios vary from around 1 in Freeman and Lewis[2] to 1 order of magnitude lower in Zavitsas et al.[4] In Zavitsas et al.,[4] the methanol-free formaline solutions were neutralized prior to the reactions with P.

(3) In all cases, the total concentration of formaldehyde and its derivatives ($[F_T]$, as defined by eq A.29 in the Appendix) was measured through the (direct or modified version of) the hydroxylamine hydrochloride method.[10,16] But while Zavitsas et al.[4] report the time evolutions of $[F_T]$, Freeman and Lewis[2] and Higuchi et al.[6] only report the initial F_T concentrations.

(4) The total concentration of P and its methylolated derivatives ($[P_{o,p_T}]$, as defined by eq A.30), was determined as follows. Zavitsas et al.[4] employed gas−liquid chromatography (GLC) to measure the acetylated derivatives of all of the phenolic species, with the acetylations carried out in two steps: first, all hemiformals were reconverted into hydroxymethylphenols with SO_2−pyridine, and then all hydroxymethylphenols (i.e., both the original and reconverted) were acetylated with pyridine−acetic anhydride.[14] In Freeman and Lewis[2] and Higuchi et al.,[6] $[P_{o,p_T}]$ was respectively determined by paper chromatography and high-pressure liquid chromatography.

The following is noted in Table 2.

(1) In Freeman and Lewis,[2] the kinetic mechanism was limited to eqs 2. In contrast, Zavitsas et al.[2] adopted the most comprehensive reaction scheme, but erroneously assumed that methylene glycol was the main reacting species.

(2) The seven k_i (i = 1, 2, ..., 7) hydroxymethylation constants of eqs 1 and 2 were estimated as follows. Freeman and Lewis[2] developed a sequential procedure that first involved the graphical estimation of k_6 and k_7 from the measurements of expts 4 and 5, respectively. Then, a successive approximation method was applied to estimate (a) k_5 from the measurements of expt 3, (b) k_3 and k_4 from the measurements of expt 2, and (c) k_1 and k_2 from the measurements of expt 1 (reproduced in Figure 1). In the other two publications, all seven k_i constants were simultaneously adjusted to the measurements of Figures 2 and 3. For such calculations, Zavitsas et al.[4] employed a maximization method of multiple correlation coefficients, while Higuchi et al.[6] employed a finite difference procedure. Also, Zavitsas et al.[4] adjusted different k_i values for the dilute and concentrated reaction systems, suggesting that the "dilute" kinetic constants obtained in expts 1 and 3 were valid for molar fractions of water ≥ 90%. Higuchi et al.[6] developed Arrhenius expressions for the seven $\acute{k}_i$s on the basis of averaged values at 20, 30, and 40 °C, and such expressions were employed to calculate the k_i values of Table 2. Also, Higuchi et al.[6] found no significant dependence between the k_i values and the initial NaOH:P ratios.

(3) Large variations are observed in the k_i values of Table 2. Compare, for example, the values at 30 °C of Freeman and Lewis[2] with those of Zavitsas et al.[4] Higuchi et al.[6] and Gardziella et al.[1] justified such variations to differences in the ionic strengths of the corresponding experiments. However, the $\acute{k}_i$s are also importantly affected by the adopted set of side reactions. Thus, the constants by Zavitsas et al.[4] are generally higher than those of Freeman and Lewis[2] and Higuchi et al.,[6] because Zavitsas et al.[4] admitted that F is partially as paraformaldehyde and derived hemiformals.

(4) In relation to eqs 3−8, Zavitsas et al.[4] adopted constant $K_{o,p}$ values, even though the ionic strength (μ) was varied between 0.03 and 0.1. Similarly, Higuchi et al.[6] adopted constant $K_{o,p}$ values, even though μ was varied between 0.5 and 1 and T between 20 and 40 °C.

(5) Zavitsas et al.[4] simplified eqs 12 and 18 by limiting the chain lengths to n = 3 and l = 2, respectively.

(6) Note that none of the base publications included the hydration/dehydration of F (eq 10).

