

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

Swelling Equilibria for Ionized Temperature-Sensitive Gels in Water and in Aqueous Salt Solutions

### Permalink

<https://escholarship.org/uc/item/1k10g3p4>

### Journal

Journal of chemical physics, 92(3)

### Authors

Beltran, S.

Hooper, H.H.

Blanch, H.W.

et al.

### Publication Date

1989-07-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Chemical Sciences Division

To be submitted for publication

### Swelling Equilibria for Ionized Temperature-Sensitive Gels in Water and in Aqueous Salt Solutions

S. Beltran, H.H. Hooper, H.W. Blanch, and J.M. Prausnitz

July 1989



1 LOAN COPY 1  
1 Circulates 1  
1 for 2 weeks 1

Bldg. 50 Library.

LBL-27572

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

# Swelling Equilibria for Ionized Temperature-Sensitive Gels in Water and in Aqueous Salt Solutions

*Sagrario Beltran, Herbert H. Hooper, Harvey W. Blanch, and John M. Prausnitz\**

Chemical Engineering Department  
University of California

and

Materials and Chemical Sciences Division  
Lawrence Berkeley Laboratory  
1 Cyclotron Road  
Berkeley, CA 94720

## ABSTRACT

Swelling equilibrium data in water and in aqueous NaCl solutions are presented for thermally-sensitive N-isopropylacrylamide (NIPA) hydrogels containing 0-4 mole percent quaternized amine (positively ionizable) comonomer. We report the effect of gel charge and solution ionic strength on the temperature-induced collapse of NIPA gels. Experimental swelling equilibria are compared with predictions based on a recently proposed oriented-quasichemical model. This model has been shown previously to describe lower critical solution behavior in *uncharged* aqueous polymer solutions and gels (i.e., aqueous NIPA gel). We apply the model here to *ionized* NIPA gel. Semiquantitative predictions are obtained for the effects of gel charge and solution ionic strength on temperature-dependent swelling behavior.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

\*To whom correspondence should be addressed

submitted for publication July, 1989

## INTRODUCTION

Phase transitions in polymer gels have attracted much attention since the first observation of gel collapse by Tanaka<sup>1</sup>. Initial work was directed primarily at partially ionized polyacrylamide gels (or related derivatives) which collapse in mixed solvent (acetone/water) systems as solvent composition is varied<sup>2-6</sup>. In recent years, crosslinked gels of N-isopropylacrylamide (NIPA) and of N,N'-diethylacrylamide (NDEA) have been shown to exhibit discontinuous or nearly-discontinuous volume transitions in water in response to an increase in temperature<sup>7-12</sup>. These *temperature-sensitive* gels have received attention for their scientific interest<sup>11,12</sup> and for their potential technical importance in a variety of applications including solute recovery<sup>10</sup>, drug delivery<sup>9</sup>, and immobilized-enzyme reactors<sup>13</sup>.

Temperature-induced collapse of polymer gels is analogous to lower-critical-solution phase separation in aqueous polymer solutions, and to the coil-globule transition of a single polymer chain in solution. For example, aqueous poly(NIPA) solutions exhibit a lower critical solution temperature (LCST) at approximately 31°C<sup>14</sup>; the end-to-end dimension of an infinitely-dilute isopropylacrylamide polymer in water decreases dramatically as temperature rises above 31°C<sup>15</sup>; and crosslinked NIPA gels exhibit volume collapse as temperature exceeds approximately 33°C. LCST behavior in aqueous polymer solutions is due to specific, orientation-dependent interactions<sup>16</sup>. This behavior cannot be explained by conventional polymer-solution theories (e.g., Flory-Huggins)<sup>17</sup>.

Many potential applications of temperature-sensitive gels require incorporation of fixed ionizable groups within the gel. Ionic groups may be used for imparting to a gel specific solute-binding or exclusion properties, or for increasing the water absorption capacity of a gel. Thus, the effect of gel charge on temperature-induced phase transitions is of interest. While swelling equilibria in water have been reported previously for temperature-sensitive gels containing weakly ionizable groups<sup>10,18-21</sup>, in this work we examine swelling equilibria for NIPA gels containing a *strongly* dissociating quaternized-amine comonomer. The effect of ionic strength on swelling behavior for ionized temperature-sensitive gels has not been studied previously. We report here temperature-dependent swelling behavior in water and in aqueous sodium chloride solutions for NIPA gels copolymerized with methacrylamidopropyltrimethylammonium chloride (MAPTAC).

