

Thermodynamic Analysis of Hydrogel Swelling in Aqueous Sodium Chloride Solutions

Sheik Tanveer^a and Chau-Chyun Chen^{a, *}

^a Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, USA

* Corresponding author. Tel.: +1 806.834.3098. Email address: chauchyun.chen@ttu.edu

ORCID: Chau-Chyun Chen: 0000-0003-0026-9176

Abstract

A comprehensive thermodynamic model is presented for swelling and salt partitioning of poly (n-isopropyl acrylamide) hydrogels in aqueous sodium chloride (NaCl) solutions at 298 K. Together with a Helmholtz energy expression for network elastic energy, a modified electrolyte Nonradom Two-Liquid activity coefficient model is used to represent both the long-range electrostatic interactions and the short-range van der Waals interactions present in the gel phase. The model parameters include one network parameter per hydrogel system plus two binary parameters per interaction pair in the polymer-solvent-salt systems. With semiquantitative agreement with experimental data for both hydrogel swelling and salt partitioning up to salt saturation, the analysis suggests the ion hydration between NaCl and water is the root cause for hydrogel deswelling in aqueous NaCl solution at high NaCl concentrations, i.e., NaCl weight fraction > 0.03 . On the other hand, the strong repulsive interactions between NaCl and hydrogel polymer is the dominant factor for salt partitioning.

Keywords: Electrolyte NRTL Model; Hydrogel Swelling; Polymer NRTL Model; Salt Partitioning;

1. Introduction

Hydrogels are three-dimensional hydrophilic crosslinked viscoelastic network of polymer chains. They can be natural, such as collagen, or synthetic, such as poly (n-isopropyl acrylamide) hydrogels. Crosslinking gives hydrogels the physical structure and elasticity in their network, making it possible to stretch or shrink. Depending on surrounding conditions such as temperature, pressure, solvent composition, salt content, and pH, hydrogels exhibit significant volume changes without changing their structural properties [1]. An increase in hydrogel volume is known as swelling, and collapse is known as deswelling. This abrupt volume transition is influenced by chemical properties of the polymer chain [2] such as the presence of hydrophobic groups [3], the crosslink density, and interactions of polymer segments with solvents and salts . Hydrogels that respond on external stimulus is called “intelligent” hydrogels [3, 4]. Intelligent hydrogels have a broad range of applications, including enhanced oil recovery [5], contact lenses [6], drug delivery [7], biosensors, pharmaceutical applications, and separation processes [3].

n-Isopropyl acrylamide (IPAAm) hydrogels, perhaps the most studied thermo-sensitive intelligent hydrogel, have many interesting applications. IPAAm hydrogels can be used to transport and release the drug inside the human body [3]. During the fracking process, self-suspending particles called proppants may be encapsulated with IPAAm hydrogel to make it highly viscous and prevent it from settling down inside the fracking site [5]. In addition, IPAAm hydrogels are well-known for application in biosensors and tissue engineering [8].

IPAAm hydrogel swelling is very sensitive to temperature and solvent composition. IPAAm hydrogels are soluble in water (H₂O) and have a lower critical solution temperature (LCST) at around 305 K [4]. The presence of co-solvents or salts in solution has dramatic effects

on the hydrogel swelling behavior. In pure water or organic solvents such as ethanol, IPAAm hydrogels show high swelling, whereas it deswells when the hydrogel is exposed in specific mixed solvent compositions [2, 9, 10]. Also, the gradual addition of salts, such as NaCl, in water decreases the hydrogel swelling, and the hydrogel shrinks abruptly after specific salt concentrations [11, 12]. Park and Hoffman [13] reported temperature-dependent salt-induced phase transition behavior (i.e., LCST) in aqueous solutions. Later, Du et al. [12] claimed the polymer-salt interactions play a critical role in the shift of LCST.

A few thermodynamic studies have been reported in the literature for the swelling behavior of IPAAm hydrogels under the influence of aqueous salt solutions. Hooper et al. [14] presented a thermodynamic model to describe hydrogel swelling in aqueous salt solutions. They investigated both IPPAm hydrogels and “ionized” IPPAm hydrogels formed by copolymerization with ionic co-monomers. Defining a “swelling pressure” as the difference between the osmotic pressures of the two phases, they calculated the swelling pressure with three contributions: the elastic term from elasticity of deformed chain during swelling/deswelling, the mixing term from polymer/solvent mixing, and the ionic term based on ideal Donnan equilibrium to account for the “presence of mobile and bound ions.” Three “exchange energy” parameters in the mixing term were used to regress isothermal swelling data. Partitioning of solvents and salts in the coexisting phases (the gel phase and the bulk liquid phase) was not addressed. Later Maurer and Prausnitz [15] presented a comprehensive thermodynamic framework to describe swelling behavior of nonionic and ionic hydrogels in mixed organic solvents and aqueous salt solutions. The framework rigorously established the partitioning relationships for the solvents and salts in the coexisting phases. Built on this thermodynamic framework, Islam et al. [10] investigated the swelling behavior of IPAAm hydrogels in aqueous organic solvents with

polymer Nonrandom Two-Liquid (NRTL) activity coefficient model [16]. Having successfully correlated both the swelling data and the solvent partitioning data, they found that the swelling is governed by the solvent compositions in the bulk solution, and the gels collapse when the mixed solvent from an ideal solution with the hydrogel polymer.