The mathematical models of the base publications are subsets of the more general model that is presented in the Appendix, and Table 3 compares the final sets of adopted equations. Each of the base models were simulated in this work with their corresponding set of kinetic parameters (Table 2).
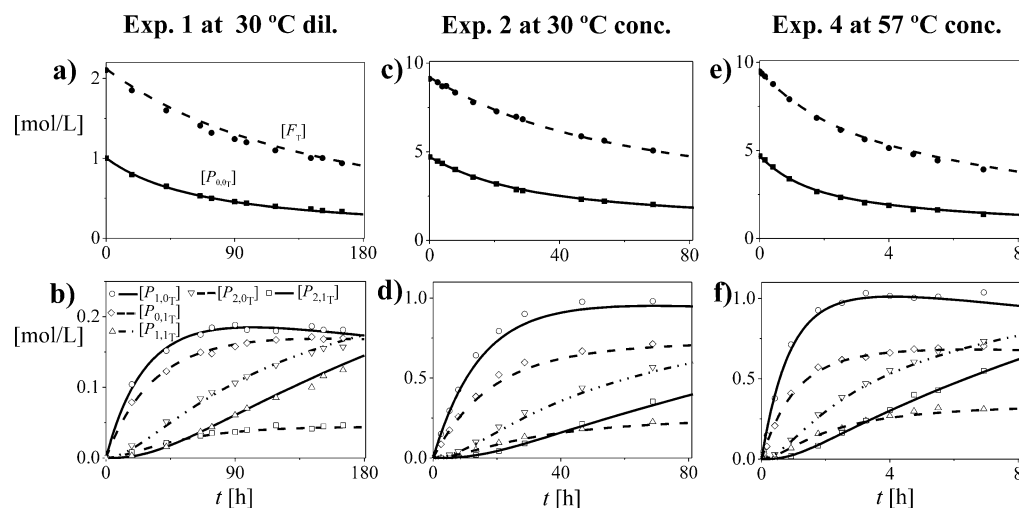
Figure 2. Experiments 1, 2, and 4 by Zavitsas et al.:[4] measurements (in symbols) and simulation results (in curves), as calculated in this work with the corresponding model equations and parameters of Tables 3 and 2. Time evolutions of total formaldehyde and phenol (a, c, e) and total hydroxymethylphenols (b, d, f).
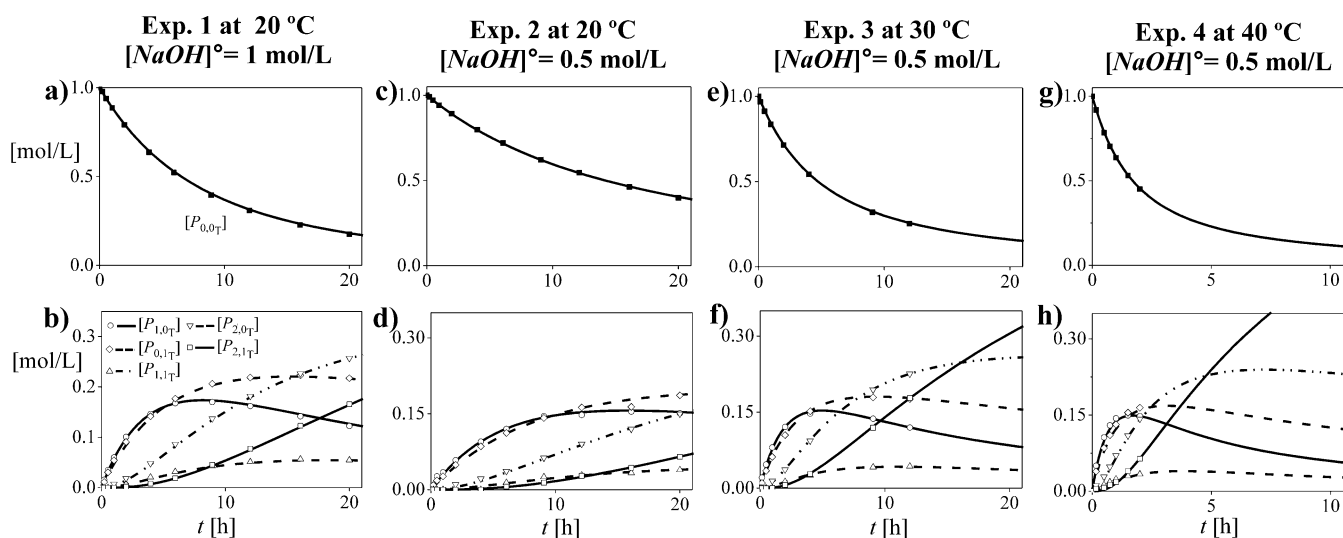
Figure 3. Experiments 1−4 by Higuchi et al.:[6] measurements (in symbols) and simulation results (in curves), as calculated in this work with the corresponding model equations and parameters of Tables 3 and 2. Time evolutions of total phenol (a, c, e, g) and total hydroxymethylphenols (b, d, f, h).

The computer programs were written in Matlab, and the differential equations were solved with an integration routine appropriate for nonstiff systems. The simulation results are presented in Figures 1−3. In Figures 2 and 3, the model predictions appropriately reproduce the experimental data, and (as expected) they almost coincide with the predictions in the base publications. Due to a lack of computing facilities at the time of the publication, no model predictions are presented in Freeman and Lewis,[2] and instead the experimental measurements were simply interpolated by adjustment curves (not shown here). In Figure 1, large differences are observed between the measurements and model predictions calculated in this work when employing the published model and parameters.[2] Possibly, such differences are due to propagation of errors into the adjusted k_i values along a sequential procedure that did not include a final global adjustment.[2]

The following is noted in Table 3.

(1) Zavitsas et al.[4] and Higuchi et al.[6] assumed instantaneous acid dissociation reactions. But while Higuchi et al.[6] also included the instantaneous self-ionization of water, Zavitsas

et al.[4] neglected such reaction, or the contribution of $[OH^-]$ toward the charge balance, and replaced eq A.9 for $[OH^-]$-independent expressions (Table 3).

(2) Zavitsas et al.[4] assumed instantaneous equilibriums for the polymerizations and hemiformal reactions, and therefore eqs A.11, A.12, and A.20−A.24 were replaced by the algebraic expressions of Table 3. Zavitsas et al.[4] also considered the effect of the generation of hemiformals from hydroxymethylphenols on the measurements of $[F_T]$ and $[P_{o,p_T}]$.

■ READJUSTED GENERAL MODEL AND RESIMULATION OF PUBLISHED EXPERIMENTS

The mentioned experiments were resimulated with the model equations listed in the last column of Table 3 and the kinetic parameters of Tables 4 and 5. The parameters of Table 4 were directly taken from the literature. Due to a lack of information concerning some of their values, the following additional assumptions were adopted.

