Mathematical modeling of urea-formaldehyde resins: specific acid-base catalysis

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INTRODUCTION

Urea formaldehyde (U-F) base resins are obtained by reaction between urea (U) and formaldehyde (F) and are used mainly as adhesives in the manufacture of wood panels. The hydroxymethylation-condensation mechanism is very complex since it is catalyzed by acids and bases [Eqs. (1)-(4)][1].

$$—NH_2 + F \underset{k_{m1}}{\overset{k_{m1}}{\rightleftarrows}} —NHCH_2OH \quad (1)$$

$$—NHCH_2OH + F \underset{k_{m2}}{\overset{k_{m2}}{\rightleftarrows}} —N(CH_2OH)_2 \quad (2)$$

$$—NH_2 + —NHCH_2OH \underset{k'_{MB}}{\overset{k_{MB}}{\rightleftarrows}} —NHCH_2NH— + H_2O \quad (3)$$

$$2\,—NHCH_2OH \underset{k'_{EB}}{\overset{k_{EB}}{\rightleftarrows}} —NHCH_2OCH_2NH— + H_2O \quad (4)$$

By-side reactions involve: *i*) the hydration/dehydration[2] of F and its polymerization [Eqs. (5) and (6)];

$$F + H_2O \underset{k_d}{\overset{k_h}{\rightleftarrows}} HOCH_2OH \qquad K_{MG}=[HOCH_2OH]/[F][H_2O] \quad (5)$$

$$HO(CH_2O)_{n-1}H + HOCH_2OH \underset{k_{MG2I}}{\overset{k_{MG2}}{\rightleftarrows}} HO(CH_2O)_nH + H_2O \quad (6)$$

and *ii*) the ionization of U in water [Eqs. (7) and (8)]:

$$U + H_2O \rightleftarrows UH^+ + OH^- \qquad K_U=[UH^+][OH^-]/[U] \quad (7)$$

$$2H_2O \rightleftarrows H_3O^+ + OH^- \qquad K_W=[H_3O^+][OH^-] \quad (8)$$

Also, hydroxymethylureas undergo hydrolysis in alkaline conditions [Eq. (9)]:[3]

$$—CH_2OH + {}^-OH \rightleftarrows —CH_2O^- + H_2O \qquad K_h=[—CH_2O^-]/[—CH_2OH][OH^-] \quad (9)$$

where $[—CH_2OH]=[—NHCH_2OH]+2[—N(CH_2OH)_2]$.

EXPERIMENTAL METHODS

Four experiments were carried out at 48 °C and 60 °C, pH 4 and 9 for initial molar ratios $[F]°/[U]°= 2$ with $[F]°=0.4$ mol/L. Along the reactions the total free F (F_T), the molar ratio $r_1=[-N\underline{H}]/[-N\underline{H}_2]$, and the number average molecular weight ($\overline{M}_n$) were measured by the sulphite method, nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC).

MATHEMATICAL MODELING

The model is based on the material and charge balances of Ecs. 1-9. The following hypotheses were considered: i) constant reaction volume; ii) the U has 3 (of 4) reactive H; iii) $k_{MB}=k_{EB}$ and $k'_{MB}=k'_{EB}$; iv) instantaneous equilibrium of hydration/ dehydration of F, (Eq. 5); v) chain length n = 2 of the poly(oxymethylene glycol) (Eq. 6); vi) instantaneous equilibrium of the ionization reaction of U (Eq. 7); vii) instantaneous equilibrium of the self-ionization of water (Eq. 8) viii) instantaneous equilibrium of the hydrolysis of hydroxymethylureas (Eq. 9). The computer program was written in Matlab R 2011a, and the systems of equations were solved by routines for non-linear systems (ode 15s). The kinetic hydroxymethylation-condensation constants were all adjusted in this work, to fit the measurements of Fig. 1 and Table 2. The parameters of the model are shown in Table 1.

Table 1. Parameters of the model.*

(L/mol s^{-1})	*Arrhenius expressions*	(s^{-1})	*Arrhenius expressions*
k_{m1}	$1.13\times10^{11}e^{(-7917/T)}$	k'_{m1}	$2.56\times10^{23}e^{(-22000/T)}$
k_{m2}	$2.66\times10^{16}e^{(-14500/T)}$	k'_{m2}	$1.36\times10^{12}e^{(-13667/T)}$
k_{EB}, k_{MB}	$1.01\times10^{2}e^{(-3917/T)}$	k'_{EB}, k'_{MB}	$8.37\times10^{6}e^{(-9750/T)}$

∗ K_{MG}, k_{MG2}, k'_{MG2I}, K_U, K_h, K_W were taken from the literature.[3,4,5,6]

RESULTS AND DISCUSSION

F_T decreases with temperature and pH (Figure 1) whereas $\overline{M}_n$ increases (Table 2).

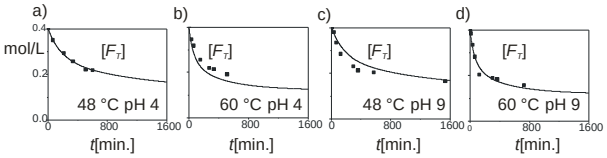

Figure 1: Evolution of F_T. Measurements (in symbol) and model predictions (in continuous trace).

Table 2. Measurements of NMR and SEC at pH 9. Simulation results between brackets.

	$r_1=[-N\underline{H}]/[-N\underline{H}_2]$		$\overline{M}_n$	
t (min.)	48 °C	60 °C	48 °C	60 °C
60	3.88(0.19)	3.34 (0.56)	74(54.84)	84(68.38)
540	4.4(2.54)	4.2 (6.5)	101(99.94)	117 (138)

The theoretical predictions showed an acceptable concordance with the volumetric, chromatographic and spectroscopic measurements.

CONCLUSIONS

A new mathematical model was developed that allows to predict the specific acid-base catalysis of the hydroxymethylation-condensation of the U employing a single set of model parameters in all pH range. The Arrhenius expressions of the hydroxymethylation-condensation kinetic constants were estimated.

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