

[Supporting information]

1. Role of Binding isotherm model

The fraction of occupied binding sites (θ) is represented below:

$$\theta = \frac{\Gamma}{\Gamma_{\infty}} = \frac{c_{surf}}{K_L + c_{surf}} \quad (S1)$$

where Γ is the concentration of the bound surfactant at the interface; Γ_{∞} is the maximum possible concentration of the bound surfactant at the interface; c_{surf} is the concentration of the surfactant in the bulk solution; K_L is a Langmuir constant related to the energy of binding per molecule, respectively.

Depending on the value of Langmuir constant (K_L), binding isotherm curves are varied significantly as below in Figure S1.

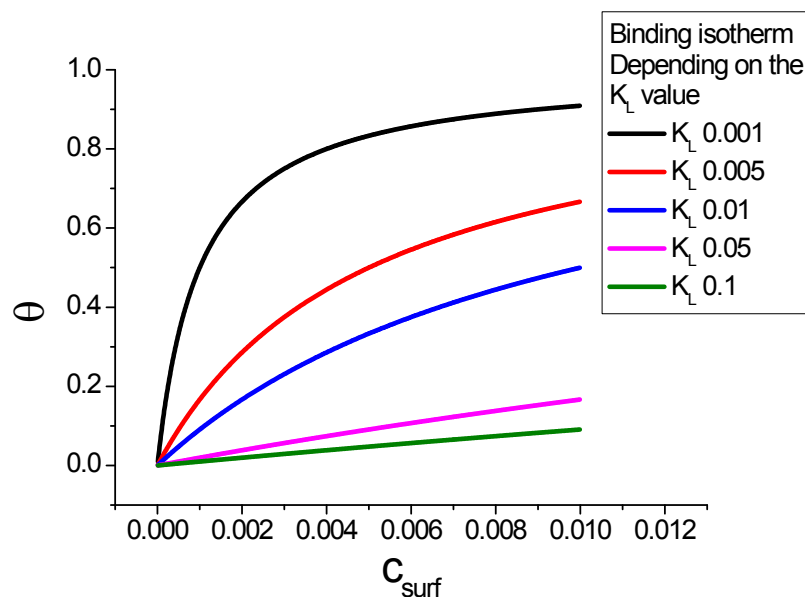


Figure S1. Binding isotherm curves calculated by Langmuir isotherm model depending on the value of K_L .

As the energy of binding is increased (as the value of K_L is increased), surfactant molecules became hard to be bound onto the interface (the value of θ is decreased). The binding isotherms are determined by K_L value adjusting the VPTT increment of hydrogel in surfactant solution (Case II). In addition, contribution of electrostatic interaction from bound surfactant is supplemented by adding the interfacial tension contribution. Generalized form of Langmuir isotherm suggested by Borwankar and Wasan considers the electric potential of bound species onto the interface, and enhanced swelling ability of the hydrogel is successfully described (Case III).

2. Phase Equilibrium Calculation

2.1. Calculation Procedure

Surfactant-free Solution (Case I)

Step 1	Read the predetermined parameters (r_i , m_c , ϕ_{g0}), and experimental data (Swelling Ratio (SR), T).
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Step 2	Obtain the adjustable parameters (ε_{12}/k , $\delta\varepsilon_{12}/k$) which minimize the error with experimental data by evaluating that net chemical potential of component 1 (Water) equal zero ($\Delta\mu_{1,net} = \Delta\mu_{1,mix} + \Delta\mu_{1,ela} = 0$).
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Step 3	Using the obtained adjustable parameters (ε_{12}/k , $\delta\varepsilon_{12}/k$), calculate the ϕ_1^{gel} value when net chemical potential of component 1 is zero at T_1 . : Print [$SR \left(= \frac{\phi_{g0}}{1 - \phi_1^{gel}} \right), T_1$].
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Repeat "Steps 3" with increasing (or decreasing) the T

Surfactant Solution (Case II and III)

Case II

Step 1	Read the predetermined parameters (r_i , m_c , ϕ_{g0} , $\frac{\mu_0^s - \mu_0}{kT}$, δ), obtained
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	parameters (ε_{12}/k , $\delta\varepsilon_{12}/k$) from Case I, and experimental data about the all-range of surfactant concentration (Swelling Ratio (SR), T , c_{surf}).
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Step 2	Obtain the adjustable parameters ($\delta\varepsilon_{BS,w}/k$, K_L) which minimize the error with volume phase transition temperature (VPTT) of experimental data by evaluating that net chemical potential of component 1 (Water) equal zero ($\Delta\mu_{1,net} = \Delta\mu_{1,mix} + \Delta\mu_{1,ela} = 0$).
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Step 3	Using the obtained adjustable parameters ($\delta\varepsilon_{BS,w}/k$, K_L), calculate the ϕ_1^{gel} value when net chemical potential of component 1 is zero at T_1 . : Print [$SR \left(= \frac{\phi_{g0}}{1 - \phi_1^{gel}} \right), T_1$].
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Repeat “Steps 3” with increasing (or decreasing) the T
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Case III