Table 4. Model Parameters Directly Taken from the Literature ($pK_{o,p}^{\circ}$ Values Shown in Parentheses)

		Arrhenius expressions (T in K)	values at given temp				ref
			20 °C	30 °C	40 °C	57 °C	
acid dissocn reacn: eqs 3–8:	$K_{0,0}^{\circ}$ (mol/L)	$1.062 \times 10^{-10} e^{2415.5[(1/298)-(1/T)]}$	0.925×10^{-10} (10.03)	1.21×10^{-10} (9.92)	1.57×10^{-10} (9.81)	2.33×10^{-10} (9.63)	Zavitsas et al.[17]
	$K_{1,0}^{\circ}$ (mol/L)	$1.062 \times 10^{-10} e^{2717.4[(1/298)-(1/T)]}$	0.909×10^{-10} (10.04)	1.23×10^{-10} (9.91)	1.64×10^{-10} (9.78)	2.57×10^{-10} (9.59)	Zavitsas et al.[17]
	$K_{0,1}^{\circ}$ (mol/L)	$1.489 \times 10^{-10} e^{2264.5[(1/298)-(1/T)]}$	1.31×10^{-10} (9.88)	1.69×10^{-10} (9.77)	2.14×10^{-10} (9.67)	3.11×10^{-10} (9.51)	Zavitsas et al.[17]
	$K_{1,1}^{\circ}$ (mol/L)	$1.489 \times 10^{-10} e^{2465.8[(1/298)-(1/T)]}$	1.29×10^{-10} (9.89)	1.71×10^{-10} (9.77)	2.21×10^{-10} (9.66)	3.32×10^{-10} (9.48)	Zavitsas et al.[17]
	$K_{2,0}^{\circ}$ (mol/L)	$1.918 \times 10^{-10} e^{2365.1[(1/298)-(1/T)]a}$	1.68×10^{-10} (9.78)	2.19×10^{-10} (9.66)	2.81×10^{-10} (9.55)	4.14×10^{-10} (9.38)	Zavitsas et al.[17]
	$K_{2,1}^{\circ}$ (mol/L)	$2.470 \times 10^{-10} e^{2264.5[(1/298)-(1/T)]}$	2.17×10^{-10} (9.66)	2.80×10^{-10} (9.55)	3.56×10^{-10} (9.45)	5.16×10^{-10} (9.29)	Zavitsas et al.[17]
self-ionization of water: eq 9	K_w° (mol²/kg²)	$10^{(-3249.3/(273+T))[(1/298)-(1/T)]}$	7.03×10^{-15} (14.2)	1.57×10^{-14} (13.8)	3.29×10^{-14} (13.5)	1.03×10^{-13} (13.0)	Marshall et al.[18]
hydration/dehydrn. of F: eq 10	$K_{MG} = k_h/k_d$ (L/mol)	$e^{-2.325+2579/T}$	650	486	370	242	Siling and Akselrod[12]
poly(oxymethylene glycol) formation: eqs 11 and 12	$k_{MG_i} = k_{MG_n}$ (L mol⁻¹ s⁻¹)	$(1 + 247.3 \times 10^{-pH} + e^{(-0.8380-3102/T)\times10^{9pH}})e^{(23.12-8551/T)}$	0.00232^b	0.00609^b	0.0150^b	0.0613^b	Hahnenstein et al.[19]
	$k'_{MG_i} = k_{MG_i}/K_{MG_i}$ (mol⁻¹ s⁻¹)	$k_{MG_i}/e^{0.01449+560.9/T}$	0.000338^b	0.000943^b	0.00246^b	0.0110^b	Hahnenstein et al.[20]
	$k'_{MG_n} = k_{MG_n}/K_{MG_n}$ (L mol⁻¹ s⁻¹)	$k_{MG_n}/e^{-0.1084+460.4/T}$	0.000538^b	0.00149^b	0.00384^b	0.0169^b	Hahnenstein et al.[20]
hemiformals formation: eqs 16 and 18	k_{PHF_i}, k_{PHF_n} (L mol⁻¹ s⁻¹)	—	0	0	0	0	—
	k'_{PHF_i}, k'_{PHF_n} (L mol⁻¹ s⁻¹)	—	0	0	0	0	—

^{a}Interpolated values from $K_{1,1}^{\circ}$ and $K_{2,1}^{\circ}$. ^{b}Calculated at pH = 8.3.

Table 5. Arrhenius Expressions and k_i Constants of Equations 2 (Recalculated from the Values in Zavitsas et al.[4])

	Arrhenius expressions (T in K)	values at given temp			
		20 °C	30 °C	40 °C	57 °C
k_1 (L mol^{-1} s^{-1})	$5.29 \times 10^{10} e^{-7525/T}$	0.371	0.867	1.92	6.61
k_2 (L mol^{-1} s^{-1})	$1.22 \times 10^{10} e^{-7214/T}$	0.248	0.558	1.19	3.91
k_3 (L mol^{-1} s^{-1})	$6.44 \times 10^{9} e^{-6850/T}$	0.453	0.979	2.02	6.22
k_4 (L mol^{-1} s^{-1})	$1.87 \times 10^{9} e^{-6540/T}$	0.379	0.791	1.58	4.62
k_5 (L mol^{-1} s^{-1})	$5.21 \times 10^{10} e^{-7522/T}$	0.370	0.862	1.91	6.57
k_6 (L mol^{-1} s^{-1})	$5.01 \times 10^{9} e^{-6563/T}$	0.937	1.96	3.92	11.6
k_7 (L mol^{-1} s^{-1})	$2.44 \times 10^{9} e^{-6707/T}$	0.279	0.595	1.21	3.64

(1) The acid dissociation reactions (eqs 3−8), the self-ionization of water (eq 9), and the hydration/dehydration of F (eq 10) are all in instantaneous equilibrium.

(2) The kinetic constants of eqs 16 and 18 were not found in the literature and were therefore neglected by imposing the following: $k_{PHF_1} = k'_{PHF_1} = k_{PHF_l} = k'_{PHF_l} = 0$. Similarly, the following were neglected: $[-CH_2O(CH_2O)_lH]$ in eq A.29 and $[PH_{o,p_T}]$ in eq A.30.

(3) In eq A.29, the chain lengths of the generated poly(oxymethylene glycols) $[HO(CH_2O)_nH]$ were allowed to vary from $n = 2$ to $n = 6$.

