

Supplementary material

The effect of saccharides on equilibrium swelling of thermo-responsive gels

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1 Appendix A: Swelling in pure water

The specific Helmholtz free energy (per unit volume in the initial state) Ψ of a TR gel is given by Eq. (6). Combining Eqs. (1) and (6) to (8) and using Eq. (13), we find that

$$\Psi = \mu^0 C_f + k_B T_0 C_f \left(\ln \frac{C_f v}{1 + C_f v} + \frac{\chi}{1 + C_f v} \right) + \sum_{m=1}^2 W_m(I_{e1}^{(m)}, I_{e2}^{(m)}, I_{e3}^{(m)}). \quad (\text{S-1})$$

Differentiation of Eq. (S-1) with respect to time implies that

$$\begin{aligned} \dot{W} &= \left[\mu^0 + k_B T_0 \left(\ln \frac{C_f v}{1 + C_f v} + \frac{1}{1 + C_f v} + \frac{\chi}{(1 + C_f v)^2} \right) \right] \dot{C}_f \\ &+ \sum_{m=1}^2 \left(\frac{\partial W_m}{\partial I_{e1}^{(m)}} \dot{I}_{e1}^{(m)} + \frac{\partial W_m}{\partial I_{e2}^{(m)}} \dot{I}_{e2}^{(m)} + \frac{\partial W_m}{\partial I_{e3}^{(m)}} \dot{I}_{e3}^{(m)} \right), \end{aligned} \quad (\text{S-2})$$

the superscript dot stands for the derivative with respect to time t . The derivatives of the principal invariants $I_{e1}^{(m)}$, $I_{e2}^{(m)}$, $I_{e3}^{(m)}$ of the tensors $\mathbf{B}_e^{(m)}$ ($m = 1, 2$) read

$$\dot{I}_{e1}^{(m)} = 2\mathbf{B}_e^{(m)} : \mathbf{D}, \quad \dot{I}_{e2}^{(m)} = 2 \left(I_{e2}^{(m)} \mathbf{I} - I_{e3}^{(m)} (\mathbf{B}_e^{(m)})^{-1} \right) : \mathbf{D}, \quad \dot{I}_{e3}^{(m)} = 2I_{e3}^{(m)} \mathbf{I} : \mathbf{D}, \quad (\text{S-3})$$

where the colon denotes convolution,

$$\mathbf{L} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} \quad (\text{S-4})$$

is the velocity gradient, and

$$\mathbf{D} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^\top) \quad (\text{S-5})$$

is for the rate-of-strain tensor. It follows from Eqs. (S-2) and (S-3) that

$$\dot{W} = K \dot{C}_f + 2\mathbf{K} : \mathbf{D}, \quad (\text{S-6})$$

where

$$\begin{aligned} K &= \mu^0 + k_B T_0 \left[\ln \frac{C_f v}{1 + C_f v} + \frac{1}{1 + C_f v} + \frac{\chi}{(1 + C_f v)^2} \right], \\ \mathbf{K} &= \sum_{m=1}^2 \left[\frac{\partial W_m}{\partial I_{e1}^{(m)}} \mathbf{B}_e^{(m)} - I_{e3}^{(m)} \frac{\partial W_m}{\partial I_{e2}^{(m)}} (\mathbf{B}_e^{(m)})^{-1} + \left(I_{e2}^{(m)} \frac{\partial W_m}{\partial I_{e2}^{(m)}} + I_{e3}^{(m)} \frac{\partial W_m}{\partial I_{e3}^{(m)}} \right) \mathbf{I} \right]. \end{aligned} \quad (\text{S-7})$$

To develop constitutive equations for a TR gel under isothermal deformation, we apply the free energy imbalance inequality

$$\dot{\Psi} - u_{\text{mec}} - u_{\text{dif}} \leq 0, \quad (\text{S-8})$$

where u_{mec} and u_{dif} denote works (per unit volume in the initial state and unit time) produced by stresses and diffusion of solvent molecules.

The specific mechanical work is determined by the conventional formula

$$u_{\text{mec}} = J \boldsymbol{\Sigma} : \mathbf{D}, \quad (\text{S-9})$$

where $\boldsymbol{\Sigma}$ is the Cauchy stress tensor, and

$$J = \det \mathbf{F}. \quad (\text{S-10})$$

The specific work produced by solvent transport is determined by

$$u_{\text{dif}} = \mu \dot{C}_f + \bar{u}_{\text{dif}} \quad (\text{S-11})$$

with

$$\bar{u}_{\text{dif}} \geq 0. \quad (\text{S-12})$$

Eq. (S-8) is satisfied when the functions C_f and \mathbf{F} are connected by the molecular incompressibility condition (3). To account for this relation, we differentiate Eq. (3) with respect to time and find that

$$\dot{C}_f v - J \mathbf{I} : \mathbf{D} = 0. \quad (\text{S-13})$$

We multiply Eq. (S-13) by an arbitrary function Π (pressure treated as a Lagrange multiplier) and add the result to Eq. (S-8). Using Eqs. (S-6), (S-9) and (S-11), we arrive at

$$(K + \Pi v - \mu) \dot{C}_f + [2\mathbf{K} - J(\boldsymbol{\Sigma} + \Pi \mathbf{I})] : \mathbf{D} - \bar{u}_{\text{dif}} \leq 0. \quad (\text{S-14})$$

Keeping in mind that C_f and \mathbf{D} are arbitrary functions and using Eq. (S-12), we conclude that inequality (S-14) is fulfilled, provided that the chemical potential μ of water molecules reads

$$\mu = \mu^0 + k_B T_0 \bar{\mu}, \quad \bar{\mu} = \ln \frac{Q}{1+Q} + \frac{1}{1+Q} + \frac{\chi}{(1+Q)^2} + \frac{\Pi v}{k_B T_0}, \quad (\text{S-15})$$

and the Cauchy stress tensor $\boldsymbol{\Sigma}$ is given by

$$\boldsymbol{\Sigma} = -\Pi \mathbf{I} + \frac{2}{1+Q} \sum_{m=1}^2 \left[\frac{\partial W_m}{\partial I_{e1}^{(m)}} \mathbf{B}_e^{(m)} - I_{e3}^{(m)} \frac{\partial W_m}{\partial I_{e2}^{(m)}} (\mathbf{B}_e^{(m)})^{-1} + \left(I_{e2}^{(m)} \frac{\partial W_m}{\partial I_{e2}^{(m)}} + I_{e3}^{(m)} \frac{\partial W_m}{\partial I_{e3}^{(m)}} \right) \mathbf{I} \right], \quad (\text{S-16})$$

where $Q = C_f v$ stands for degree of swelling.

Eqs. (S-15) and (S-16) serve as the constitutive equations for the mechanical response and swelling of a TR gel in water. Adopting the neo-Hookean expressions (9) for the functions W_m , we present Eq. (S-16) in the form

$$\boldsymbol{\Sigma} = -\Pi \mathbf{I} + \frac{1}{1+Q} \left[G_1(\mathbf{B}_e^{(1)} - \mathbf{I}) + G_2(\mathbf{B}_e^{(2)} - \mathbf{I}) \right], \quad (\text{S-17})$$

where G_1 and G_2 denote the elastic moduli.