Step 1	Read the predetermined parameters (r_i , m_c , ϕ_{g0} , $\frac{\mu_0^s - \mu_0}{kT}$, δ), obtained parameters (ε_{12}/k , $\delta\varepsilon_{12}/k$, $\delta\varepsilon_{BS,w}/k$, K_L) from Case I and II, and experimental data about the all-range of surfactant concentration (Swelling Ratio (SR), T , c_{surf}).
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Step 2	Obtain the adjustable parameter (ψ_s) which minimize the error with swollen state of experimental data by evaluating that net chemical potential of component 1 (Water) equal zero ($\Delta\mu_{1,net} = \Delta\mu_{1,mix} + \Delta\mu_{1,ela} = 0$).
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Step 3	Using the obtained adjustable parameter (ψ_s), calculate the ϕ_1^{gel} value when net chemical potential of component 1 is zero at T_1 . : Print [$SR \left(= \frac{\phi_{g0}}{1 - \phi_1^{gel}} \right), T_1$].
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Repeat “Steps 3” with increasing (or decreasing) the T
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2.2. Discussion of phase equilibrium calculation

To describe the swelling equilibrium of the hydrogel system in surfactant solution, we compare the three cases of modeling (Case I, II and III) in this work. Using the MDL model as a representative mixing contribution, phase equilibrium calculation is presented in terms of chemical potential. Calculation results for the thermosensitive swelling of the poly(N-vinylcaprolactam) (PNVCL) gel in a 4.01mM sodium dodecyl sulfate (SDS) surfactant solution are utilized in this section.

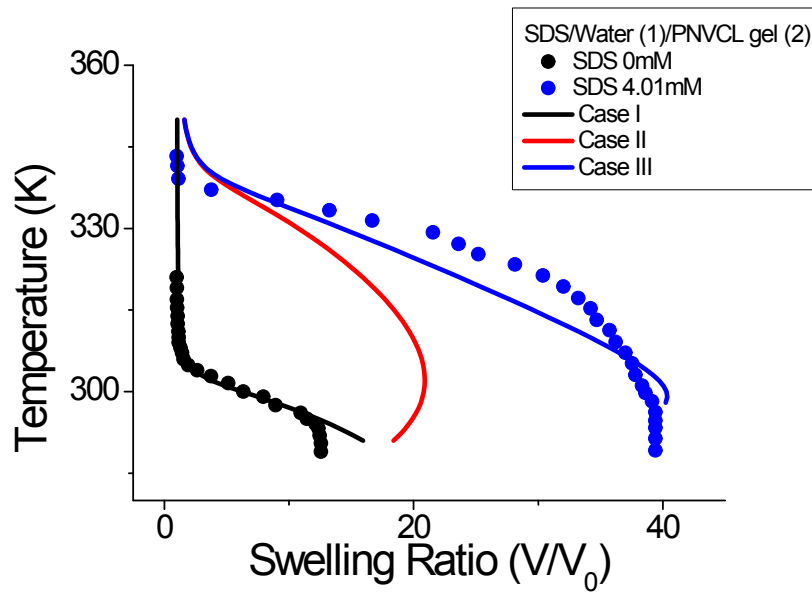


Figure S2. Experimental results of the thermosensitive swelling behavior of the PNVC gel in SDS solution and the modeling results for Case I, II and II. Dots and lines represent experimental results and modeling results, respectively.