Following the framework of Maurer and Prausnitz [15], Hüther et al. [11] investigated the swelling of IPAAm hydrogels in aqueous NaCl solutions. To estimate the activity coefficients of the solvent and salts for IPAAm hydrogels immersed in aqueous salt solutions, they extended the Pitzer activity coefficient model [17] by substituting species concentrations with “relative surface fractions” and incorporating a free volume expression with the Pitzer model to account for “additional differences in the size of the species” [2]. A modified Phantom network theory proposed by James and Guth [18] was used to estimate the elastic energy of the gel. While they reported satisfactory results in correlating the data on the degree of swelling and the partitioning of NaCl in the coexisting phases, the Pitzer model formulation is exceedingly cumbersome for engineering calculations. Specifically, to model swelling behavior of IPAAm hydrogels in aqueous NaCl solutions at 298 K, the extended Pitzer model requires 20 pure component parameters, 12 binary interaction parameters, and 10 tertiary interaction parameters. These interaction parameters arise from the ionic strength-dependent virial expansion of the excess Gibbs free energy expression for the solution.

This work presents a new attempt to perform thermodynamic analysis on swelling and salt partitioning of IPAAm hydrogels in aqueous NaCl solutions. Following the thermodynamic framework of Maurer and Prausnitz [15], we substitute the extended Pitzer model of Hüther et al. [11] with a modified electrolyte Nonrandom Two-Liquid (eNRTL) activity coefficient model for aqueous electrolyte solutions [19-22]. Specifically, we expand the eNRTL model by integrating

the segment concept of polymer NRTL model [16] into eNRTL and we further account for the configurational entropy of mixing polymers and solvents.

The paper is arranged as follows: Section 2 details the IPAAm hydrogels examined in this work; Section 3 presents the thermodynamic equilibrium conditions for swelling equilibria; Section 4 summarizes the parameter estimation methodologies; Section 5 discusses the model results and then followed by concluding remarks.

2. IPAAm Hydrogels

This work investigates the swelling of IPAAm hydrogels in aqueous NaCl solutions with data from Hüther et al. [11]. Details of the synthesis procedure have been reported by Hüther et al. [2] and Hüther et al. [11]. The following terms are used to describe the hydrogel swelling behavior.

Mass of swollen hydrogel, m_{gel} , is the sum of the mass of IPAAm monomer, m_{mon} , the mass of crosslinker, m_c , and the mass of solvent, m_{sol} , in the swollen hydrogel.

$$m_{gel} = m_{mon} + m_c + m_{sol}, \quad (1)$$

Mass fraction of the polymerizable substance in the swollen hydrogel, w_{gel} , is the ratio of the sum of the monomer mass and the crosslinker mass to the swollen gel mass, m_{gel} .

$$w_{gel} = \frac{m_{mon} + m_c}{m_{gel}}, \quad (2)$$

The crosslinker mole fraction, x_c , is the ratio of the moles of crosslinker, n_c , to the sum of the moles of monomer, n_{mon} , and the moles of crosslinker.

$$x_c = \frac{n_c}{n_{mon} + n_c}, \quad (3)$$

Degree of swelling, q , is the ratio of the swollen gel mass to the dry (i.e., solvent free) gel mass, m_{gel}^{dry} .

$$q = \frac{m_{gel}}{m_{gel}^{dry}}, \quad (4)$$

The IPAAm hydrogel polymer chains form a tetra-functional network. For such crosslinked polymer network, we treat the polymer segments between two crosslink points as one polymer chain, i.e.

$$n_{chain} = 2n_c, \quad (5)$$

where n_{chain} denotes the moles of polymer chains in hydrogel. The number of polymer segments between two crosslink points, r , can be defined as

$$r = \frac{1-x_c}{2x_c}, \quad (6)$$

and the molar volume of the polymer chain, v_{chain} , is defined as the product of r and the molar volume of the polymer segment, v_s .

$$v_{chain} = rv_s, \quad (7)$$

In the study by Hüther et al. [11], w_{gel} was fixed at 0.08 and 0.1, and x_c was fixed at 0.01, 0.015, and 0.02, respectively. For all the hydrogels, the initiator concentration in the polymerization reaction was fixed at the range of $(1.81-1.84) \times 10^{-4}$ gram/gram of polymerizable solution. The study reported data for the degree of swelling and the salt concentration in the coexisting phases. Following the naming convention established in our prior study on modeling swelling of IPAAm hydrogels in aqueous organic solvents [10], we name the four hydrogels examined in this study as G1 to G4, and their corresponding hydrogel properties, w_{gel} and x_c , are given in Table 1. All the hydrogels show a high degree of swelling at low salt concentrations,

i.e., NaCl mass fraction of $\sim 10^{-4}$ in the bulk liquid phase, and collapse at high salt concentrations, i.e., NaCl mass fraction of $\sim 10^{-2}$ in the bulk liquid phase.