We now analyze unconstrained equilibrium swelling of a TR gel in a water bath with a fixed temperature T . Pressure in the bath is disregarded,

$$\Pi^{\text{bath}} = 0. \quad (\text{S-18})$$

Under equilibrium conditions, Q depends on temperature T only: $Q = Q(T)$. The deformation gradient reads

$$\mathbf{F} = \lambda \mathbf{I}, \quad (\text{S-19})$$

where the coefficient λ is calculated from Eq. (3),

$$\lambda = (1+Q)^{\frac{1}{3}}. \quad (\text{S-20})$$

Combining Eqs. (S-17), (S-19) and (S-20) and using Eq. (5), we find that

$$\boldsymbol{\Sigma} = \Sigma \mathbf{I}, \quad \Sigma = -\Pi + \frac{1}{1+Q} \left\{ G_1 \left[\left(\frac{1+Q}{1+Q_0} \right)^{\frac{2}{3}} - 1 \right] + G_2 \left[(1+Q)^{\frac{2}{3}} - 1 \right] \right\}. \quad (\text{S-21})$$

The Cauchy stress tensor $\boldsymbol{\Sigma}$ obeys the equilibrium equation

$$\boldsymbol{\nabla} \cdot \boldsymbol{\Sigma} = \mathbf{0}, \quad (\text{S-22})$$

where $\boldsymbol{\nabla}$ stands for the gradient in the actual state, and the boundary condition at the surface of a gel sample

$$\mathbf{n} \cdot \boldsymbol{\Sigma} = \mathbf{0}, \quad (\text{S-23})$$

where \mathbf{n} is the unit normal vector. Combining Eqs. (S-21) to (S-23), we conclude that

$$\Sigma = 0.$$

Inserting Eq. (S-21) into this equality and using Eq. (5), we find that

$$\Pi = \frac{1}{1+Q} \left\{ G_1 \left[\left(\frac{1+Q}{1+Q_0} \right)^{\frac{2}{3}} - 1 \right] + G_2 \left[(1+Q)^{\frac{2}{3}} - 1 \right] \right\}. \quad (\text{S-24})$$

The chemical potential of water molecules inside a gel is determined by Eq. (S-15). Its chemical potential in the bath is given by the same equality where the terms describing interactions between water molecules and segments of chains are neglected,

$$\mu^{\text{bath}} = \mu^0. \quad (\text{S-25})$$

Substituting expressions (S-15) and (S-25) into the equilibrium condition

$$\mu = \mu^{\text{bath}}, \quad (\text{S-26})$$

and using Eq. (S-24), we arrive at the equation

$$\ln \frac{Q}{1+Q} + \frac{1}{1+Q} + \frac{\chi}{(1+Q)^2} + \frac{g_1}{1+Q} \left[\left(\frac{1+Q}{1+Q_0} \right)^{\frac{2}{3}} - 1 \right] + \frac{g_2}{1+Q} \left[(1+Q)^{\frac{2}{3}} - 1 \right] = 0, \quad (\text{S-27})$$

where

$$g_m = \frac{G_m v}{k_B T_0} \quad (m = 1, 2)$$

are dimensionless elastic moduli.

2 Appendix B: Swelling in solution of additives

We now analyze the thermo-mechanical response of a TR gel in an aqueous (solvent-1) solution of an additive (solvent-2).

The specific energy of cosolvent molecules not interacting with each other and with segments of polymer chains is given by

$$\Psi_1 = \mu_1^0 C_1 + \mu_2^0 C_2, \quad (\text{S-28})$$

where C_1, C_2 are concentrations of these molecules in the gel, and μ_1^0, μ_2^0 are their chemical potentials when all mutual interactions are disregarded. Using Eqs. (21) and (24), we present Eq. (S-28) in the form

$$\Psi_1 = (\mu_1^0 \phi_1^{\text{bath}} + \mu_2^0 \phi_2^{\text{bath}}) C_f. \quad (\text{S-29})$$

For a TR gel in the swollen state, where hydrophobic segments do not form aggregates (serving as physical bonds between chains), the strain energy density of the polymer network reads

$$\Psi_2 = W_1(I_{e1}^{(1)}, I_{e2}^{(1)}, I_{e3}^{(1)}). \quad (\text{S-30})$$

The specific energy of interaction between segments of chains and cosolvent molecules is determined by Eq. (22),

$$\begin{aligned} \Psi_{\text{int}} = & k_{\text{B}}T_0C_{\text{f}} \left[\ln \frac{C_{\text{f}}v}{1+C_{\text{f}}v} + \frac{\chi_{13}\phi_1^{\text{bath}} + \chi_{23}\phi_2^{\text{bath}} + \chi_{12}\phi_1^{\text{bath}}\phi_2^{\text{bath}}C_{\text{f}}v}{1+C_{\text{f}}v} \right. \\ & \left. + (\phi_1^{\text{bath}} \ln \phi_1^{\text{bath}} + \phi_2^{\text{bath}} \ln \phi_2^{\text{bath}}) \right]. \end{aligned} \quad (\text{S-31})$$

The specific Helmholtz free energy (per unit volume in the initial state) Ψ of a TR gel in a binary solution is given by Eq. (6),

$$\begin{aligned} \Psi = & \left[(\mu_1^0\phi_1^{\text{bath}} + \mu_2^0\phi_2^{\text{bath}}) + k_{\text{B}}T_0(\phi_1^{\text{bath}} \ln \phi_1^{\text{bath}} + \phi_2^{\text{bath}} \ln \phi_2^{\text{bath}} + \chi_{12}\phi_1^{\text{bath}}\phi_2^{\text{bath}}) \right] C_{\text{f}} \\ & + k_{\text{B}}T_0C_{\text{f}} \left(\ln \frac{C_{\text{f}}v}{1+C_{\text{f}}v} + \frac{\chi_{*}}{1+C_{\text{f}}v} \right) + W_1(I_{\text{e}1}^{(1)}, I_{\text{e}2}^{(1)}, I_{\text{e}3}^{(1)}), \end{aligned} \quad (\text{S-32})$$

where

$$\chi_{*} = \chi_{13}\phi_1^{\text{bath}} + \chi_{23}\phi_2^{\text{bath}} - \chi_{12}\phi_1^{\text{bath}}\phi_2^{\text{bath}}. \quad (\text{S-33})$$

Differentiating Eq. (S-32) with respect to time (under the assumption that χ_{*} is independent of C_{f}), we find that

$$\begin{aligned} \dot{W} = & \left[(\mu_1^0\phi_1^{\text{bath}} + \mu_2^0\phi_2^{\text{bath}}) + k_{\text{B}}T_0(\phi_1^{\text{bath}} \ln \phi_1^{\text{bath}} + \phi_2^{\text{bath}} \ln \phi_2^{\text{bath}} + \chi_{12}\phi_1^{\text{bath}}\phi_2^{\text{bath}}) \right. \\ & \left. + k_{\text{B}}T_0 \left(\ln \frac{C_{\text{f}}v}{1+C_{\text{f}}v} + \frac{1}{1+C_{\text{f}}v} + \frac{\chi_{*}}{(1+C_{\text{f}}v)^2} \right) \right] \dot{C}_{\text{f}} \\ & + \left(\frac{\partial W_1}{\partial I_{\text{e}1}^{(1)}} \dot{I}_{\text{e}1}^{(1)} + \frac{\partial W_1}{\partial I_{\text{e}2}^{(1)}} \dot{I}_{\text{e}2}^{(1)} + \frac{\partial W_1}{\partial I_{\text{e}3}^{(1)}} \dot{I}_{\text{e}3}^{(1)} \right). \end{aligned} \quad (\text{S-34})$$