In relation to eq 10, Schecker and Schulz[11] developed the following expression for the variation of k_h with pH and temperature:

$$k_h / [L/(mol\ s)]$$
$$= [1 + 870 \times 10^{-pH} + 6.3 \times 10^{(pH-8)}] e^{(8.962 - 1913/T)}$$
(20)

At pH = 8.5 and $T = 30$ °C, eq 20 yields $k_h = 295.68$ L mol^{-1} s^{-1}. This value is considerably larger than k_d (=k_h/K_{MG} = 0.608 s^{-1}) and is also larger than any of the k_i constants in Table 5. This justifies the instantaneous equilibrium for eq 10. Equation A.10 in the Appendix is also a consequence of such instantaneous equilibrium.
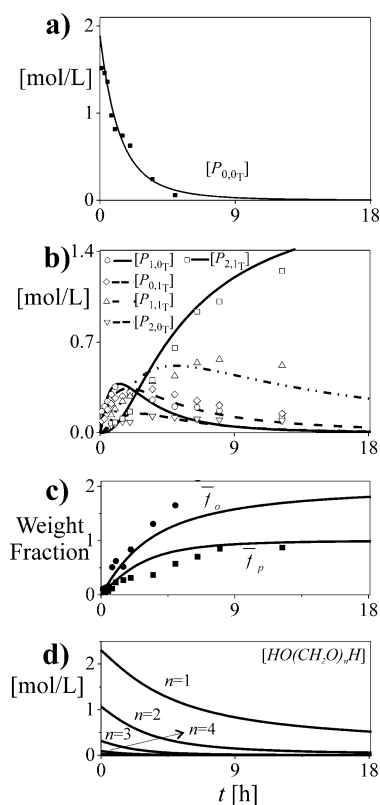
The k_i kinetic constants by Zavitsas et al.[4] (Table 2) were recalculated through the following equation, to take into account eq A.10 and the fact that the reactive species is F and not methylene glycol:

$$k_{i,Z} \equiv k_i K_{MG} [H_2O] \qquad (i = 1, 2, ..., 7)$$
(21)

Figure 4. Experiment 1 of Freeman and Lewis:[2] measurements (in symbols) and simulation results (in curves), as calculated with the new global model and parameters of Tables 4 and 5. Time evolutions of total phenol (a), total hydroxymethylphenols (b), number-average functionalities of o- and p-hydroxymethyl groups (c), and methylene glycol ($n = 1$) and poly(oxymethylene glycols) ($n \geq 2$) (d).

where k_i and $k_{i,Z}$ are the original and recalculated constants by Zavitsas et al.[4] Table 6 presents the recalculated constants at 30 and 57 °C for the two system concentrations. Kinetic constants are not expected to be affected by concentration, however. Thus, their averages at 30 and 57 °C were calculated (Table 6), and Arrhenius expressions were derived from such averages (Table 5). Finally, the Arrhenius expressions were used to calculate the new corrected k_i values at 20, 30, 40, and 57 °C (Table 5). These new values are about 5 orders of magnitude higher than those of the base publications (Table 2). This is a consequence of having introduced eq 10, for which the

Table 6. Recalculation of the Kinetic Constants by Zavitsas et al.[4] through Equation 21 and Corresponding Averaged Values ($\bar{k}_{i,Z}$)

	$T = 30$ °C			$T = 57$ °C		
	$k_{i,Z}$ (L mol^{-1} s^{-1})			$k_{i,Z}$ (L mol^{-1} s^{-1})		
i	$[H_2O]^0 = 47$ mol/L	$[H_2O]^0 = 21$ mol/L	$\bar{k}_{i,Z}$ (L mol^{-1} s^{-1})	$[H_2O]^0 = 47$ mol/L	$[H_2O]^0 = 21$ mol/L	$\bar{k}_{i,Z}$ (L mol^{-1} s^{-1})
1	0.882	0.848	0.865[a]	5.832	7.373	6.603[a]
2	0.627	0.487	0.557[a]	3.877	3.936	3.906[a]
3	1.099	0.862	0.980[a]	5.661	6.804	6.232[a]
4	0.796	0.788	0.792[a]	4.117	5.146	4.631[a]
5	0.946	0.780	0.863[a]	6.381	6.778	6.580[a]
6	2.344	1.577	1.960[a]	12.317	10.755	11.536[a]
7	0.561	0.629	0.595[a]	3.031	4.248	3.640[a]

[a]Values employed for calculating the Arrhenius expressions of Table 5.

Figure 5. Experiments 1, 2, and 4 by Zavitsas et al.:[4] measurements (in symbols) and simulation results (in curves), as calculated with the new global model and parameters of Tables 4 and 5. Time evolutions of total formaldehyde and phenol (a, e, i), total hydroxymethylphenols (b, f, j), number-average functionalities of o- and p-hydroxymethyl groups (c, g, k), and methylene glycol ($n = 1$) and poly(oxymethylene glycols) ($n \geq 2$) (d, h, l).

concentration of the true reactive species ($[F]$) is much lower than the measurements of $[F_T]$.

The analyzed experiments were resimulated with the equations listed in the last column of Table 3 and the model parameters of Tables 4 and 5. The initial concentrations, $[NaOH]^0$, $[H_2O]^0$, $[F_T]^0$, and $[P_{0,0_T}]^0$, are given in Table 1, and the initial concentrations of poly(oxymethylene glycols) were calculated through eqs A.10, A.13, A.14, and A.29.