3. Equilibrium conditions for hydrogel swelling in Aqueous Sodium Chloride Solutions

When IPAAm hydrogels are immersed in aqueous NaCl solutions, both water molecules and salt species permeate inside the gel phase until equilibrium is achieved. As described by Maurer and Prausnitz [15], at a given temperature and pressure, energy of the system, which includes the Gibbs free energy of the coexisting phases (G^b for the surrounding bulk liquid phase and G^{gel} for the gel phase) and the Helmholtz free energy of the elastic polymer membrane, A^m , should reach a minimum at thermodynamic equilibrium:

$$G^b(T, p, n^b) + G^{gel}(T, p, n^{gel}) + A^m(T, V^{gel}) \rightarrow \text{minimum} \quad (8)$$

where superscript b denotes bulk liquid phase; superscript gel denotes gel phase; T is the system temperature; p is the pressure of the bulk phase; n is the number of moles; V^{gel} is the volume of the gel phase at equilibrium. In the present work, T is 298.15 K and p is fixed at 1 bar.

From Eq. 8, Maurer and Prausnitz [15] derived the following phase equilibrium condition.

$$\ln a_i^b(T, p, n_k^b) = \ln a_i^{gel}(T, p, n_k^{gel}) + \frac{v_i^{gel} \left(\frac{\partial A^m}{\partial V^{gel}} \right)}{RT}, \quad (9)$$

where a is the activity; i is the species index for solvents and salts; n is the number of moles; k denotes all other species; v is the molar volume; R is the universal gas constant. In Eq. 9, the derivative term arising from the Helmholtz energy of the gel network is expressed as

$$\left(\frac{\partial A^m}{\partial V} \right)_T = \frac{3CRTn_{chain}}{2V} \left(\frac{V}{V_0} \right)^{2/3}, \quad (10)$$

with V_0 is the volume of the hydrogel at stress-free condition (i.e. at preparation), and C is the adjustable hydrogel network parameter. Details of the Helmholtz energy expression are available in the literature [2, 10].

Activity of salt NaCl can be expressed as Eq. 11.

$$a_{NaCl} = (a_{Na^+})(a_{Cl^-}), \quad (11)$$

As mentioned earlier, a modified version of the eNRTL activity coefficient model is used to model the hydrogel system. Briefly, the modified eNRTL model presents the excess Gibbs free energy of the aqueous hydrogel electrolyte solution, g^{ex} , as the sum of three contributions: (1) $g^{ex,lc}$ for the short-range van der Waals interaction contribution, (2) $g^{ex,PDH}$ for the long-range ion-ion interaction contribution, and (3) $g^{ex,comb}$ for the contribution from combinatorial entropy of mixing of species in the system.

$$g^{ex} = g^{ex,lc}(x, \alpha_{ij}, \tau_{ij}) + g^{ex,PDH}(x) + g^{ex,comb}(x, \phi), \quad (12)$$

here x denotes the mole fractions of species in solution; α_{ij} and τ_{ij} denote the nonrandomness factor and the asymmetric binary interaction parameters for each interacting pair of species i and j , respectively; ϕ denotes volume fractions of the species. Details of the model are given in **Supporting Information**. With α_{ij} typically fixed at value of 0.2 to 0.3 [19], there are two adjustable binary interaction parameters, τ_{ij} , per interacting pair of species $i - j$.

We calculate activity coefficient of component i , γ_i , from g^{ex} .

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial g^{ex}}{\partial n_i} \right)_{T,P,n_{j \neq i}}, \quad (13)$$

The activity coefficient of the IPAAm segment, γ_{IPAAm} , is calculated from the activity coefficient of the IPPAm polymer chain, $\gamma_{polymer}$.

$$\ln \gamma_{IPAAm} = \frac{\ln \gamma_{polymer}}{r}, \quad (14)$$

Note that water and polymer IPAAm are treated as solvent species. The reference states for solvents are pure liquid state while the reference state for electrolytes is the infinite dilution state in aqueous solution. We use a correction term, commonly known as “Born term” [21], to change the reference state for electrolytes from the infinite dilution state in mixed solvent to that in aqueous solution in the calculation of the long-range ion-ion interaction contribution to the activity coefficient of ions. Details of the “Born term” correction are discussed in the **Supporting Information**. Walker et al. [23] reported dielectric constant of an IPAAm hydrogel ($w_{gel} = 0.1$, $x_c = 0.15$) as 72, from which we calculated dielectric constant of IPAAm polymer as 53. We retrieved the molar volume of species from Hüther et al. [11], which set 18.06 cm³/mol for water, Na⁺, and Cl⁻, whereas, for IPAAm segment, the value is 101.38 cm³/mol. The molar volume of NaCl is calculated as the sum of the corresponding values of Na⁺ and Cl⁻.