It follows from Eqs. (S-3) and (S-34) that

$$\dot{W} = K\dot{C}_{\text{f}} + 2\mathbf{K} : \mathbf{D}, \quad (\text{S-35})$$

where

$$\begin{aligned} K = & (\mu_1^0\phi_1^{\text{bath}} + \mu_2^0\phi_2^{\text{bath}}) + k_{\text{B}}T_0(\phi_1^{\text{bath}} \ln \phi_1^{\text{bath}} + \phi_2^{\text{bath}} \ln \phi_2^{\text{bath}} + \chi_{12}\phi_1^{\text{bath}}\phi_2^{\text{bath}}) \\ & + k_{\text{B}}T_0 \left[\ln \frac{C_{\text{f}}v}{1+C_{\text{f}}v} + \frac{1}{1+C_{\text{f}}v} + \frac{\chi_{*}}{(1+C_{\text{f}}v)^2} \right], \\ \mathbf{K} = & \frac{\partial W_1}{\partial I_{\text{e}1}^{(1)}} \mathbf{B}_{\text{e}}^{(1)} - I_{\text{e}3}^{(1)} \frac{\partial W_1}{\partial I_{\text{e}2}^{(1)}} (\mathbf{B}_{\text{e}}^{(1)})^{-1} + \left(I_{\text{e}2}^{(1)} \frac{\partial W_1}{\partial I_{\text{e}2}} + I_{\text{e}3}^{(1)} \frac{\partial W_1}{\partial I_{\text{e}3}^{(1)}} \right) \mathbf{I}. \end{aligned} \quad (\text{S-36})$$

Substituting Eq. (S-36) into the free energy imbalance inequality (S-8) and repeating the transformations performed in Appendix A, we arrive at the formula for the chemical potential of solvent molecules in the gel

$$\mu = (\mu_1^0\phi_1^{\text{bath}} + \mu_2^0\phi_2^{\text{bath}}) + k_{\text{B}}T_0(\phi_1^{\text{bath}} \ln \phi_1^{\text{bath}} + \phi_2^{\text{bath}} \ln \phi_2^{\text{bath}} + \chi_{12}\phi_1^{\text{bath}}\phi_2^{\text{bath}}) + k_{\text{B}}T_0\bar{\mu} \quad (\text{S-37})$$

with

$$\bar{\mu} = \ln \frac{Q}{1+Q} + \frac{1}{1+Q} + \frac{\chi_*}{(1+Q)^2} + \frac{\Pi v}{k_B T_0}, \quad (\text{S-38})$$

and the stress-strain relation for the Cauchy stress tensor Σ

$$\Sigma = -\Pi \mathbf{I} + \frac{2}{1+Q} \left[\frac{\partial W_1}{\partial I_{e1}^{(1)}} \mathbf{B}_e^{(1)} - I_{e3}^{(1)} \frac{\partial W_1}{\partial I_{e2}^{(1)}} (\mathbf{B}_e^{(1)})^{-1} + \left(I_{e2}^{(1)} \frac{\partial W_1}{\partial I_{e2}} + I_{e3}^{(1)} \frac{\partial W_1}{\partial I_{e3}^{(1)}} \right) \mathbf{I} \right]. \quad (\text{S-39})$$

When the functions W_1 is described by the neo-Hookean expression (9), Eq. (S-39) is simplified,

$$\Sigma = -\Pi \mathbf{I} + \frac{G_1}{1+Q} (\mathbf{B}_e^{(1)} - \mathbf{I}). \quad (\text{S-40})$$

Under unconstrained equilibrium swelling of a TR gel in an aqueous solution of an additive, osmotic pressure Π in the gel is determined by an analog of Eq. (S-24),

$$\Pi = \frac{G_1}{1+Q} \left[\left(\frac{1+Q}{1+Q_0} \right)^{\frac{2}{3}} - 1 \right], \quad (\text{S-41})$$

the chemical potential of solvent molecules inside the gel is given by Eq. (S-37), and their chemical potential in the bath is given by the same equality where the terms describing interactions between solvent molecules and segments of chains are neglected,

$$\mu^{\text{bath}} = (\mu_1^0 \phi_1^{\text{bath}} + \mu_2^0 \phi_2^{\text{bath}}) + k_B T_0 (\phi_1^{\text{bath}} \ln \phi_1^{\text{bath}} + \phi_2^{\text{bath}} \ln \phi_2^{\text{bath}} + \chi_{12} \phi_1^{\text{bath}} \phi_2^{\text{bath}}). \quad (\text{S-42})$$

Substituting expression (S-37) and (S-42) into the equilibrium condition (S-26), and using Eqs. (S-38) and (S-41), we find that

$$\ln \frac{Q}{1+Q} + \frac{1}{1+Q} + \frac{\chi_*}{(1+Q)^2} + \frac{g_1}{1+Q} \left[\left(\frac{1+Q}{1+Q_0} \right)^{\frac{2}{3}} - 1 \right] = 0. \quad (\text{S-43})$$

Eq. (S-43) with χ_* given by Eq. (S-33) provides the governing equation for equilibrium degree of swelling Q of a TR gel in an aqueous solution of additives.

3 Appendix C: Partitioning of additives

The specific free energy of molecules of solvent-1 and solvent-2 not interacting with each other and with segments of polymer chains is given by Eq. (S-28), where C_1 , C_2 denote concentration of molecules of solvent-1 and solvent-2 in the gel, and μ_1^0 , μ_2^0 are chemical potentials of these molecules when all mutual interactions are disregarded.

The specific energy of the polymer network is determined by Eq. (S-30), where W_1 is the specific mechanical energy stored in polymer chains of the covalently cross-linked network.

The specific energy of interaction between segments of chains and cosolvent molecules is determined by Eq. (2),

$$\Psi_{\text{int}} = k_{\text{B}}T_0 \left[\left(C_1 \ln \frac{C_1 v}{1 + C_{\text{f}}v} + C_2 \ln \frac{C_2 v}{1 + C_{\text{f}}v} \right) + \frac{\chi_{13}C_1 + \chi_{23}C_2 + \chi_{12}C_1C_2v}{1 + C_{\text{f}}v} \right].$$

The Helmholtz free energy of a TR gel (per unit volume in the initial configuration) equals the sum of the above three terms, see Eq. (6), which implies that

$$\begin{aligned} \Psi = & \mu_1^0 C_1 + \mu_2^0 C_2 + W_1(I_{\text{e}1}^{(1)}, I_{\text{e}2}^{(1)}, I_{\text{e}3}^{(1)}) + k_{\text{B}}T_0 \left[C_1 \ln \frac{C_1 v}{1 + (C_1 + C_2)v} \right. \\ & \left. + C_2 \ln \frac{C_2 v}{1 + (C_1 + C_2)v} + \frac{\chi_{13}C_1 + \chi_{23}C_2 + \chi_{12}C_1C_2v}{1 + (C_1 + C_2)v} \right]. \end{aligned} \quad (\text{S-44})$$

Differentiating Eq. (S-44) with respect to time and using Eq. (S-3), we find that

$$\dot{\Psi} = K_1 \dot{C}_1 + K_2 \dot{C}_2 + 2\mathbf{K} : \mathbf{D}. \quad (\text{S-45})$$