Prange et al<sup>22</sup> recently presented a theoretical framework for describing LCST phenomena in aqueous polymer solutions and gels. This framework accounts for the competition between specific (hydrogen-bonding) and non-specific (dispersion-force) interactions which results in LCST behavior in aqueous polymer systems at normal temperatures and pressures. Hooper et al<sup>23</sup> extended this model to polyelectrolyte gels and compared model

predictions with *isothermal* swelling measurements for ionized acrylamide/MAPTAC copolymer gels in water and in salt solutions. In this work we consider simultaneously the effects of temperature, gel ionization, and solution ionic strength on the swelling properties of NIPA/MAPTAC gels (which are sensitive to all three variables). Swelling measurements are compared with predictions based on the model presented in Refs. (22) and (23).

## EXPERIMENTS

Gels were prepared by free-radical copolymerization of NIPA and MAPTAC, using N,N'-methylenebisacrylamide (BIS) as the crosslinker. The synthesis procedure is similar to that discussed in Ref. (23) with differences described below. All monomers were dissolved in 100ml water (in a nitrogen-filled glove box) and 0.01g each of ammonium persulfate and sodium metabisulfite were added to initiate reaction. The gels were formed between glass plates (10x10cm) separated by 1.0mm Teflon spacers. The plates were chilled to 10°C before injecting the monomer solution; after injecting solution, the plates were transferred from the glove box to a refrigerator and allowed to react at 10°C. (Temperature control is essential to prevent thermally-induced phase separation during polymerization). After 48 hours, the gel slabs were removed from the plates and sliced into 1-cm disks using a punch. The disks were soaked in distilled, deionized water (replaced daily) for one week.

The volume fraction of monomers in the initial (100ml water) reacting solution was 0.12 for all gels prepared here. Also, each gel was prepared with a crosslink content of 0.01 mole BIS per mole of all monomers (i.e., 0.01 mole fraction BIS on a diluent-free basis). The only gel-composition parameter varied here was the relative amount of charged comonomer (MAPTAC) in the gel. Five gels were prepared containing, respectively, 0, 0.01, 0.02, 0.03, and 0.04 mole fraction MAPTAC (on a diluent-free basis); we refer to these gels by their respective mole *percent* MAPTAC.

Gel volumes (water absorption capacities) were measured in the temperature range 10-70°C in water and in aqueous sodium chloride solutions in the concentration range  $10^{-5}$  to 1.0M. Capacities were determined gravimetrically and by volume change as discussed in Ref. (23). At each temperature, gel samples were allowed to equilibrate at least 24 hours before recording the volume. Gels placed in salt solutions were equilibrated for seven days (with solutions replaced daily) at 10°C. The solution temperature was then increased, held constant for at least 24 hours, and the gel volume recorded. All swelling measurements were performed in triplicate; standard deviations of the measured swelling capacities were generally less than 2% of the mean. Temperature was measured with a calibrated

thermocouple which is accurate to within  $\pm 0.05^\circ\text{C}$ .

## EXPERIMENTAL RESULTS

Figure 1 presents swelling equilibria in water for uncharged NIPA gel in the range  $10\text{-}70^\circ\text{C}$ . The gel undergoes a continuous volume change as a function of temperature; this change is most dramatic in the region  $30\text{-}35^\circ\text{C}$  (the *transition* region). Both continuous<sup>9,20,21</sup> and discontinuous<sup>8,10</sup> transitions have been observed for NIPA gels in water. The gel is close to a critical point, and changes in gel crosslink density<sup>12</sup>, external osmotic pressure<sup>11</sup>, and initiator type<sup>24</sup> have been shown to result in a crossover of the transition from first-order to second-order behavior. Regardless of the order of the transition, a large volume change is always observed in the temperature range  $30\text{-}35^\circ\text{C}$ .