2.2.1. Effect of temperature on the phase equilibrium

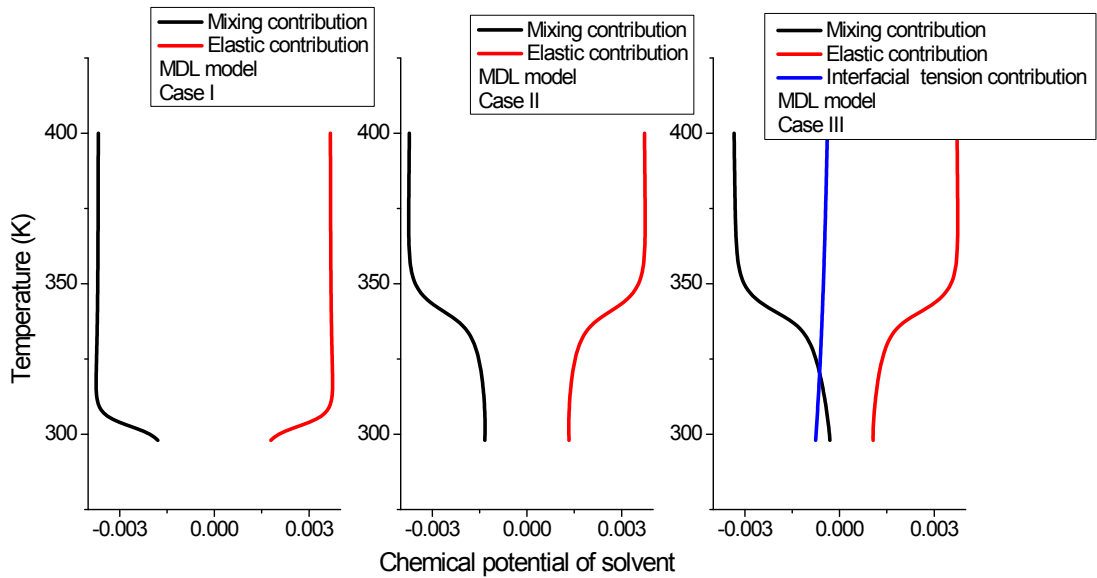


Figure S3. Effect of temperature on each contribution of chemical potential of solvent at equilibrium condition: (a) Case I, (b) Case II and (c) Case III.

In case I, mixing and elastic contributions are combined to describe the swelling behavior of the hydrogel system as Figure S3(a). For mixing contribution of case II, combination of the binding isotherm and the secondary lattice term are added. As a results, descriptions of increased transition temperature are represented in Figure S3(b) and red line of Figure S2. The interfacial tension contribution accounting for the electrostatic interaction of bound surfactants is included in Figure S3(c), which gives minus contribution to the net chemical potential. Effect of this minus contribution generates the enhanced swelling ability in modeling and will be explained by the phase equilibrium calculation in isothermal condition.

2.2.2. Phase Equilibrium in Isothermal condition

In isothermal condition, equilibrium swelling ratio at gel system is determined by finding the volume fraction of solvent which meet the roots of the net chemical potential. According to the collapsed/swelling condition, the net chemical potential curves by volume fraction of solvent (ϕ) represent different shape. Three isothermal conditions (T1: 400K, T2: 320K, and T3: 298K) and three modeling cases (Case I, II and III) are treated in Figure S3 and S4. Classification of collapsed and swollen state according to the three cases of calculation results is listed in Table S1.

Table S1. Collapsed/Swollen state at each temperature

Temperature	Case I	Case II	Case III
T1 (400K)	Collapsed	Collapsed	Collapsed
T2 (320K)	Collapsed	Swollen	Swollen
T3 (298K)	Swollen	Swollen	Swollen

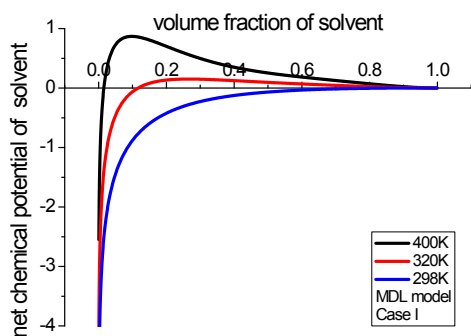


Figure S4. Net chemical potential curves at three temperatures: (a) Case I and (b) Case II.

As we mentioned above, different shape of curves are represented in Figure S3 depending on the collapsed and swollen state. Figure S4 shows two collapsed-type curves (at 400K and 320K) which have only one root and maxima near the pure gel phase and one swollen-type curves (at 298K) which have only one root and maxima near the pure solvent phase.