Here

$$\begin{aligned} K_1 &= \mu_1^0 + k_{\text{B}}T_0 \left[\ln \phi_1 + \phi_{\text{n}} + \chi_{13}\phi_{\text{n}}^2 + \phi_2 \left((\chi_{13} - \chi_{23} + \chi_{12})\phi_{\text{n}} + \chi_{12}\phi_2 \right) \right], \\ K_2 &= \mu_2^0 + k_{\text{B}}T_0 \left[\ln \phi_2 + \phi_{\text{n}} + \chi_{23}\phi_{\text{n}}^2 + \phi_1 \left((\chi_{23} - \chi_{13} + \chi_{12})\phi_{\text{n}} + \chi_{12}\phi_1 \right) \right], \\ \mathbf{K} &= \frac{\partial W_1}{\partial I_{\text{e}1}^{(1)}} \mathbf{B}_{\text{e}}^{(1)} - I_{\text{e}3}^{(1)} \frac{\partial W_1}{\partial I_{\text{e}2}^{(1)}} (\mathbf{B}_{\text{e}}^{(1)})^{-1} + \left(I_{\text{e}2}^{(1)} \frac{\partial W_1}{\partial I_{\text{e}2}^{(1)}} + I_{\text{e}3}^{(1)} \frac{\partial W_1}{\partial I_{\text{e}3}^{(1)}} \right) \mathbf{I}, \end{aligned} \quad (\text{S-46})$$

and we use notation (20),

$$\phi_1 = \frac{C_1 v}{1 + C_{\text{f}}v}, \quad \phi_2 = \frac{C_2 v}{1 + C_{\text{f}}v}, \quad \phi_{\text{n}} = \frac{1}{1 + C_{\text{f}}v} \quad (\text{S-47})$$

with

$$C_{\text{f}} = C_1 + C_2.$$

We now substitute Eq. (S-45) into the free energy imbalance inequality (S-8) with u_{mec} given by Eq. (S-9) and u_{dif} determined by the formula

$$u_{\text{dif}} = \mu_1 \dot{C}_1 + \mu_2 \dot{C}_2 + \bar{u}_{\text{dif}}. \quad (\text{S-48})$$

Repeating the transformations described in Appendix A, and adopting the neo-Hookean expression (9) for the elastic potential W_1 , we arrive at Eq. (S-39) for the Cauchy stress

tensor and the following relations for the chemical potentials of solvent-1 and solvent-2 molecules:

$$\mu_1 = \mu_1^0 + k_B T_0 \bar{\mu}_1, \quad \mu_2 = \mu_2^0 + k_B T_0 \bar{\mu}_2, \quad (\text{S-49})$$

where

$$\begin{aligned} \bar{\mu}_1 &= \ln \phi_1 + \phi_n + \chi_{13} \phi_n^2 + (\chi_{13} - \chi_{23} + \chi_{12}) \phi_2 \phi_n + \chi_{12} \phi_2^2 + \frac{\Pi v}{k_B T_0}, \\ \bar{\mu}_2 &= \ln \phi_2 + \phi_n + \chi_{23} \phi_n^2 + (\chi_{23} - \chi_{13} + \chi_{12}) \phi_1 \phi_n + \chi_{12} \phi_1^2 + \frac{\Pi v}{k_B T_0}. \end{aligned} \quad (\text{S-50})$$

The chemical potentials of solvent-1 and solvent-2 molecules in the bath are determined by Eqs. (S-49) and (S-50), where all terms describing interactions between the polymer network and cosolvents are disregarded:

$$\mu_1^{\text{bath}} = \mu_1^0 + k_B T_0 \bar{\mu}_1^{\text{bath}}, \quad \mu_2^{\text{bath}} = \mu_2^0 + k_B T_0 \bar{\mu}_2^{\text{bath}} \quad (\text{S-51})$$

with

$$\bar{\mu}_1^{\text{bath}} = \ln \phi_1^{\text{bath}} + \chi_{12} (\phi_2^{\text{bath}})^2, \quad \bar{\mu}_2^{\text{bath}} = \ln \phi_2^{\text{bath}} + \chi_{12} (\phi_1^{\text{bath}})^2. \quad (\text{S-52})$$

Under equilibrium swelling of a TR gel in a bath with volume fractions of cosolvents ϕ_1^{bath} and ϕ_2^{bath} , pressure Π is determined by Eq. (S-41), and the quantities ϕ_1 , ϕ_2 and ϕ_n are found from the equations

$$\mu_1 = \mu_1^{\text{bath}}, \quad \mu_2 = \mu_2^{\text{bath}} \quad (\text{S-53})$$

and the condition

$$\phi_1 + \phi_2 + \phi_n = 1. \quad (\text{S-54})$$

Substitution of expressions (S-49)–(S-52) into Eq. (S-53) results in the nonlinear equations

$$\begin{aligned} & \ln \phi_1 + \phi_n + \chi_{13} \phi_n^2 + (\chi_{13} - \chi_{23} + \chi_{12}) \phi_2 \phi_n + \chi_{12} \phi_2^2 + g_1 \phi_n \left[\left(\frac{\phi_n}{\phi_{n0}} \right)^{-\frac{2}{3}} - 1 \right] \\ &= \ln \phi_1^{\text{bath}} + \chi_{12} (\phi_2^{\text{bath}})^2, \\ & \ln \phi_2 + \phi_n + \chi_{23} \phi_n^2 + (\chi_{23} - \chi_{13} + \chi_{12}) \phi_1 \phi_n + \chi_{12} \phi_1^2 + g_1 \phi_n \left[\left(\frac{\phi_n}{\phi_{n0}} \right)^{-\frac{2}{3}} - 1 \right] \\ &= \ln \phi_2^{\text{bath}} + \chi_{12} (\phi_1^{\text{bath}})^2, \end{aligned} \quad (\text{S-55})$$

where $\phi_{n0} = (1 + Q_0)^{-1}$.

Subtracting the last equality in Eq. (S-55) from the first one and using Eq. (S-54), we find, after simple algebra, that

$$\ln \frac{\phi_1}{\phi_2} + (\chi_{13} - \chi_{23})\phi_n + \chi_{12}(\phi_2 - \phi_1) = \ln \frac{\phi_1^{\text{bath}}}{\phi_2^{\text{bath}}} + \chi_{12}(\phi_2^{\text{bath}} - \phi_1^{\text{bath}}). \quad (\text{S-56})$$

It follows from Eq. (S-47) that

$$\phi_1 = \frac{\varphi_1 Q}{1 + Q}, \quad \phi_2 = \frac{\varphi_2 Q}{1 + Q}, \quad \phi_n = \frac{1}{1 + Q}. \quad (\text{S-57})$$

Insertion of Eq. (S-57) into Eq. (S-56) implies that

$$\ln \frac{\varphi_1}{\varphi_2} + \frac{\chi_{13} - \chi_{23}}{1 + Q} + \chi_{12}(\varphi_2 - \varphi_1) \frac{Q}{1 + Q} = \ln \frac{\phi_1^{\text{bath}}}{\phi_2^{\text{bath}}} + \chi_{12}(\phi_2^{\text{bath}} - \phi_1^{\text{bath}}).$$