Figure 2 shows swelling behavior at  $10^\circ\text{C}$  in water and in aqueous NaCl solutions for gels with varying MAPTAC concentration. (Pure water is denoted on the graph as  $10^{-7}\text{M}$  NaCl). Gel swelling in water, and in salt solutions at low ionic strength, is highly dependent on the degree of gel ionization (%MAPTAC). As salt concentration rises, the ionized gels deswell; at about  $0.1\text{M}$  NaCl all gels have approximately the same water content. The behavior seen in Figure 2 is similar to that observed elsewhere. This behavior can be explained on the basis of Donnan-equilibria arguments<sup>23</sup>.

Temperature-dependent swelling equilibria for gels with varying %MAPTAC were measured for three of the ionic strengths shown in Figure 2: deionized water,  $10^{-3}\text{M}$  NaCl, and  $10^{-1}\text{M}$  NaCl. Figure 3 presents results for measurements in water. Like the uncharged NIPA gel, the ionized gels exhibit large (continuous) changes in water content as a function of temperature. The temperature range where the volume change is greatest (i.e., the transition region) increases strongly with gel ionization. In addition, the volume change appears to become less dramatic (more continuous) as %MAPTAC increases.

Some workers have observed discontinuous volume transitions for ionized NIPA gels<sup>21</sup> and for ionized NDEA gels<sup>18,19</sup>. However, others have reported continuous transitions for ionized NIPA<sup>20</sup> and NDEA<sup>10</sup> gels. In light of these conflicting observations, we conducted additional studies to confirm that our measurements of continuous transitions were not the result of slow equilibration near a possible critical (discontinuous) transition. The transition region for different gels was approached from both higher and lower temperatures using swollen-gel samples and using samples which were initially dry (i.e., dried in a vacuum oven). After 12 hours, all samples with the same MAPTAC content had identical swelling capacities (within  $\pm 2\%$ ) corresponding to the continuous temperature-volume curves in Figure 3. In addition, some samples were held in the transition region for longer

times (up to 5 days); no change in gel water content was observed after the first 12 hours.

A plausible explanation for the reported differences in transition behavior for ionized temperature-sensitive gels is that the effect of the ionizable comonomer is not restricted to its ionic character. The chemical and physical nature of the comonomer (in addition to its ionic character and to its concentration within the gel) may influence the type of transition observed. In Refs. (18), (19), and (21) (where discontinuous transitions were observed), the ionizable comonomer was either sodium acrylate or sodium methacrylate. In Ref. (20) (continuous transition), the gel contained N-(acryloxy)succinimide. Clearly, other factors (e.g., network composition and preparation procedure) may contribute to the observed differences in transition behavior for ionized gels (as with uncharged NIPA gels). Thus, more data are required before definitive conclusions may be reached regarding the transition behavior of ionized temperature-sensitive gels.

Figure 4 presents swelling equilibria for NIPA/MAPTAC gels in  $10^{-3}$ M NaCl solutions. The gels exhibit swelling curves similar to those seen in Figure 3. However, in analogy to the behavior observed in Figure 2, the ionized gels absorb less water in  $10^{-3}$ M NaCl than in deionized water. Increasing ionic strength thus decreases the apparent magnitude of the volume transition for ionized gels.

Figure 5 shows swelling measurements for NIPA/MAPTAC gels in 0.1M NaCl solutions. In Figure 2 we noted that at 0.1M NaCl (and 10°C) gel charge density has little effect on swelling capacity. Figure 5 confirms this effect over the range 10-70°C. Thus, at ionic strengths of 0.1M (or greater), gel charge density has a minimal effect on swelling behavior, and the ionized gels exhibit temperature-volume curves which are in near-quantitative agreement with those for the uncharged NIPA gel. This *damping* of charge effects at (relatively) moderate ionic strengths has important implications for proposed applications of ionized gels. In particular, Donnan exclusion of ionized solutes from a charged gel will not be observed at ionic strengths above 0.1M; therefore, solute recovery operations relying on Donnan exclusion<sup>10</sup> will be ineffective at ionic strengths near or larger than 0.1M.

The swelling data presented in this section are available in tabular form as supplemental material.



