

Supplemental Information – 2 – Model Equations for 4,4'-MDI

Symbols and abbreviations

Subscripts

0	initial (at time = 0)
A	for mass transfer
C	in organic phase
U	for urea formation
W	in aqueous phase, or for hydrolysis

Symbols

$D[f(t)]$	= $df(t)/dt$ (differential of the function $f(t)$ with time)
k	reaction or mass transfer rate constant
L_0	initial overall loading
$MDA(t)$	concentration of 4,4'-methylene dianiline
$MDI(t)$	concentration of 4,4'-methylene diphenyl diisocyanate (aqueous phase)
$MDI_c(t)$	loading of 4,4'-methylene diphenyl diisocyanate (organic phase)
$MIA(t)$	concentration of 4-(4'-aminobenzyl)-isocyanato benzene
r	reaction rate
t	time
S_0	solubility limit
$U(t)$	concentration (loading) of ureas
W_0	55 mol/L (pure water concentration)

Model equations

Chemical reaction rate in the aqueous phase

Rates for the reactions of Schemes 1 and 2 are expressed using standard rate equations:

Hydrolysis

$$r_1 = k_W \cdot MDI(t) \cdot W_0$$

$$r_2 = 0.5 k_W \cdot MIA(t) \cdot W_0$$

Urea formation

$$r_3 = k_U \cdot \text{MDI}(t) \cdot \text{MIA}(t)$$

$$r_4 = 2 k_U \cdot \text{MDI}(t) \cdot \text{MDA}(t)$$

$$r_5 = 0.5 k_U \cdot \text{MIA}(t) \cdot \text{MIA}(t)$$

$$r_6 = k_U \cdot \text{MIA}(t) \cdot \text{MDA}(t)$$

Note: coefficients are based on the number of reactive NCO or amino groups (see Schemes 1 and 2).

Mass transfer between the organic and aqueous phases

Expresses the driving force (deviation from equilibrium) and its reduction as a function of remaining MDI in the organic phase:

$$r_7 = k_A \cdot (S_0 - \text{MDI}(t)) \cdot \text{MDI}_C(t)$$

Note: in this equation, MDI_C(t) fulfills two roles: (1) the solubility limit is a function of the remaining MDI concentration in an organic particle (which decreases as more ureas are being formed), and (2) takes into account that increased loading typically also leads to increased surface area of the particles, which would not be considered by the “constant” k_A.

Chemical reaction rate in the organic phase

Express a potential (minimal) formation of MDA from the organic phase, as well as the predominant reaction to form ureas:

$$r_8 = k_W \cdot \text{MDI}_C(t) \cdot W_0 / 2000$$

$$r_9 = k_U / 2000 \cdot \text{MDI}_C(t) \cdot 1$$

Note: the factor 2000 for the “fast” urea formation scenario is explained in the main article. For the “slow” scenario, a 10-fold greater factor was used in r₉. The factor “1” in r₉ expresses the average availability of amino-groups (including those in ureas) over time. This simplification is permitted since (1) in essence every water molecule reacts away two MDI molecules in the organic phase (since the concentration of water is so low, MIA predominantly reacts with MDI to form a urea, rather than hydrolyzing itself), and (2) with time, any NCO groups in ureas are increasingly hydrolyzed to amino groups. This simplification affords significant reduction in modeling effort for the organic phase.

Continuity equations

The equations below are standard equations expressing the conservation of mass. The rates r_7 , r_8 , and r_9 , as well as the continuity equation for $MDI_c(t)$ are only used where relevant (heterogeneous conditions).

$$D[MDI(t)] = -r_1 - r_3 - r_4 + r_7$$

$$D[MIA(t)] = r_1 - r_2 - r_3 - 2r_5 - r_6$$

$$D[MDA(t)] = r_2 - r_4 - r_6 + r_8$$

$$D[U(t)] = r_3 + r_4 + r_5 + r_6 + r_9$$

$$D[MDI_c(t)] = -r_7 - r_8 - r_9$$

Initial conditions

Initially, only unreacted MDI is present, and there is no organic phase if $L_0 \leq S_0$:

$$MDI(0) = L_0 \text{ or } S_0, \text{ whichever is smaller}$$

$$MDI_c(0) = (L_0 - S_0) \text{ or } 0, \text{ whichever is greater}$$

$$MIA(0) = 0$$

$$MDA(0) = 0$$

$$U(0) = 0$$