Bearing in mind that

$$\varphi_1 = 1 - \varphi_2, \quad \phi_1^{\text{bath}} = 1 - \phi_2^{\text{bath}},$$

we conclude that

$$\ln \frac{1 - \varphi_2}{\varphi_2} + \frac{\chi_{13} - \chi_{23}}{1 + Q} + \chi_{12}(2\varphi_2 - 1) \frac{Q}{1 + Q} = \ln \frac{1 - \phi_2^{\text{bath}}}{\phi_2^{\text{bath}}} + \chi_{12}(2\phi_2^{\text{bath}} - 1). \quad (\text{S-58})$$

It follows from Eqs. (23) and (S-58) that

$$\ln \frac{1 - P\phi_2^{\text{bath}}}{P(1 - \phi_2^{\text{bath}})} + \frac{\chi_{13} - \chi_{23} + \chi_{12}}{1 + Q} + 2\chi_{12}\phi_2^{\text{bath}} \left(\frac{PQ}{1 + Q} - 1 \right) = 0. \quad (\text{S-59})$$

At small volume fractions of additives in the bath, $\phi_2^{\text{bath}} \ll 1$, Eq. (S-59) is simplified,

$$\ln P = \frac{\chi_{13} - (\chi_{23} - \chi_{12})}{1 + Q}.$$

Combination of this equality with Eq. (29) results in the formula

$$P = \exp\left(\frac{\chi_{13} - K}{1 + Q}\right). \quad (\text{S-60})$$

Keeping in mind that for a TR gel,

$$\chi_{13} = \chi_0 + \chi_1 T,$$

we find from Eq. (S-60) that

$$P = \exp\left(\frac{\chi_0 + \chi_1 T - K}{1 + Q}\right). \quad (\text{S-61})$$

Tables

Table S-1: Material parameters for PNIPA gel in water and NaCl solution (Fig. S-1A,B)

	T_c °C	β_2	\bar{g}_2/g_1
Water	32.0	1.23	7.7
NaCl solution	24.0	1.23	7.9

Table S-2: Material parameters for PNIPA gel in water (Fig. S-2A)

χ_0	χ_1	χ_{\max}	Q_0	g_1	\bar{g}_2	β_2
-2.098	0.079	0.555	12.81	0.024	4.5	0.1

Table S-3: Material parameters for PNIPA gel in water (Fig. 1-A)

χ_0	χ_1	χ_{\max}	Q_0	g_1	\bar{g}_2	β_2
-2.098	0.079	0.563	18.5	0.011	0.13	0.1

Table S-4: Parameter K for PNIPA gel in aqueous solutions of saccharides (Figs. 1-B,C,D)

Saccharides	K
Galactose	8.3
Glucose	7.0
Sucrose	4.8

Figures

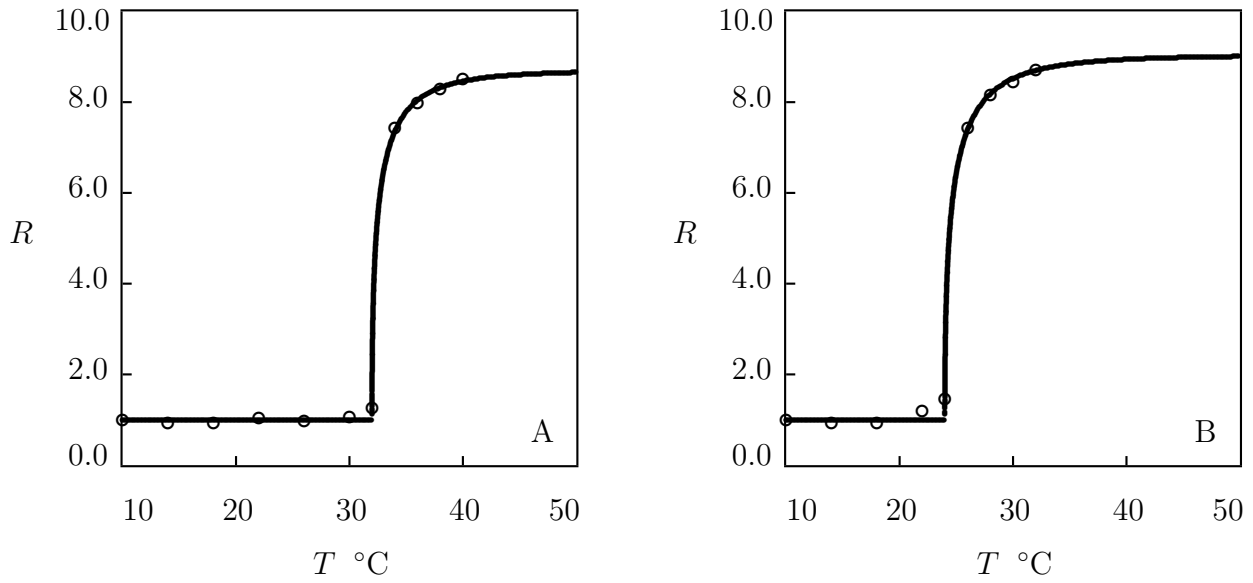


Figure S-1: The ratio of Young's moduli $R = E(T)/E(T_0)$ with $T_0 = 10$ °C versus temperature T . Circles: experimental data [50] on PNIPA gel in pure water (A) and aqueous solution of NaCl with concentration 0.5 mol/L (B). Solid lines: results of simulation.

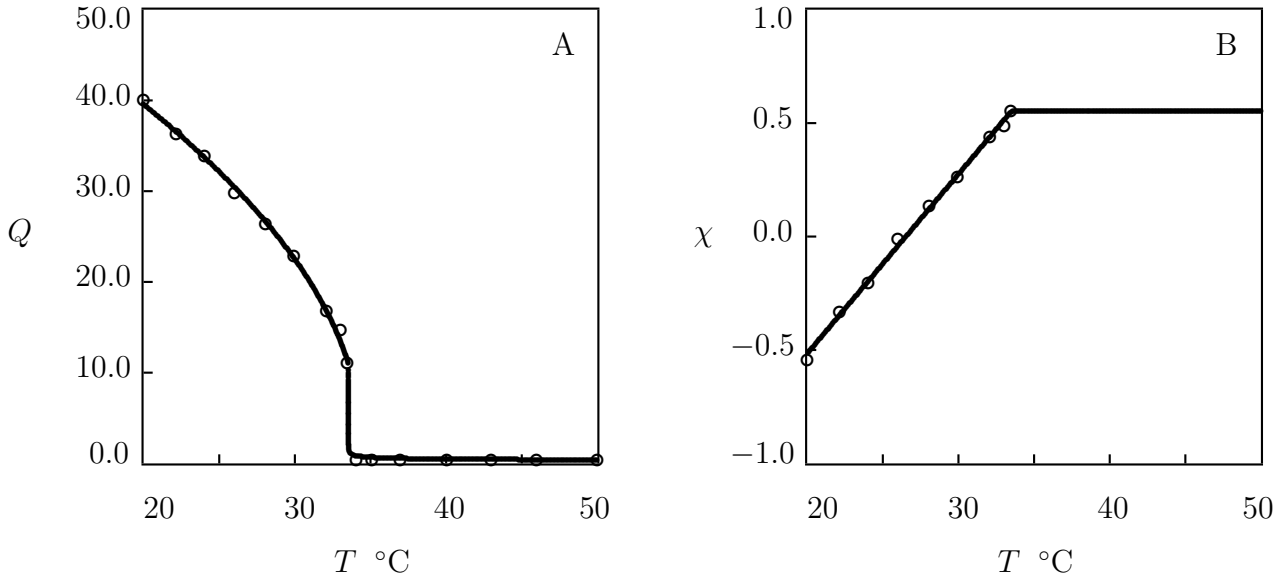


Figure S-2: A – Degree of swelling Q versus temperature T . Circles: experimental data [53] on PNIPA gel prepared by irradiation of polymer solution with $\Gamma = 20$ kGy. Solid line: results of simulation. B – Parameter χ versus temperature T . Circles: treatment of observations. Solid line: results of simulation.