4. Parameter estimation

Data on degree of swelling and NaCl concentrations in the coexisting phases for the hydrogels, G1 to G4, are available from Hüther et al. [11]. To model the hydrogel systems, we require the hydrogel network parameter C for each hydrogel and two binary interaction parameters per pair of the polymer-water-salt ternary mixture. For the gels G1, G2, and G3, we retrieved the network parameter C from Islam et al. [10]. We retrieved the binary interaction parameters for the H₂O:(Na⁺ Cl⁻) pair from Yan and Chen [24] and the binary interaction parameters for the IPAAm segment:H₂O pair from Islam et al. [10]. The binary interaction parameters for the IPAAm segment:(Na⁺ Cl⁻) pair for the hydrogels and the network parameter C

for G4 are identified in this work. The network parameter C for the hydrogels are given in Table 1 while the binary interaction parameters for the pairs are reported in Table 2.

The objective function, F , to be minimized in the regression is formulated similar to as that in ASPEN Properties[®] (version 10) [25] and can be written as

$$F = \sum_{k=1}^K W_k \sum_{l=1}^L \sum_{m=1}^M \left(\frac{E_{lm} - EM_{lm}}{\sigma_{lm}} \right)^2, \quad (15)$$

where K is the total number of data groups; k is the data group index; W_k is the relative weight of data group k which is set to unity; L is the total number of data points in a data group; l is the data index, M is the total number of measured variables; m is the measured variable index; E is the calculated quantity; EM is the experimental value; σ is the standard deviation.

We calculate moles of water and salts in the gel phase for a given degree of swelling data and NaCl concentration in the coexisting phases. Therefore, the measurable variables are the moles of water, $n_{w,gel}$, and the moles of salt NaCl, $n_{NaCl,gel}$, in the gel phase.

Standard deviation of $n_{w,gel}$ and $n_{NaCl,gel}$, $\sigma_{n_{w,gel}}$ and $\sigma_{n_{NaCl,gel}}$ in Eq. 15 are estimated from standard deviation of q and $w_{NaCl,gel}$, σ_q and $\sigma_{w_{NaCl,gel}}$, by the error propagation correlation [26] as follows

$$\sigma_{n_{w,gel}} = \frac{W_{polymer}}{M_w} \sqrt{\{(q-1)\sigma_{w_{NaCl,gel}}\}^2 + \{(1-w_{NaCl,gel})\sigma_q\}^2}, \quad (16)$$

and,

$$\sigma_{n_{NaCl,gel}} = \frac{W_{polymer}}{M_{NaCl}} \sqrt{\{(q-1)\sigma_{w_{NaCl,gel}}\}^2 + (w_{NaCl,gel}\sigma_q)^2}, \quad (17)$$

where $w_{NaCl,gel}$ denotes the mass fraction of NaCl in the gel phase on a polymer free basis; $W_{polymer}$ is the mass of the polymer chain between two crosslink points; M_w and M_{NaCl} are the molecular weight of water and NaCl, respectively;

As suggested by Hüther et al. [2], C parameter can be estimated using swelling data available at pure solvents. As swelling data is not available for G4 at pure solvents, we regress swelling data available at low salt concentrations, i.e., at the NaCl mass fraction of 6.6×10^{-5} in the bulk liquid, to identify C parameter for G4 as listed in Table 1.

We correlate data available for gel G2 to identify parameters for the IPAAm segment:(Na⁺ Cl⁻) pair. As the gels G1 to G4 differ slightly in their characterization properties, we assume that G1, G3, and G4 can be expressed with the same binary interaction parameters for the IPAAm segment:(Na⁺ Cl⁻) pair as those identified for G2. We excluded the data points from the regression the experimental data points where NaCl concentration in the gel phase were not reported. We could not identify one of the binary parameters in the IPAAm segment:(Na⁺ Cl⁻) pair very well; hence set the value to zero as reported in Table 2.

5. Model results and discussions

Figure 1(a) to Figure 1(d) show the model results for the degree of swelling and salt partitioning for G1 to G4, respectively. Note that Figure 1(a), (c) and (d) are the model predictions based on the interaction parameters identified from the data for G2 while Figure 1(b) shows the correlation results for G2. The model results are in semi-quantitative agreement with the experimental data. Figure 1 shows, from G1 to G3, the degree of swelling q decreases with increasing crosslinking density χ_c . For a given hydrogel, q stays relatively constant against the

NaCl mass fraction in the bulk phase, $w_{NaCl,bulk}$, up to ~ 0.01 . Within the range of $0.01 - 0.03$ of $w_{NaCl,bulk}$, deswelling occurs and a sharp drop in q is observed for all the hydrogels. At higher NaCl concentrations, i.e., at $w_{NaCl,bulk} > 0.03$, the hydrogels are in totally collapsed state. Figure 1 also shows that, at $w_{NaCl,bulk} < 0.03$, the NaCl concentrations in the coexisting phases are the same. At $w_{NaCl,bulk} \sim 0.03$, the NaCl concentration in the gel phase reach their maxima. At $w_{NaCl,bulk} > 0.03$ up to salt saturation, the NaCl concentration in the gel phase decreases. Note that the NaCl concentration in the gel phase is reported as a mass fraction on a polymer-free basis.