## COMPARISON OF EXPERIMENT WITH THEORY

LCST behavior is observed in polymer solutions when: (1) the polymer and solvent exhibit large differences in thermal expansion, or (2) specific, orientation-dependent interactions occur between polymer and solvent. In both cases, the phase separation is entropically driven; however, the origin of this driving force is significantly different in the two cases. While compressibility effects are dominant in nonpolar systems at temperatures approaching the solvent critical temperature (e.g., poly(styrene)/acetone<sup>25</sup>), specific interactions are dominant in polar, or hydrogen-bonding systems at normal temperatures and pressures (i.e., conditions remote from the solvent's critical point). Aqueous polymer solutions (e.g., NIPA gels) represent systems in which specific (hydrogen-bonding) interactions are the driving force for LCST behavior.

Free-volume<sup>26</sup> and lattice-fluid<sup>27</sup> equations of state can describe LCST behavior resulting from compressibility effects in nonpolar systems. However, these models do not account for orientation-dependent interactions and thus cannot describe LCST behavior in aqueous polymer solutions. Recently, lattice models have been proposed which account for specific interactions and describe LCST behavior in polar and hydrogen-bonding systems<sup>22,28</sup>. We have applied such a model for describing LCST behavior in the uncharged NIPA gel/water system<sup>22</sup>. Here, we apply an extension of this model for polyelectrolyte gels<sup>23</sup> for describing swelling behavior in ionized NIPA/MAPTAC copolymer gels.

The classical solution theory of Flory and Huggins<sup>17</sup> does not account for free-volume effects or for specific interactions, and thus cannot describe the mechanisms responsible for LCST behavior in either non-polar or specifically interacting systems. Nevertheless, LCST behavior can be predicted by classical Flory-Huggins theory if the polymer/solvent interaction parameter is given an *unreasonable* temperature- or composition-dependence. This approach, while physically unappealing, has been used for describing LCST behavior in NIPA and NDEA gels<sup>19,21</sup>.

At equilibrium, the osmotic pressure difference ( $\Pi$ ) of solvent between a gel (phase ') and surrounding solution (phase '') is zero, i.e.,

$$\Pi = \frac{-\Delta\mu}{V_1} = \frac{-(\mu'_1 - \mu''_1)}{V_1} = 0 \quad (1)$$

where  $V_1$  is the molar volume of solvent and  $\mu_1$  represents the solvent chemical potential. Assuming that the swelling pressure  $\Pi$  is the sum of contributions from polymer/solvent mixing, network elasticity, and ion/solvent mixing, and substituting expressions discussed in Ref. (23) for these contributions, we obtain:

$$\begin{aligned} \Pi = 0 &= \Pi_{\text{mixing}} + \Pi_{\text{elastic}} + \Pi_{\text{ion}} \\ &= -\frac{RT}{V_1} \left[ \ln \phi_1 + \phi_2 - \frac{1}{2} z_1^\alpha q_1 \ln \frac{[\Gamma_{11}^{\alpha\alpha}]_{\text{pure}}}{[\Gamma_{11}^{\alpha\alpha}]_{\text{mix}}} - \frac{1}{2} z_1^\beta q_1 \ln \frac{[\Gamma_{11}^{\beta\beta}]_{\text{pure}}}{[\Gamma_{11}^{\beta\beta}]_{\text{mix}}} - \frac{1}{2} z_1^D q_1 \ln \frac{[\Gamma_{11}^{DD}]_{\text{pure}}}{[\Gamma_{11}^{DD}]_{\text{mix}}} \right] \\ &\quad - \frac{RT}{V_1} (\phi_2^0/x_c) \lambda^{-1} [1 + K(\lambda)] + RT \sum_j (c_j^{\text{gel}} - c_j^{\text{ext}}) \end{aligned} \quad (2)$$

Here,  $R$  is the gas constant,  $T$  is temperature,  $\phi_1$  and  $\phi_2$  represent (respectively) the volume fraction of solvent and polymer in the gel,  $q_1$  and the  $z_1$ 's are solvent structural parameters,  $\alpha$ ,  $\beta$ , and  $D$  represent different types of contact (interacting) sites on a segment, the  $\Gamma_{11}$ 's are non-random factors (representing the extent of non-random mixing around each type of contact site),  $\phi_2^0$  is the volume fraction of the gel at preparation,  $x_c$  denotes the average number of segments per network chain (where a segment is defined as having the same volume as that of a solvent molecule),  $\lambda = (\phi_2^0/\phi_2)^{1/3}$ , and  $c_j^{\text{gel}}$  and  $c_j^{\text{ext}}$  represent, respectively, the concentration of mobile ions within the gel and in the surrounding solution.