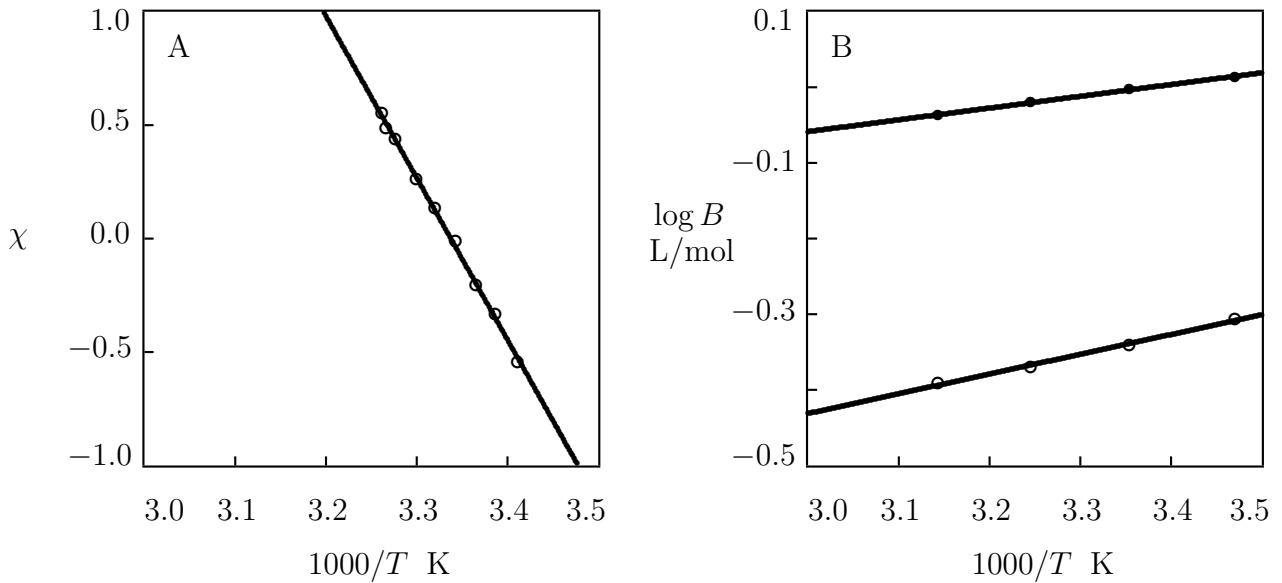


Figure S-3: A – Parameter χ versus temperature T . Circles: treatment of observations [53] on PNIPA gel. Solid line: approximation of the data by the equation $\chi = \chi_0 - E_a/(RT)$ with $E_a = 59.3$ kJ/mol. B – Viscosity B -coefficient versus temperature T . Symbols: experimental data [60] on aqueous solutions of glucose (\circ) and sucrose (\bullet). Solid lines: approximation of the data by the Arrhenius law with $E_a = 5.0$ (glucose) and 3.0 (sucrose) kJ/mol.

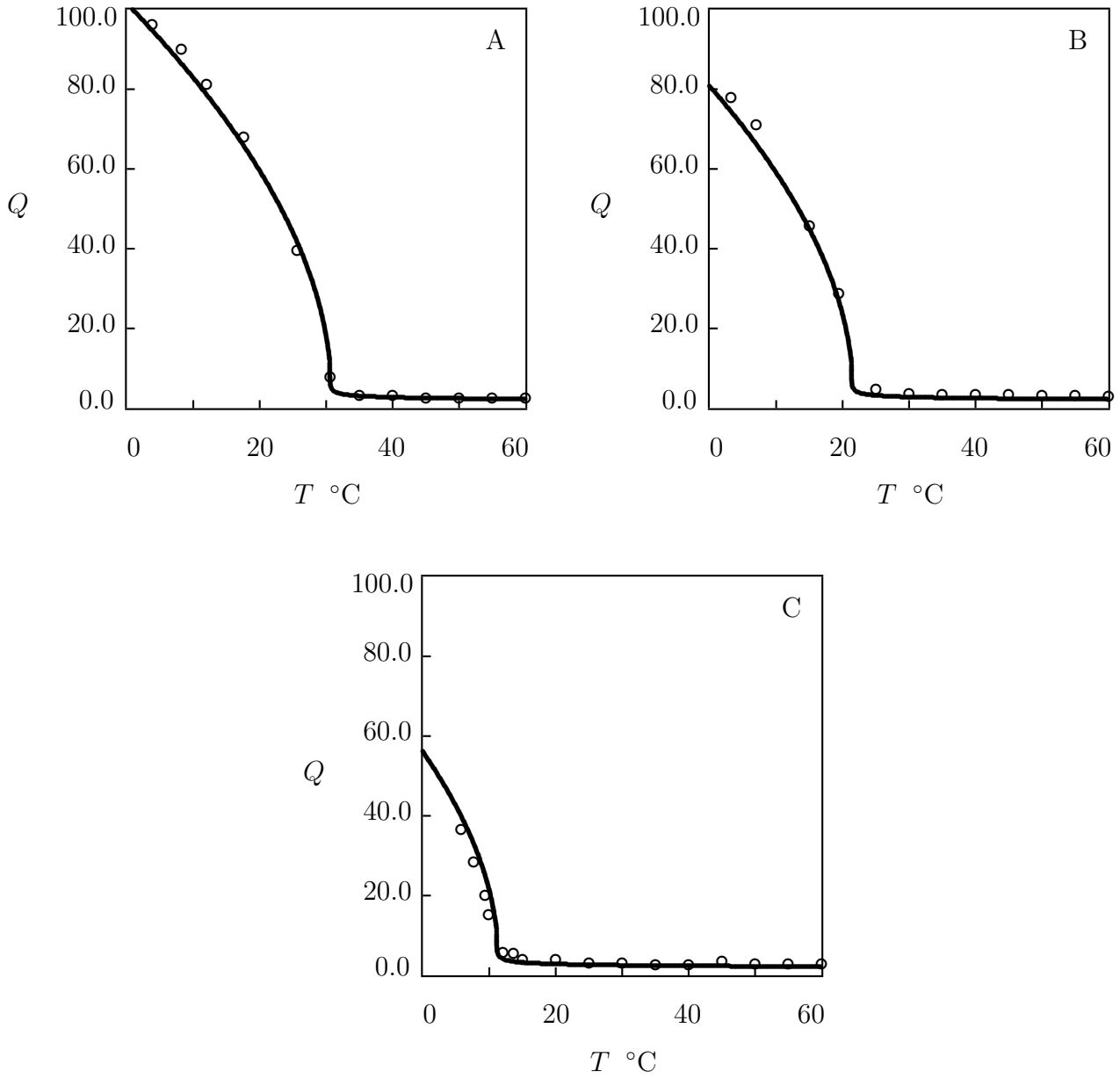


Figure S-4: Degree of swelling Q versus temperature T . Circles: experimental data [8] on PNIPA gel in aqueous solutions of galactose with volume fractions $\phi_2^{\text{bath}} = 0.305$ (A), 0.112 (B) and 0.213 (C). Solid lines: predictions of the model.