The drop in the NaCl concentration in the gel phase at $w_{NaCl,bulk} > 0.03$ can be explained with the NaCl activity coefficients in the gel phase. Figure 2 shows the mole fraction scale mean ionic activity coefficients of NaCl in the bulk solution and the gel phase for hydrogel G2. At $w_{NaCl,bulk} < 0.03$, the NaCl activity coefficients in the bulk solution and the gel phase are almost the same and remain relatively unchanged. At $w_{NaCl,bulk} > 0.03$, the hydrogel deswells, the NaCl activity coefficient in the gel phase increases sharply to the order of hundreds due to the strong repulsive interaction between the NaCl and the increased IPAAm polymer content in the gel phase, and $w_{NaCl,gel}$ drops sharply in comparison to $w_{NaCl,bulk}$. The repulsive interactions between organic components and electrolytes in aqueous solutions have been reported by Chen and Song [27].

Figure 2 further shows the water activity coefficients, mole fractions, and activities in the bulk solution and the gel phase together with the IPAAm segment activity coefficient in the gel phase as functions of the NaCl concentration in the bulk phase for hydrogel G2. At $w_{NaCl,bulk} < 0.03$, the hydrogels are swollen, the water activity coefficients in both the bulk phase and the gel

phase are around unity and remain relatively unchanged. With increasing NaCl concentration in the bulk phase, the water activity coefficient in the bulk phase shown in Figure 2(a) drops below unity and it weakens the water activity shown in Figure 2(b), the driving force for hydrogel swelling. Figure 1(b) shows that the hydrogel eventually deswells and collapses at $w_{NaCl,bulk} > 0.03$. Note that the water activity coefficient in the deswelled gel phase is lower than that of water in the bulk solution, together with the less than unity activity coefficient of IPAAM segment in the gel phase, are the results of the strong attractive interactions between water and hydrophilic IPAAM segment in the gel phase.

Figure 3 shows the natural logarithm of mole fraction scale mean ionic activity coefficient contributions of salt NaCl in the gel phase for hydrogel G2. It is evident that the dominant contribution to the activity coefficient of NaCl is the local interaction term which exhibits strong repulsive interactions between NaCl and IPAAM in the gel phase.

Figure 4 presents sensitivity of the binary interaction parameters of the IPAAM segment: (Na⁺ Cl⁻) pair, upon degree of swelling and partitioning of NaCl salt for hydrogel G2 at 298.15 K. There are two binary interaction parameters for the IPAAM segment:(Na⁺ Cl⁻) pair, i.e., $\tau_{IPAAM:(Na^+ Cl^-)}$ and $\tau_{(Na^+ Cl^-):IPAAM}$. Our investigation indicates that the model results for both the degree of swelling and the NaCl concentrations in the gel phase are insensitive to the change in the parameter $\tau_{(Na^+ Cl^-):IPAAM}$. Given the few data points at high NaCl concentrations in the bulk phase, the $\tau_{(Na^+ Cl^-):IPAAM}$ parameter cannot be identified and it is set to the value of 0.

Conclusions

A modified electrolyte NRTL activity coefficient model has been successfully used in thermodynamic analysis on swelling of IPAAm hydrogels immersed in aqueous NaCl solutions at 298 K. The model satisfactorily represents both the swelling data and the salt partitioning data of IPAAm hydrogels in aqueous NaCl solutions for concentrations up to salt saturation. While it is well known that hydrogel swelling is determined by minimization of system Gibbs energy, our investigation reveals that the swelling and deswelling of IPAAm hydrogels in aqueous NaCl is determined by the water activity in the aqueous solution, the result of the attractive interactions between water and NaCl. IPAAm hydrogels are fully swollen in water and dilute aqueous NaCl solutions. However, in concentrated NaCl solutions, the driving force for swelling weakens as the water activity coefficient in the bulk solution drops due to the ion hydration between NaCl and water. On the other hand, NaCl is pushed out of IPAAm hydrogels due to the strong repulsive interactions between NaCl and IPAAm.

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Figure 1: Degree of swelling q of IPAAm hydrogels and mass fraction of salt NaCl in the gel phase (polymer-free basis) with change in NaCl mass fraction in the bulk solution for various hydrogels at 298.15 K: blue lines are model results for the degree of swelling and red lines are for the mass fraction of NaCl in the gel phase; blue circles are experimental data [11] the degree of swelling red triangles are for the mass fraction of NaCl in the gel phase. a) G1, b) G2, c) G3, and d) G4.

Figure 2: (a) Model prediction for activity coefficients (mole fraction based) with change in NaCl mass fraction in the bulk solution for G2 at 298.15 K: (left y-axis) activity coefficient of H₂O in the bulk solution (—•) and the gel phase (—); (right y-axis) mean ionic activity coefficient of NaCl in the bulk solution (—•) and the gel phase (—), and activity coefficient of IPAAm segment in the gel phase (—).

(b) Model results for mole fractions and activities of H₂O with change in NaCl mass fraction in the bulk solution for G2 at 298.15 K: mole fraction of H₂O in the bulk solution (—•) and the gel phase (—); activity of H₂O in the bulk solution (—•) and the gel phase (—).