The first line in Equation (2) gives the contribution to the swelling pressure from polymer/solvent mixing. The first two terms in this expression represent the random (athermal) Flory-Huggins combinatorial contribution, while the last three terms represent the energetic and non-random mixing contributions (discussed in Ref. 22). The non-random mixing contribution is significant for mixtures in which strong, orientation-dependent interactions occur; it is this contribution which enables the model to describe LCST behavior in aqueous polymer solutions<sup>22</sup>.

The second line in Equation (2) gives the contributions to the swelling pressure from network elasticity and from ion/solvent mixing. The affine network model<sup>17</sup> is usually used for describing the elastic contribution to gel swelling. However, this model gives a poor description of elastic properties when applied over large ranges of strain, and is particularly unsuitable for swollen networks (which behave closer to the phantom network limit<sup>29</sup>). Here, we use for the elastic contribution the constrained junction theory of Flory and Erman<sup>30</sup>; this model interpolates between affine and phantom network behavior, and accounts for nonaffine displacement of network junctions under strain. The function  $K(\lambda)$  in Equation (2) is given by Equation (16) (and related equations) in Ref. (31). The last term in Equation (2) is the van't Hoff expression for ideal ion/solvent mixing<sup>17</sup>.

Equation (2) is the equilibrium criterion for solvent (water) concentration within the gel. The distribution of mobile ions (added salt) between the gel and solution is described here assuming ideal Donnan equilibria<sup>17</sup>:

$$\left( \frac{c_i^{gel}}{c_i^{ext}} \right) = \left[ \frac{c_i^{ext}}{c_i^{gel} + \frac{i\phi_2}{V_u}} \right] \quad (3)$$

where  $c_i$  refers to the concentration of added salt,  $i$  represents the fraction of monomer units containing bound charges, and  $V_u$  denotes the molar volume of a monomer unit. When salt is not present in the external solution (i.e., for swelling in deionized water), Equation (3) is not needed. In that case, all  $c_i^{ext}$  in Equation (2) are zero, and  $c_i^{gel}$  is given by the concentration of counterions within the gel.

Equations (2) and (3) describe the gel water content (or, equivalently,  $\phi_2$ ) and the salt concentration within the gel ( $c_i^{gel}$ ) as a function of temperature and external salt concentration ( $c_i^{ext}$ ). For comparison with experiment, we define here the parameters which appear in these equations. Structural parameters in the polymer/solvent mixing expression are the same as those in Ref. (22):  $q_1 (=r_1) = 1.0$ ,  $z_1^\alpha = z_1^\beta = 2.0$ ,  $z_2^\alpha = z_2^\beta = 1.07$ , and  $V_1 = 18.0 \text{ cm}^3/\text{mol}$ . Gel-composition parameters in the elastic expression are determined from the synthesis conditions as:  $\phi_2^g = 0.12$ , and  $x_c = 283$ . The degree of gel ionization (parameter  $i$  in Equation (3)) is determined from the %MAPTAC for a given gel, and we estimate  $V_u = 101.0 \text{ cm}^3/\text{mol}$ .

The above parameters are fixed by gel and solution conditions and are not adjustable. Three *adjustable* energy parameters are required for determining the non-random factors ( $\Gamma_{11}$ 's) in Equation (2)<sup>22</sup>; these parameters characterize specific interactions between different contact sites in the solution. These energy parameters must be obtained from experimental data. Our goal here is to examine the ability of Equations (2) and (3) to describe the effects of gel charge and solution ionic strength on the swelling behavior of a temperature-sensitive gel. We thus obtain the adjustable energy parameters from swelling equilibria for uncharged NIPA gel in water (Figure 1), and use these parameters to predict swelling for ionized NIPA/MAPTAC gels in water and in salt solutions.

Energy parameters optimized to swelling equilibria for the uncharged NIPA gel are (using the notation of Ref (22)):  $\omega^{DD} = 202$ ,  $\omega^{\alpha\beta} = -710$ , and  $\omega^{D^*} = -119$  (in degrees Kelvin). Figure 6 presents experimental and calculated swelling equilibria for uncharged NIPA gel and for NIPA/MAPTAC copolymer gels in water and in aqueous NaCl solutions at 10°C. As found earlier<sup>23</sup>, ideal ion/solvent-mixing and Donnan-equilibria arguments predict, in semi-quantitative agreement with experiment, the effects of gel charge and solution ionic strength on swelling (at constant temperature).