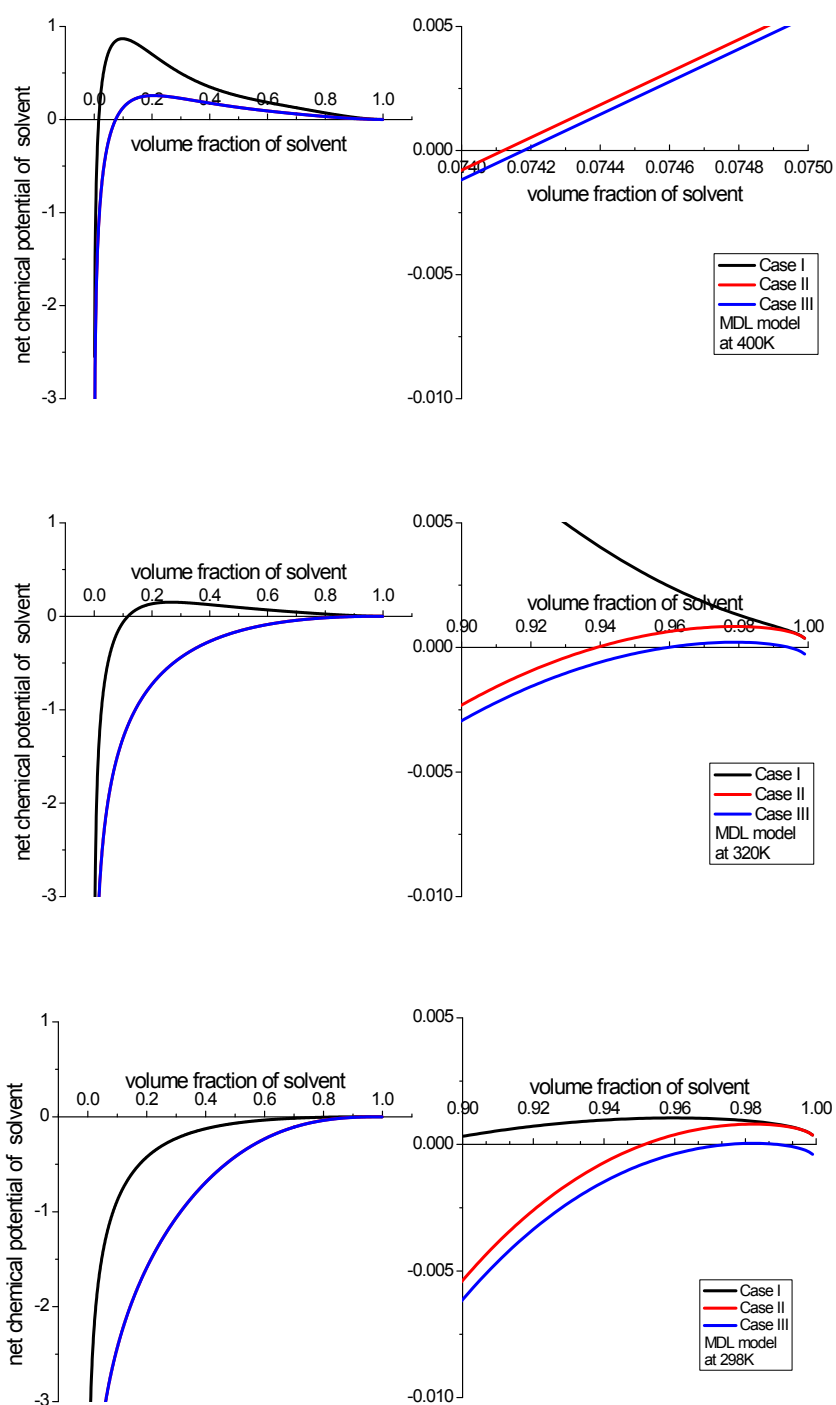


Figure S5. Net chemical potential curves by three cases of modeling: (a) 400K, (b) 320K and (c) 298K.

In Figure S5 (a2), (b2) and (c2), the net chemical potential curves of case III move slightly downward of graph compared to the case II. The minus contribution of interfacial

contribution, which is observed in sec.2.2.1., make the volume fraction of solvent at equilibrium increased, which mean the enhanced swelling ratio.