Figure 3: (left y-axis) Model prediction for the natural logarithm scale mean ionic activity coefficient (mole fraction based) of the salt NaCl, γ_{\pm}^* , in the gel phase with change in NaCl mass fraction in the bulk solution for G2 at 298.15 K: (—) for activity coefficient, (— —) for contribution from local interactions, (—•—) for contribution from long-range PDH interactions, (— — —) for contribution from the combinatorial term, and (• — —) for Born term correction; (right y-axis) (—) for dielectric constant of the gel phase, ϵ_{gel} , with change in NaCl mass fraction in bulk at 298.15 K.

Figure 4: Sensitivity of the binary parameters of the IPAAm segment:(Na⁺ Cl⁻) pair, $\tau_{(Na^+ Cl^-):IPAAm}$, upon degree of swelling q and NaCl concentration in the gel phase (polymer-free basis), $w_{NaCl,gel}$, with change in NaCl mass fraction in the bulk solution, $w_{NaCl,bulk}$ for G2 at 298.15 K: Dash lines for $\tau_{(IPAAm: Na^+ Cl^-)} = (9.814, 4)$; solid lines for $\tau_{(IPAAm: Na^+ Cl^-)} = (9.814, 0)$; dotted lines for $\tau_{(IPAAm: Na^+ Cl^-)} = (9.814, -4)$; symbols for experimental data [11]; blue for degree of swelling and red for NaCl concentration in the gel phase.