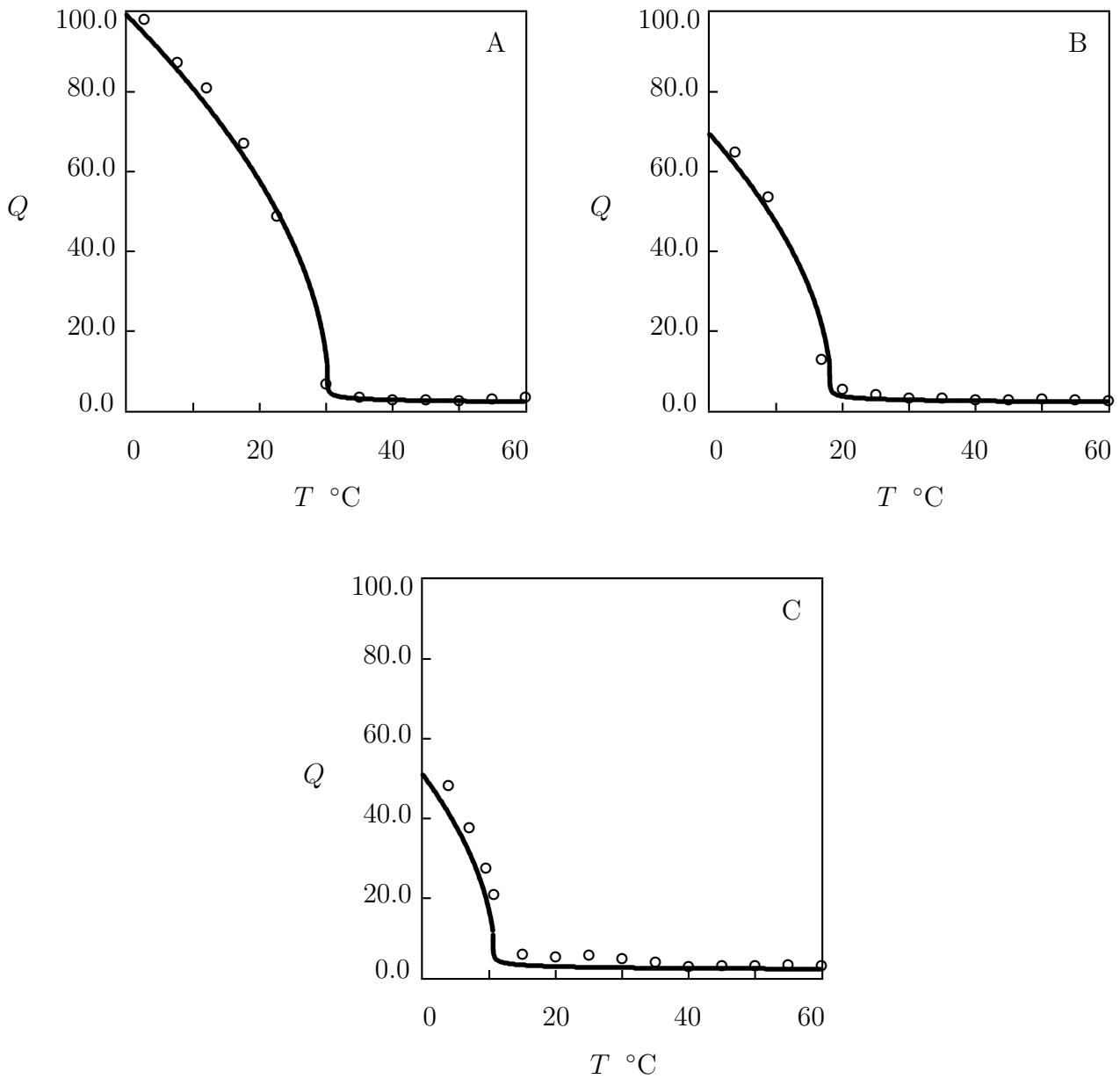


Figure S-5: Degree of swelling Q versus temperature T . Circles: experimental data [8] on PNIPA gel in aqueous solutions of sucrose with volume fractions $\phi_2^{\text{bath}} = 0.061$ (A), 0.225 (B) and 0.301 (C). Solid lines: predictions of the model.

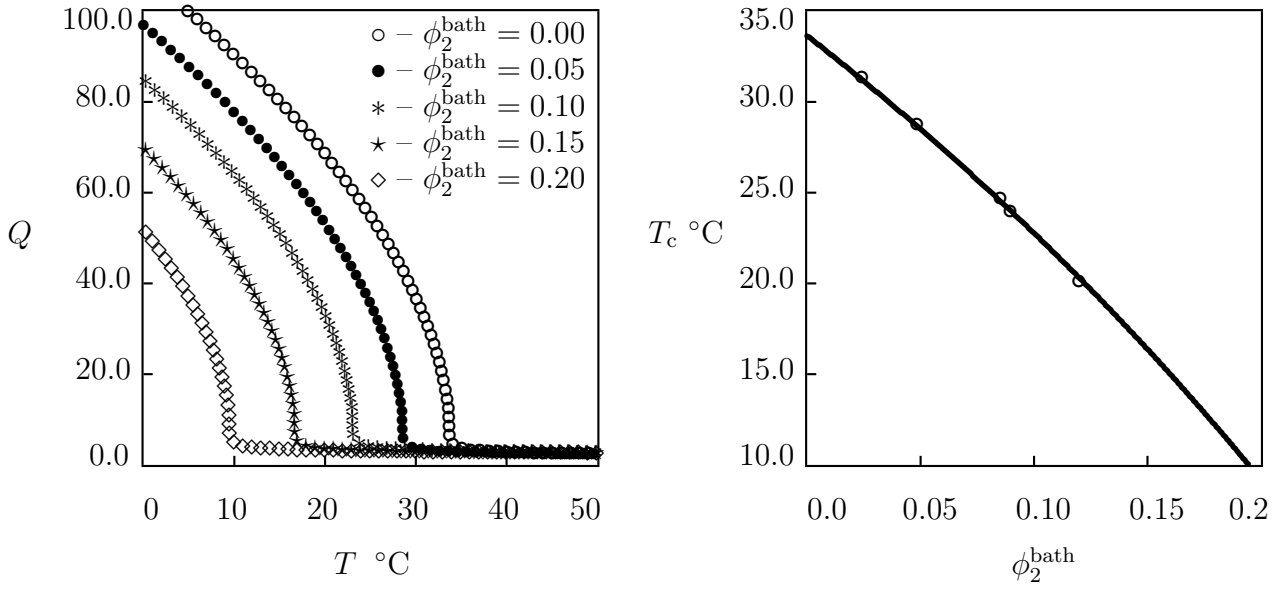


Figure S-6: A – Degree of swelling Q versus temperature T . Symbols: results of simulation for PNIPA gel in aqueous solutions of galactose with various volume fractions ϕ_2^{bath} . B – Volume phase transition temperature T_c versus volume fraction of galactose in the bath ϕ_2^{bath} . Circles: experimental data [65]. Solid line: predictions of the model.