Figure 7 presents experimental and calculated swelling equilibria in deionized water for gels containing 0, 2, and 4%MAPTAC. Analogous with Figure 6, calculated swelling capacities at low temperatures are in reasonable (though not perfect) agreement with experiment. The increase in temperature of the transition region with increasing %MAPTAC is also predicted fairly well. However, discrepancies between calculated and measured swelling behavior are apparent both in the order of the volume transition, and in the swelling capacities at high temperatures (above the transition). For gels which undergo a temperature-induced volume transition (whether continuous or discontinuous), the ion/solvent mixing expression in Equation (2) always predicts an increase in the sharpness of this transition (to 1st-order behavior) with increasing ionization<sup>21</sup>. While such a crossover has been observed (as discussed earlier), it was not seen here. In addition, the calculated swelling curves for the ionized gels (at temperatures above their predicted transitions) are nearly identical with the curve for uncharged NIPA gel. In contrast, the ionized gels were actually swollen to a significantly greater degree than the uncharged gel at high temperatures.

Figure 8 presents experimental and calculated swelling equilibria for the 4%MAPTAC gel in deionized water, and in  $10^{-3}$ M and  $10^{-1}$ M aqueous NaCl. The calculated swelling curves describe correctly the large effect of ionic strength on the temperature-dependent swelling behavior for this gel. As in Figure 7, however, discrepancies between theory and experiment are apparent.

## CONCLUSIONS

The addition of small amounts of ionic comonomer to a temperature-sensitive gel affects dramatically swelling behavior in water and in low-ionic-strength aqueous solution. At higher ionic strengths (above about 0.1M NaCl), gel charge has little effect on swelling. Charge density alone may not characterize completely the effects of an ionizable comonomer on gel swelling. Even at low concentrations the specific nature of the comonomer appears to influence swelling behavior (particularly the order of the volume transition) for temperature-sensitive gels. We are currently investigating this effect for other ionizable comonomers.

Predicted swelling equilibria agree reasonably well with experiment over the investigated range of temperature, degree of gel ionization, and solution ionic strength. Considering the neglect of specific comonomer (and electrostatic) interactions in the theoretical approach, the failure to predict *quantitatively* all features of the swelling curves is not surprising. A more elaborate approach for describing such interactions is not now justified, given

the other approximations in the theory and the lack of network structural information (i.e., effective degree of crosslinking and network heterogeneity). For further theoretical development, data are needed for well-defined model systems in which all characteristics (e.g., charge distribution, molecular potentials) are known independently. Computer simulation may provide a tool for obtaining such information; we are therefore currently pursuing simulation studies to establish the effect of charge on the temperature-induced coil-globule transition of a single polymer chain in a continuous fluid medium.

#### ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. S.B. is grateful to the Spanish Ministry of Education and Science (MEC) for a fellowship.