Parts a and b of Figure 4 compare the new model predictions with the measurements of expt 1 by Freeman and Lewis.[2] Similarly, parts a,b; e,f; and i,j of Figure 5 compare the new model predictions with the measurements of expts 1, 2, and 4 by Zavitsas et al.;[4] and parts a,b; e,f; i,j; and m,n of Figure 6 compare the new model predictions with the measurements of expts 1–4 by Higuchi et al.[6] In all cases, quite reasonable fits are observed, bearing in mind that a single set of kinetic parameters was employed. Some further simulation results are presented in Figures 4c,d; 5(c,d; g,h; k,l); and 6(c,d; g,h; k,l; o,p). Figures 4c, 5c,g,k, and 6c,g,k,o compare the predicted evolution of the average functionalities of o- and p-hydroxymethyl groups ($\bar{f}_o$ and $\bar{f}_p$, respectively), where the corresponding "measurements" were indirectly estimated through eqs A.27 and A.28. In all cases, $\bar{f}_o > \bar{f}_p$. Part d of Figure 4, parts d, h, and l of Figure 5, and parts d, h, l, and p of 6 represent the predicted evolution of poly(oxymethylene glycol) species. Negligible amounts of the higher species with $n = 5$ or 6 are observed. As expected, the concentrations of poly(oxymethylene glycols) decrease in

time, due to consumption of F, which shifts the equilibriums of eqs 10−12 toward the reagents.

■ CONCLUSION

A general mathematical model was developed for the hydroxymethylation of P in alkaline conditions at relatively low temperatures and in the absence of methanol. It calculates the evolution of reagents and products, together with global parameters such as average functionalities. The seven hydroxymethylation kinetic constants were recalculated from published data by Zavitsas et al.,[4] to take into account the hydration/dehydration of F through eqs 10 and 21, which considerably lowers the concentration of the true reactive species (F ≡ CH_2O) with respect to the measurements of total formaldehyde. Employing a single set of parameters, the model appropriately reproduces the experimental data of the base publications. The model could be further improved by relaxing some of the assumptions regarding some of the side reactions, but this would require more detailed experimental data.

The main contribution of this work is the development of a global model for the hydroxymethylation of P in basic conditions and low temperatures, which was obtained by updating and reevaluating published information. Global chemical models aim at producing good predictions in a wide range of conditions but do not claim universality for the reaction scheme or kinetic parameters. In spite of their limitations, representative global models are important to help understand and control multivariate dynamical systems such as the synthesis of
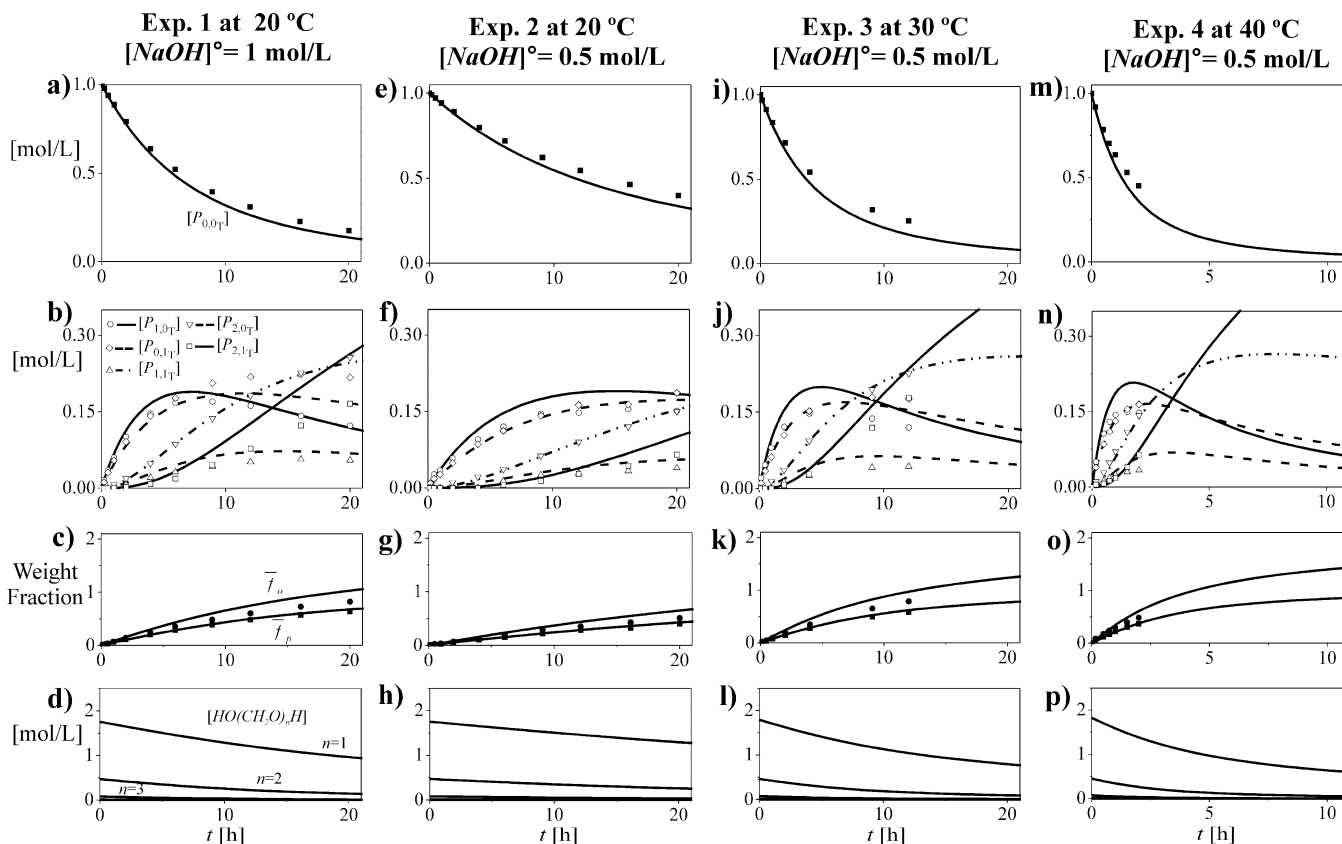
Figure 6. Experiments 1−4 by Higuchi et al.:[6] measurements (in symbols) and simulation results (in curves), as calculated with the new global model and parameters of Tables 4 and 5. Time evolutions of total phenol (a, e, i, m), total hydroxymethylphenols (b, f, j, n), number-average functionalities of o- and p-hydroxymethyl groups (c, g, k, o), and methylene glycol ($n = 1$) and poly(oxymethylene glycols) ($n \geq 2$) (d, h, l, p).