3. Limitation of MDL based model for describing the gel swelling

As we derived in our previous work, the net chemical potential of solvent for MDL with FR chain model meet equilibrium condition as follow in binary hydrogel system:

$$\begin{aligned}
\frac{\Delta\mu_{1,net}}{kT} = 0 = & \ln\left(1 - \frac{\phi_{g0}}{SR}\right) + r_1 \left(\frac{\phi_{g0}}{SR}\right) \left(\frac{1}{r_1} - \frac{1}{r_2}\right) + r_1 C_\beta \left(\frac{\phi_{g0}}{SR}\right)^2 \left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 \\
& + \frac{\phi_{g0}^{2/3}}{2m_c} \left(\frac{\phi_{g0}}{SR} - \frac{1}{2} \frac{\phi_{g0}}{SR} + \frac{3}{2} \frac{\phi_{g0}^2}{SR}\right) - \frac{1}{2m_c} \left(\frac{\phi_{g0}}{SR}\right)^2 \left(1 + \ln\left(\frac{\phi_{g0}}{SR}\right)\right) \\
& + \left[r_1 \left(\frac{\phi_{g0}}{SR}\right)^2 \left(2 + \frac{1}{r_1}\right) - 2r_2 \frac{\phi_{g0}}{SR} \left(\frac{\phi_{g0}}{SR}\right)^2 \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \right] \mathcal{E} \\
& + r_1 C_\gamma \left(1 - \frac{\phi_{g0}}{SR}\right) \left(\frac{\phi_{g0}}{SR}\right)^2 \left(\left(1 - \frac{\phi_{g0}}{SR}\right) - 2 \frac{\phi_{g0}}{SR}\right) \mathcal{E}
\end{aligned} \tag{S2}$$

Eq (S2) is simply arranged as

$$0 = A + B\mathcal{E} + C\mathcal{E}^2 \tag{S3}$$

where

$$\begin{aligned}
A &= \ln\left(1 - \frac{\phi_{g0}}{SR}\right) + r_1 \left(\frac{\phi_{g0}}{SR}\right) \left(\frac{1}{r_1} - \frac{1}{r_2}\right) + r_1 C_\beta \left(\frac{\phi_{g0}}{SR}\right)^2 \left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 \\
&\quad + \frac{\phi_{g0}^{2/3}}{2m_c} \left(\frac{\phi_{g0}}{SR}^{1/3} - \frac{1}{2} \frac{\phi_{g0}^{4/3}}{SR} + \frac{3}{2} \frac{\phi_{g0}^2}{SR}\right) - \frac{1}{2m_c} \left(\frac{\phi_{g0}}{SR}\right)^2 \left(1 + \ln\left(\frac{\phi_{g0}}{SR}\right)^2\right) \\
B &= \left[r_1 \left(\frac{\phi_{g0}}{SR}\right)^2 \left(2 + \frac{1}{r_1}\right) - 2r_1 \frac{\phi_{g0}}{SR} \left(\frac{\phi_{g0}}{SR}\right)^2 \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \right] \\
C &= r_1 C_\gamma \left(1 - \frac{\phi_{g0}}{SR}\right) \left(\frac{\phi_{g0}}{SR}\right)^2 \left(\left(1 - \frac{\phi_{g0}}{SR}\right) - 2 \frac{\phi_{g0}}{SR}\right)
\end{aligned} \tag{S4}$$

Eq. (S3) is also rearranged as below

$$\mathcal{E} = -\frac{B}{2C} \pm D^{1/2} \tag{S5}$$

where

$$D = \left(\frac{B^2}{4C^2} - \frac{A}{C}\right) \tag{S6}$$

Eq. (S5) become an imaginary quantity when eq. (S6) is negative number. The plot of eq. (S6)

as function of SR is represented as below:

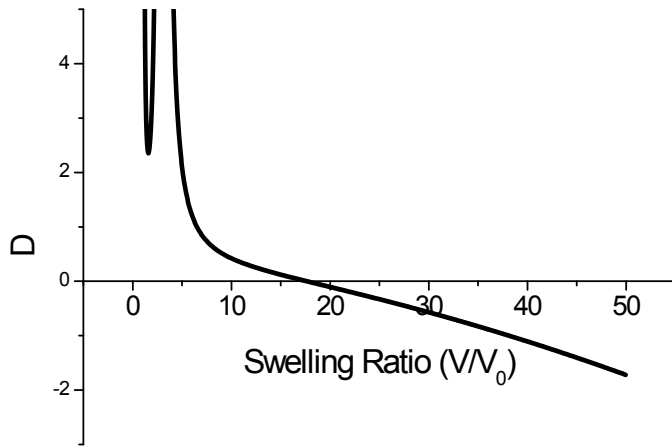


Figure S6. The behavior of determinant (D) as function of the swelling ratio (SR). ($r_1 = 1$, $r_2 = \infty$, $m_c = 100$, $\phi_{g0} = 1$).

In Figure S6, determinant (D) is negative number when swelling ratio exceeds 17.66. Thus swelling ratio over this value cannot be described under the given parameter value, and we observe that MDL base model represent limitation to describe the swelling behavior of gel system.