The reaction-diffusion model

The chemistry of the system can be summarized as

$$
\begin{aligned}
7\,\mathrm{ClO_2^-} + 2\,\mathrm{S_4O_6^{2-}} + 6\,\mathrm{H_2O} &\longrightarrow && 7\,\mathrm{Cl^-} + 8\,\mathrm{SO_4^{2-}} + 12\,\mathrm{H^+} \\
\mathrm{M\!-\!COO^-} + \mathrm{H^+} &\rightleftharpoons && \mathrm{M\!-\!COOH} \\
\mathrm{Ba^{2+}} + \mathrm{SO_4^{2-}} &\longrightarrow && \mathrm{BaSO_4}\downarrow
\end{aligned}
\tag{1}
$$
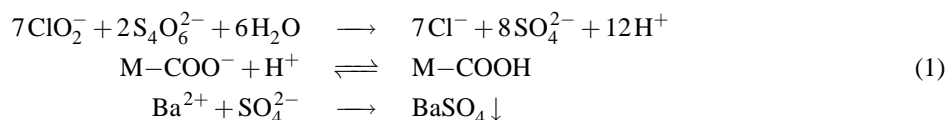
where the first reaction has an empirical rate law according to $r = k[\mathrm{ClO_2^-}][\mathrm{S_4O_6^{2-}}][\mathrm{H^+}]^2$ for small chlorite excess, while the protonation step is a fast equilibrium and the precipitation reaction is instantaneous. The concentration of chlorite ion—the reactant in excess—can be eliminated by considering the mass balance of Eq. (1) and assuming the same diffusion coefficient for thiosulfate and chlorite, yielding $[\mathrm{ClO_2^-}] = (2[\mathrm{ClO_2^-}]_0 - 7[\mathrm{S_4O_6^{2-}}]_0 + 7[\mathrm{S_4O_6^{2-}}])/2$. The governing equations then take the form

$$
\frac{\partial[\mathrm{S_4O_6^{2-}}]}{\partial t} = D\nabla^2[\mathrm{S_4O_6^{2-}}] - 2r
\tag{2}
$$

$$
\frac{\partial[\mathrm{H^+}]_t}{\partial t} = D_{\mathrm{H^+}}\nabla^2[\mathrm{H^+}] + 12r
\tag{3}
$$

$$
\frac{\partial[\mathrm{BaSO_4}]}{\partial t} = 4r
\tag{4}
$$

As a result of the fast protonation equilibrium, the temporal change in the total autocatalyst concentration $[\mathrm{H^+}]_t = [\mathrm{H^+}] + [\mathrm{-COOH}]$ can always be related to that of the free autocatalyst via

$$
\frac{\partial[\mathrm{H^+}]_t}{\partial t} = \frac{\partial[\mathrm{H^+}]}{\partial t}\left(1 + \frac{c_M K_d}{(K_d + [\mathrm{H^+}])^2}\right)
\tag{5}
$$

where K_d is the dissociation constant of the fast protonation in Eq. (1) and $c_M = [\mathrm{-COOH}] + [\mathrm{-COO^-}]$ is the amount of carboxylate groups in the gelatin.

For simplification we introduce dimensionless space and time coordinates to obtain the dimensionless forms of Eqs. (2–4) as

$$
\frac{\partial\alpha}{\partial\tau} = \widetilde{\nabla}^2\alpha - \alpha\beta^2(\kappa + 7\alpha)
\tag{6}
$$

$$
\frac{\partial\beta}{\partial\tau} = \frac{\delta\widetilde{\nabla}^2\beta}{\sigma} + \frac{6\alpha\beta^2(\kappa + 7\alpha)}{\sigma}
\tag{7}
$$

$$
\frac{\partial\gamma}{\partial\tau} = 4\alpha\beta^2(\kappa + 7\alpha)
\tag{8}
$$

where α, β, and γ are the relative concentration of tetrathionate ion, hydrogen ion, and barium sulfate precipitate with respect to the initial concentration of tetrathionate, $\delta = D_{\mathrm{H^+}}/D$. The relative chlorite excess is expressed as $\kappa = 2[\mathrm{ClO_2^-}]_0/[\mathrm{S_4O_6^{2-}}]_0 - 7$, and the autocatalyst binding as $\sigma = 1 + (K\mu)/(K + \beta)^2$, where $\mu = c_M/[\mathrm{S_4O_6^{2-}}]_0$ is the dimensionless amount of carboxylate groups in the gel and $K = K_d/[\mathrm{S_4O_6^{2-}}]_0$.