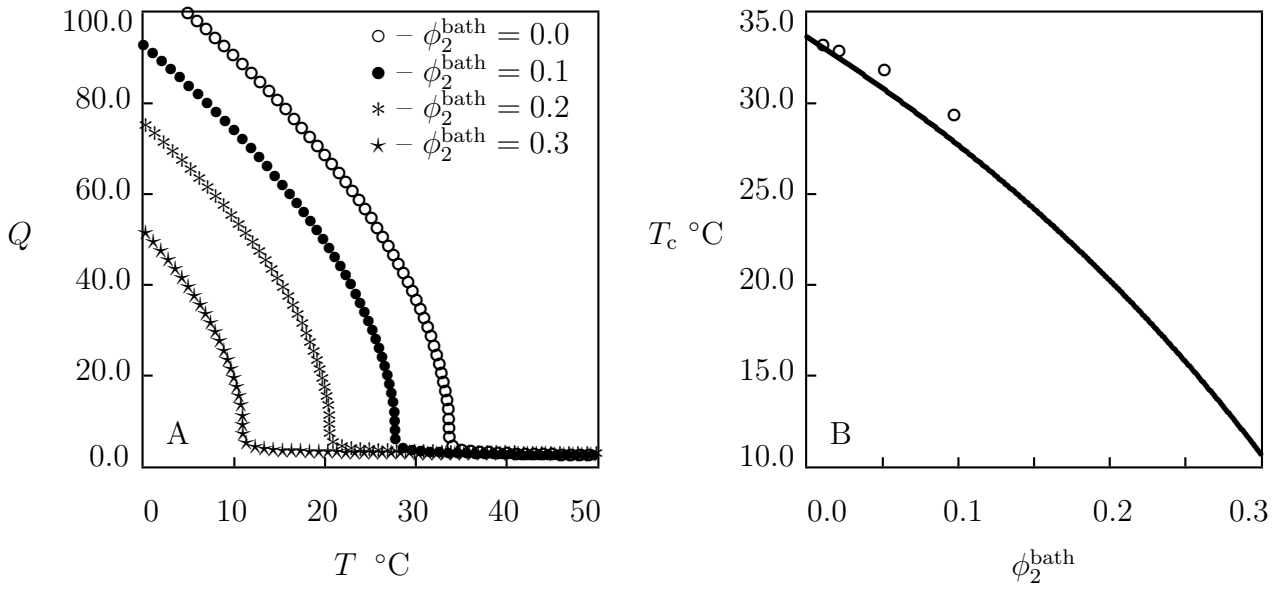


Figure S-7: A – Degree of swelling Q versus temperature T . Symbols: results of simulation for PNIPA gel in aqueous solutions of sucrose with various volume fractions ϕ_2^{bath} . B – Volume phase transition temperature T_c versus volume fraction of sucrose in the bath ϕ_2^{bath} . Circles: experimental data [67]. Solid line: predictions of the model.

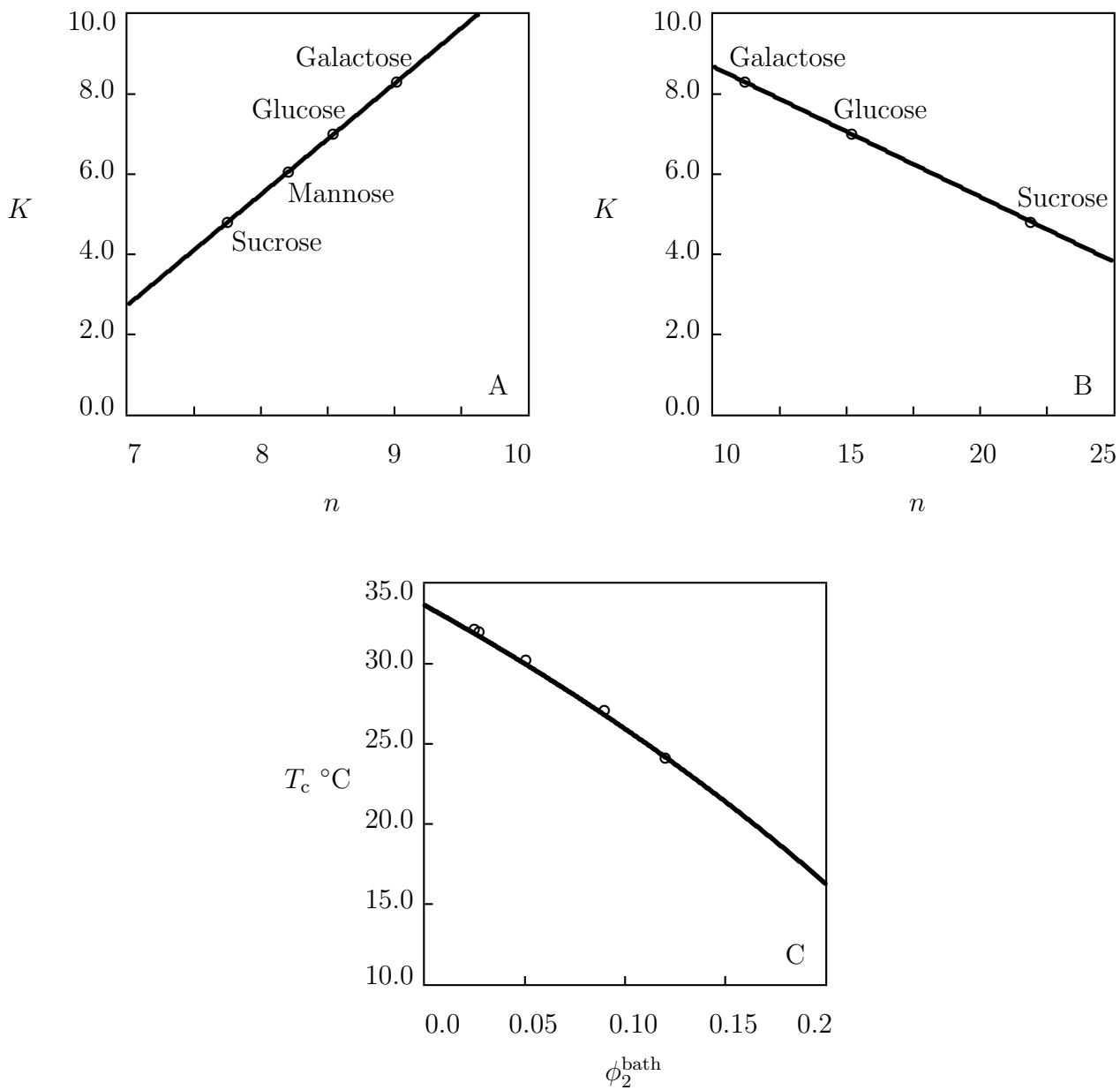


Figure S-8: A,B – Coefficient K versus hydration number n . Circles: experimental data [68,69] (A) and [70] (B). Solid lines: results of simulation. C – Volume phase transition temperature T_c versus volume fraction of mannose in the bath ϕ_2^{bath} . Circles: experimental data [65]. Solid line: predictions of the model.