P−F resins in water solution. In the new model, the kinetic parameters were directly or indirectly taken from the literature and were not readjusted to the reported measurements. In a future communication, the presented model will be extended to include condensation reactions and other phenomena, with the final aim of optimizing an industrial resol process. At present, phenol-like compounds such as lignins are being employed as partial substitution of phenol in modified resols, and to this effect, the use of ab initio methods seems promising for estimating their corresponding hydroxymethylation rate constants.[7−9]

■ APPENDIX: GENERAL MATHEMATICAL MODEL

Consider a material balance for the mechanism of eqs 2−16 and 18.

From eqs 2, the following is written:

$$\frac{d[P_{0,0}^-]}{dt} = -(k_1 + k_2)[P_{0,0}^-][F] \tag{A.1}$$

$$\frac{d[P_{1,0}^-]}{dt} = (k_1[P_{0,0}^-] - (k_3 + k_4)[P_{1,0}^-])[F] \tag{A.2}$$

$$\frac{d[P_{0,1}^-]}{dt} = (k_2[P_{0,0}^-] - k_5[P_{0,1}^-])[F] \tag{A.3}$$

$$\frac{d[P_{1,1}^-]}{dt} = (k_4[P_{1,0}^-] + k_5[P_{0,1}^-] - k_7[P_{1,1}^-])[F] \tag{A.4}$$

$$\frac{d[P_{2,0}^-]}{dt} = (k_3[P_{1,0}^-] - k_6[P_{2,0}^-])[F] \tag{A.5}$$

$$\frac{d[P_{2,1}^-]}{dt} = (k_6[P_{2,0}^-] + k_7[P_{1,1}^-])[F] \tag{A.6}$$

From the instantaneous equilibriums adopted for the dissociation reactions (eqs 3−9), one obtains:

$$[P_{o,p}^-] = \frac{K_{o,p}^{\circ}[P_{o,p}]}{(\gamma_{\pm_{o,p}}^2/\gamma_{\pm_w}^2)K_w^{\circ}/[OH^-]}$$

$$(o, p = 0, 0; 1, 0; 0, 1; 1, 1; 2, 0; 2, 1) \tag{A.7}$$

The value of $\gamma_{\pm_{o,p}}/\gamma_{\pm_w}$ could not be found in the literature, and was adopted equal to unity. The global charge balance results:

$$[Na^+] + [H_3O^+] = \sum_{o=0}^{2} \sum_{p=0}^{1} [P_{o,p}^-] + [OH^-] \tag{A.8}$$

Since $[Na^+] = [NaOH]^0$, and neglecting $[H_3O^+]$ due to the alkaline conditions, eq A.8 yields

$$[NaOH]^0 = \sum_{o=0}^{2} \sum_{p=0}^{1} [P_{o,p}^-] + [OH^-] \tag{A.9}$$

An instantaneous equilibrium for the hydration/dehydration of F (eq 10), produces

$$[HOCH_2OH] = K_{MG}[F][H_2O] \tag{A.10}$$

where the value of K_{MG} is presented in Table 4.[12]

The generation of poly(oxymethylene glycols) through eqs 11 and 12 provides

$$
\begin{aligned}
\frac{d[HO(CH_2O)_2H]}{dt} &= k_{MG_1}[HOCH_2OH]^2 - k'_{MG_1}[HO(CH_2O)_2H][H_2O] \\
&\quad - k_{MG_n}[HO(CH_2O)_2H][HOCH_2OH] \\
&\quad + k'_{MG_n}[HO(CH_2O)_3H][H_2O]
\end{aligned}
\tag{A.11}
$$

$$
\begin{aligned}
\frac{d[HO(CH_2O)_nH]}{dt} &= k_{MG_n}[HO(CH_2O)_{n-1}H][HOCH_2OH] \\
&\quad - k'_{MG_n}[HO(CH_2O)_nH][H_2O] \quad (n = 3, 4, ..., N)
\end{aligned}
\tag{A.12}
$$

Equations A.11 and A.12 are assumed in equilibrium in the initial reaction solution. Thus, the initial concentrations of poly(oxymethylene glycols) are given by

$$
[HO(CH_2O)_2H]^0 = K_{MG_1}[HOCH_2OH]^0[HOCH_2OH]^0/[H_2O]^0
\tag{A.13}
$$

$$
\begin{aligned}
[HO(CH_2O)_nH]^0 &= K_{MG_n}[HOCH_2OH]^0 \\
&\quad \times [HO(CH_2O)_{n-1}H]^0/[H_2O]^0 \quad (n = 3, 4, ..., N)
\end{aligned}
\tag{A.14}
$$

Similarly, the generation of hemiformals through eqs 13 and 14 provides

$$
\begin{aligned}
\frac{d[CH_3OCH_2OH]}{dt} &= k_{HF_1}[F][CH_3OH] - k'_{HF_1}[CH_3OCH_2OH] \\
&\quad - 2k_{HF_m}[CH_3OCH_2OH]^2 \\
&\quad + k'_{HF_m}[CH_3O(CH_2O)_2H][CH_3OH]
\end{aligned}
\tag{A.15}
$$

$$
\begin{aligned}
\frac{d[CH_3O(CH_2O)_mH]}{dt} &= k_{HF_m}[CH_3O(CH_2O)_{m-1}H][CH_3OCH_2OH] \\
&\quad - k'_{HF_m}[CH_3O(CH_2O)_mH][CH_3OH] \quad (m = 2, 3, ..., M)
\end{aligned}
\tag{A.16}
$$

Methanol is generated in eqs 14 and 15 and consumed in eq 13. This yields

$$
\begin{aligned}
\frac{d[CH_3OH]}{dt} &= -k_{HF_1}[F][CH_3OH] + k'_{HF_1}[CH_3OCH_2OH] \\
&\quad + \sum_{m=2}^{M} (k_{HF_m}[CH_3O(CH_2O)_{m-1}H][CH_3OCH_2OH] \\
&\quad - k'_{HF_m}[CH_3O(CH_2O)_mH][CH_3OH]) \\
&\quad + k_c[F]^2[OH^-] - k'_c[CH_3OH][HCOO^-]
\end{aligned}
\tag{A.17}
$$

Similarly to eqs A.13 and A.14, the initial reaction concentrations of $[CH_3OCH_2OH]$ and $[CH_3O(CH_2O)_mH]$ can be obtained from the initial concentration of methanol, and assuming equilibrium in eqs A.15 and A.16.