Figure 1

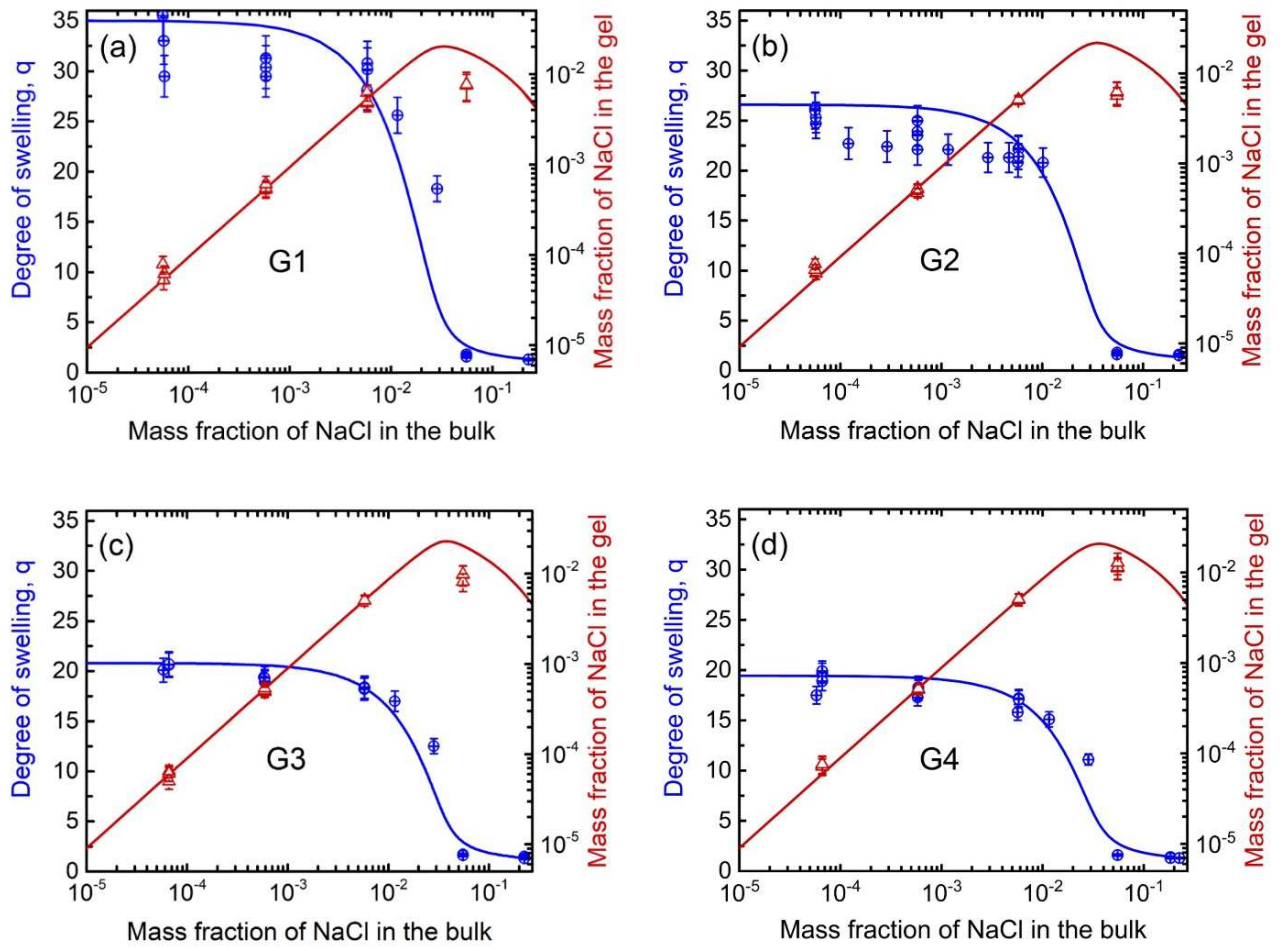


Figure 2

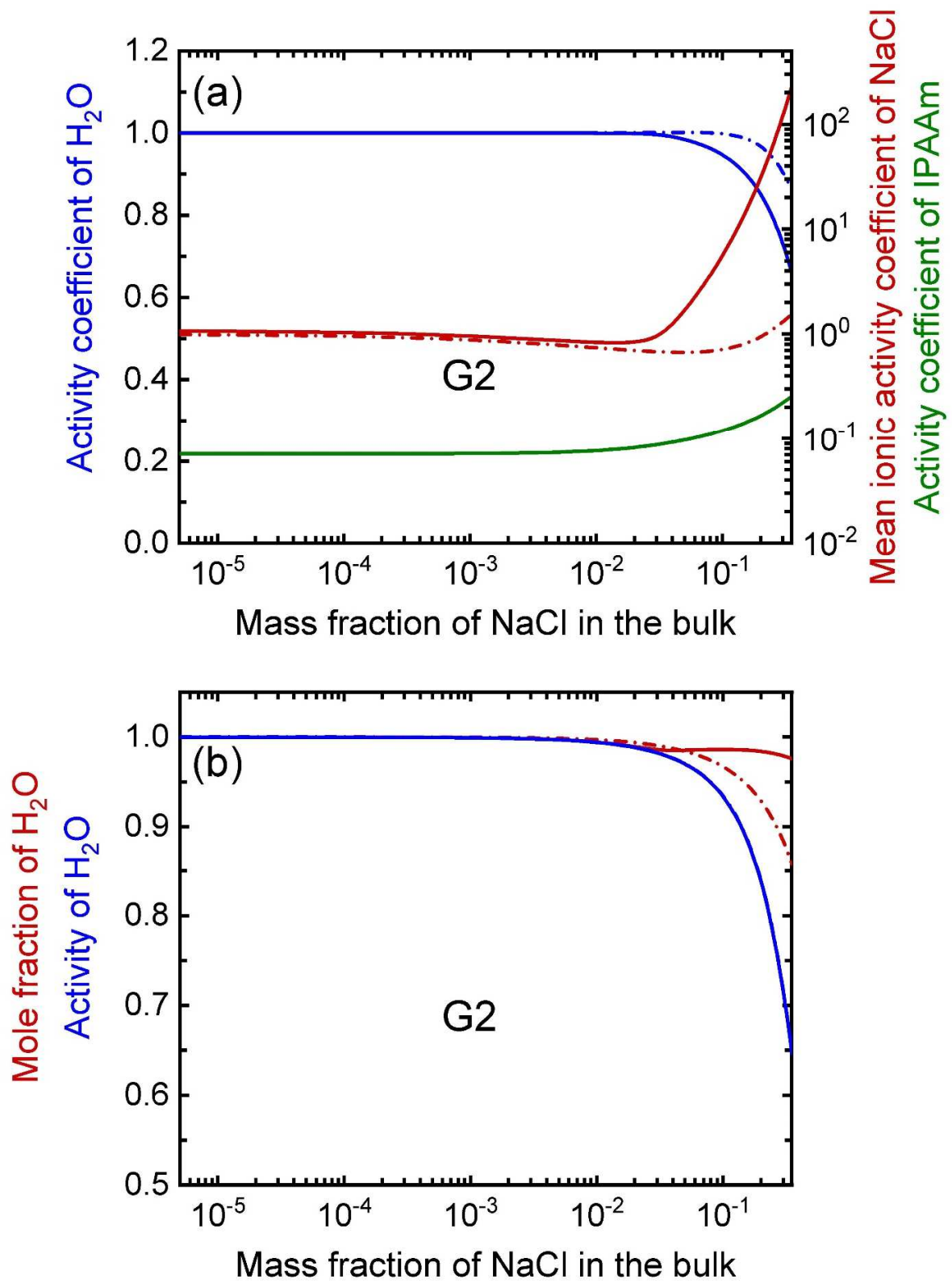


Figure 3

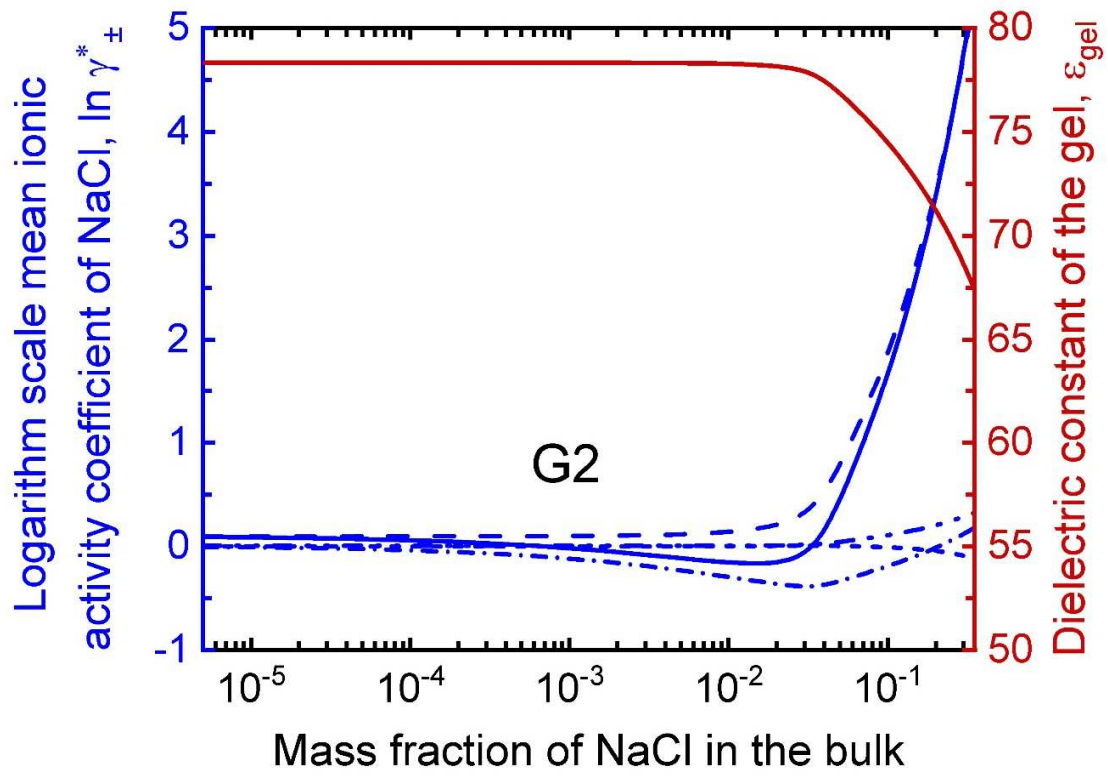


Figure 4

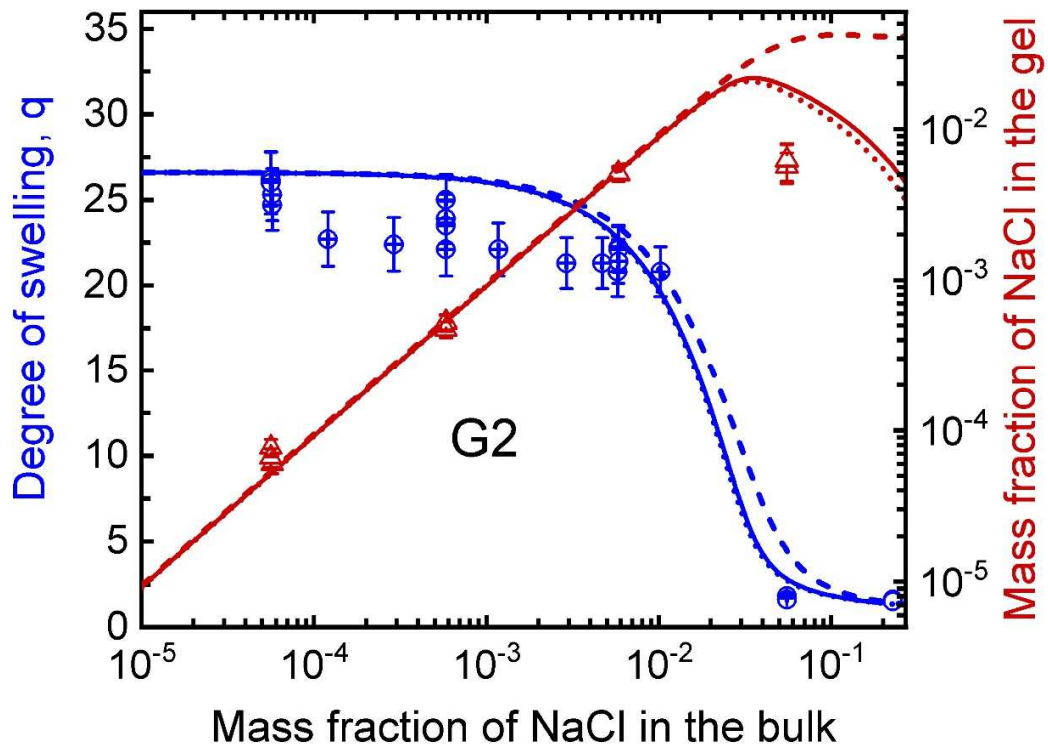


Table 1: Hydrogel properties

Gel	w_{gel} [11]	x_c [11]	r [11]	C [10]
G1	0.08	0.010	50	1.02
G2	0.08	0.015	33	1.20
G3	0.08	0.020	25	1.42
G4	0.10	0.015	33	1.40*

* Identified in this work

Table 2: eNRTL binary interaction parameters, τ_{ij} , at 298.15 K

Species, i	Species, j	τ_{ij}	τ_{ji}	α_{ij}	Source
H ₂ O	(Na ⁺ Cl ⁻)	8.866	-4.541	0.2	Yan and Chen [24]
H ₂ O	IPAAm segment	-1.977	0.195	0.3	Islam et al. [10]
IPAAm segment	(Na ⁺ Cl ⁻)	9.814	0	0.2	This work