A balance for the formate ions generated through eq 15 provides

$$
\frac{d[HCOO^-]}{dt} = k_c[F]^2[OH^-] - k'_c[CH_3OH][HCOO^-]
\tag{A.18}
$$

F is consumed in eqs 2, 13, and 15. This yields

$$
\begin{aligned}
\frac{d[F]}{dt} &= -\{(k_1 + k_2)[P^-_{0,0}] + (k_3 + k_4)[P^-_{1,0}] + k_5[P^-_{0,1}] \\
&\quad + k_6[P^-_{2,0}] + k_7[P^-_{1,1}] + k_{HF_1}[CH_3OH] \\
&\quad - k'_{HF_1}[CH_3OCH_2OH] + 2k_c[F]^2[OH^-] \\
&\quad - k'_c[CH_3OH][HCOO^-]\}[F]
\end{aligned}
\tag{A.19}
$$

Following Zavitsas et al.,[4] a common reactivity is adopted for all the generated hydroxymethylphenols through eqs 16 and 18. Thus, a balance for the total hemiformal groups obtained from the total concentration of hydroxymethyl groups $[-CH_2OH]$ produces

$$
\begin{aligned}
\frac{d[-CH_2OCH_2OH]}{dt} &= k_{PHF_1}[HOCH_2OH][-CH_2OH] \\
&\quad - k'_{PHF_1}[-CH_2OCH_2OH][H_2O] \\
&\quad - k_{PHF_l}[HOCH_2OH][-CH_2OCH_2OH] \\
&\quad + k'_{PHF_l}[-CH_2O(CH_2O)_2H][H_2O]
\end{aligned}
\tag{A.20}
$$

$$
\begin{aligned}
\frac{d[-CH_2O(CH_2O)_lH]}{dt} &= k_{PHF_l}[HOCH_2OH][-CH_2OCH_{l-1}OH] \\
&\quad - k'_{PHF_l}[-CH_2O(CH_2O)_lH][H_2O] \\
&\quad (l = 2, 3, ..., L)
\end{aligned}
\tag{A.21}
$$

Also, the total concentration of hydroxymethyl groups is

$$
[-CH_2OH] = [-CH_2OH]_o + [-CH_2OH]_p
\tag{A.22}
$$

where $[-CH_2OH]_o$ and $[-CH_2OH]_p$ are the total concentrations of o- and p-hydroxymethyl groups; i.e.,

$$
[-CH_2OH]_o = [P_{1,0_T}] + 2[P_{2,0_T}] + [P_{1,1_T}] + 2[P_{2,1_T}]
\tag{A.23}
$$

$$
[-CH_2OH]_p = [P_{0,1_T}] + [P_{1,1_T}] + [P_{2,1_T}]
\tag{A.24}
$$

The water mass balance involves eqs 11, 12, 16, and 18, yielding

$$
\begin{aligned}
\frac{d[H_2O]}{dt} &= k_{MG_1}[HOCH_2OH]^2 - k'_{MG_1}[HO(CH_2O)_2H][H_2O] \\
&\quad + \sum_{n=3}^{N} (k_{MG_n}[HO(CH_2O)_{n-1}H][HOCH_2OH] \\
&\quad - k'_{MG_n}[HO(CH_2O)_nH][H_2O]) \\
&\quad + k_{PHF_1}[HOCH_2OH][-CH_2OH] \\
&\quad - k'_{PHF_1}[-CH_2OCH_2OH][H_2O] \\
&\quad + \sum_{l=2}^{L} (k_{PHF_l}[HOCH_2OH][-CH_2O(CH_2O)_{l-1}H] \\
&\quad - k'_{PHF_l}[-CH_2O(CH_2O)_lH][H_2O])
\end{aligned}
\tag{A.25}
$$

At pH < 10 and in the absence of methanol, one can write: $[CH_3OH] = [CH_3OCH_2OH] = [CH_3O(CH_2O)_mH] = [HCOO^-] = 0$. Therefore: $d[CH_3OH]/dt = d[CH_3OCH_2OH]/dt = d[CH_3O(CH_2O)_mH]/dt = d[HCOO^-]/dt = 0$ in eqs A.15−A.18, and eq A.19 reduces to

$$\frac{d[F]}{dt} = -\{(k_1 + k_2)[P_{0,0}^-] + (k_3 + k_4)[P_{1,0}^-] + k_5[P_{0,1}^-] + k_6[P_{2,0}^-] + k_7[P_{1,1}^-]\}[F] \tag{A.26}$$

The number-average functionalities of o- and p-hydroxymethyl groups are obtained from

$$\bar{f}_o = \frac{[-CH_2OH]_o}{[P_{0,0_T}]^0} \tag{A.27}$$

$$\bar{f}_p = \frac{[-CH_2OH]_p}{[P_{0,0_T}]^0} \tag{A.28}$$

Finally, the "measurement" equations for the total concentrations of formaldehyde and phenolic species ($[F_T]$ and $[P_{o,p_T}]$, respectively), are given by

$$[F]_T = [F] + [HOCH_2OH] + \sum_{n=2}^{N} n[HO(CH_2O)_nH]$$
$$+ \sum_{m=1}^{M} m[CH_3O(CH_2O)_mH]$$
$$+ \sum_{l=1}^{L} l[-CH_2O(CH_2O)_lH] \tag{A.29}$$

$$[P_{o,p_T}] = [P_{o,p}] + [P_{o,p}^-] + [PH_{o,p_T}];$$
$$\text{with } o, p = 0, 0; 1, 0; 0, 1; 1, 1; 2, 0; 2, 1 \tag{A.30}$$

where $[HO(CH_2O)_nH]$ $(n = 2, 3, ..., N)$; $[CH_3O(CH_2O)_mH]$ $(m = 1, 2, ..., M)$; and $[-CH_2O(CH_2O)_lH]$ $(l = 1, 2, ..., L)$, are respectively the molar concentrations of poly(oxymethylene glycols) obtained through eqs 11 and 12; of hemiformals obtained from methanol through eqs 13 and 14; and of hemiformals obtained from hydroxymethyl phenols through eqs 16 and 18; and PH_{o,p_T} represents an hemiformal from phenolic molecules, in turn calculated through

$$[PH_{o,p_T}] = \frac{\sum_{l=1}^{L}[-CH_2O(CH_2O)_lH]}{[-CH_2OH]}[P_{o,p_T}] \tag{A.31}$$

Note that eq A.31 assumes a common reactivity for all hydroxymethylphenols. Replacing eq A.31 into eq A.30 and then into eq A.7, one obtains

$$[P_{o,p}^-] = \frac{K_{o,p}^\circ[P_{o,p_T}]\left(1 - \dfrac{\sum_{l=1}^{L}[-CH_2O(CH_2O)_lH]}{[-CH_2OH]}\right)}{(K_{o,p}^\circ + K_w^\circ/[OH^-])}$$
$$(o, p = 0, 0; 1, 0; 0, 1; 1, 1; 2, 0; 2, 1) \tag{A.32}$$

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■ NOTATION

$F = CH_2O$

F_T = total formaldehyde, as defined by eq A.29

$\bar{f}_o, \bar{f}_p$ = number-average functionalities of o- and p-hydroxymethyl groups

k_c, k_c' = forward and backward rate constants of the Cannizzaro reaction, L^2 mol^{-2} s^{-1} and L mol^{-1} s^{-1}

k_d, k_h = Dehydration and hydration rate constants of F, s^{-1} and L mol^{-1} s^{-1}

k_i $(i = 1, 2, ..., 7)$ = hydroxymethylation rate constants, L mol^{-1} s^{-1}

k_{i_Z} $(i = 1, 2, ..., 7)$ = readjusted hydroxymethylation constants by Zavitsas et al.[4] through eq 21, L mol^{-1} s^{-1}

k_{HF_1}, k_{HF_m} = forward rate constants of hemiformals generated by methanol, L mol^{-1} s^{-1}

k_{HF_1}', k_{HF_m}' = backward rate constants of hemiformals generated by methanol, s^{-1} and L mol^{-1} s^{-1}

k_{MG_1}, k_{MG_n} = forward rate constants of poly(oxymethylene glycol) formation, L mol^{-1} s^{-1}

k_{MG_1}', k_{MG_n}' = backward rate constants of poly(oxymethylene glycol) formation, L mol^{-1} s^{-1}

k_{PHF_1}, k_{PHF_i} = forward rate constants of hemiformals generated from hydroxymethylated phenols, L mol^{-1} s^{-1}

k_{PHF_1}', k_{PHF_i}' = backward rate constants of hemiformals generated from hydroxymethylated phenols, L mol^{-1} s^{-1}

$k_{PHF_1}^*, k_{PHF_q}^*$ = forward rate constants of hemiformals generated from phenol hydroxyl groups, L mol^{-1} s^{-1}

$k_{PHF_1}^{*\prime}, k_{PHF_q}^{*\prime}$ = backward rate constants of hemiformals generated from phenol hydroxyl groups, L mol^{-1} s^{-1}

K_{HF_1}, K_{HF_n} = equilibrium constants for hemiformals generated from methanol, L/mol and dimensionless

K_{MG} = equilibrium constant for the hydration/dehydration of F, L/mol

K_{MG_1}, K_{MG_n} = equilibrium constants for the formation of poly(oxymethylene glycol), dimensionless

K_{PHF_1}, K_{PHF_l} = equilibrium constants for hemiformals formation from hydroxymethylated phenols, dimensionless

$K_{PHF_1}^*, K_{PHF_q}^*$ = equilibrium constants for the formation of hemiformals from phenol hydroxyl groups, dimensionless

$K_{o,p}$ = concentration-based acid dissociation constants, mol/L

$K_{o,p}^\circ$ = Thermodynamic acid dissociation constants, mol/L

K_w = concentration-based acid dissociation constant of water, mol^2/kg^2

K_w° = thermodynamic acid dissociation constant of water, mol^2/kg^2

P_{o,p_T} = total phenolic species with o hydroxymethyl groups in the ortho position and p in the para position, as defined by eq A.30

$P_{o,p}$ = nonionic phenolic molecule with o hydroxymethyl groups in the ortho position and p in the para position

$P_{o,p}^-$ = ionic phenolic molecule with o hydroxymethyl groups in the ortho position and p in the para position

PH_{o,p_T} = hemiformal fraction of phenolic molecules with o hydroxymethyl groups in the ortho position and p in the para position, defined by eq A.31

t = time, s

T = temperature, °C

[ ] = molar concentration, mol/L

$\gamma_{\pm o,p}$, $\gamma_{\pm w}$ = Mean-activity coefficients of each electrolytic pair and of water

superscript 0 = initial condition

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