## REFERENCES

- <sup>1</sup>T. Tanaka, *Phys. Rev. Let.* **40**, 820 (1978).
- <sup>2</sup>T. Tanaka, D. Fillmore, S. Sun, I. Nishio, G. Swislow, and Arati Shah, *Phys. Rev. Let.* **45**, 1636 (1980).
- <sup>3</sup>I. Ohmine and T. Tanaka, *J. Chem. Phys.* **77**, 5725 (1982).
- <sup>4</sup>M. Ilavsky, *Macromolecules* **15**, 782 (1982).
- <sup>5</sup>D. Nicoli, C. Young, T. Tanaka, A. Pollak, and G. Whitesides, *Macromolecules* **16**, 887 (1983).
- <sup>6</sup>Y. Hirokawa, T. Tanaka, and E. Sato, *Macromolecules* **18**, 2784 (1985).
- <sup>7</sup>J. Hrouz, M. Ilavsky, K. Ulbrich, and J. Kopecek, *Europ. Polym. J.* **17**, 361 (1981).
- <sup>8</sup>Y. Hirokawa and T. Tanaka, *J. Chem. Phys.* **81**, 6379 (1984).
- <sup>9</sup>A.S. Hoffman, A. Afrassiabi, and L.C. Dong, *J. Controlled Release* **4**, 213 (1986).
- <sup>10</sup>R.F.S. Freitas and E.L. Cussler, *Chem. Eng. Sci.* **42**, 97 (1987).
- <sup>11</sup>S. Hirotsu, *J. Chem. Phys.* **88**, 427 (1988).
- <sup>12</sup>Y. Li and T. Tanaka, *J. Chem. Phys.* **90**, 5161 (1989).
- <sup>13</sup>T.G. Park and A.S. Hoffman, *Appl. Biochem. Biotech.* **19**, 1 (1988).
- <sup>14</sup>M. Heskins and J.E. Guillet, *J. Macromol. Sci., Chem.* **A2**, 1441 (1968).
- <sup>15</sup>S. Fujishige, K. Kubota, and I. Ando, *J. Phys. Chem.* **93**, 3311 (1989).
- <sup>16</sup>J. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.* **5**, 896 (1937).
- <sup>17</sup>P.J. Flory, *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
- <sup>18</sup>M. Ilavsky, J. Hrouz, and K. Ulbrich, *Polym. Bull.* **7**, 107 (1982).
- <sup>19</sup>M. Ilavsky, J. Hrouz, and I. Havlicek, *Polymer* **26**, 1514 (1985).
- <sup>20</sup>Y. Hirose, T. Amiya, T. Hirokawa, and T. Tanaka, *Macromolecules* **20**, 1342 (1987).
- <sup>21</sup>S. Hirotsu, Y. Hirokawa, and T. Tanaka, *J. Chem. Phys.* **87**, 1392 (1987).
- <sup>22</sup>M.M. Prange, H.H. Hooper, and J.M. Prausnitz, *AIChE J.* **35**, 803 (1989).

- 23 H.H. Hooper, J.P. Baker, H.W. Blanch, and J.M. Prausnitz, *Macromolecules*, submitted (1989).
- 24 S. Hirotsu and A. Onuki, *J. Phys. Soc. Jpn.* in press (1989).
- 25 L. Zeman and D. Patterson, *J. Phys. Chem.* 76, 1214 (1972).
- 26 P.J. Flory, *Discuss. Faraday Soc.* 49, 7 (1970).
- 27 I.C. Sanchez and R.H. Lacombe, *Macromolecules* 11, 1145 (1978).
- 28 I.C. Sanchez and A.C. Balazs, *Macromolecules* 22, 2325 (1989).
- 29 J.E. Mark and B. Erman, *Rubberlike Elasticity. A Molecular Primer*; Wiley & Sons: NY, 1988.
- 30 P.J. Flory and B. Erman, *Macromolecules* 15, 800 (1982).
- 31 B. Erman and P.J. Flory, *Macromolecules* 19, 2353 (1986).

## List of Figure Captions

**Figure 1.** Swelling equilibria for poly N-isopropylacrylamide gel in water. Error bars are smaller than data symbols.

**Figure 2.** Swelling equilibria at 10°C for NIPA/MAPTAC copolymer gels in water and in aqueous salt solutions. Results at  $10^{-7}$  M NaCl represent swelling in deionized water.

**Figure 3.** Swelling behavior in water for NIPA/MAPTAC copolymer gels. The gels are all temperature-sensitive, but do not exhibit discontinuous volume transitions.

**Figure 4.** Swelling behavior in  $10^{-3}$  M NaCl for NIPA/MAPTAC copolymer gels. Swelling capacities for charged gels are smaller than for the corresponding gels in Figure 3.

**Figure 5.** Swelling behavior in 0.1M NaCl for NIPA/MAPTAC copolymer gels. The effect of charge on swelling capacity is significantly reduced from that observed in Figures 3 and 4. (Note expanded capacity scale).

**Figure 6.** Comparison of experimental and calculated swelling equilibria for NIPA/MAPTAC copolymer gels in water and in aqueous NaCl solutions at 10°C.

**Figure 7.** Experimental and calculated temperature-dependent swelling behavior for NIPA/MAPTAC gels in water.

**Figure 8.** Experimental and calculated temperature-dependent swelling behavior for 4%MAPTAC gel in water and in  $10^{-3}$  and  $10^{-1}$  M aqueous NaCl.



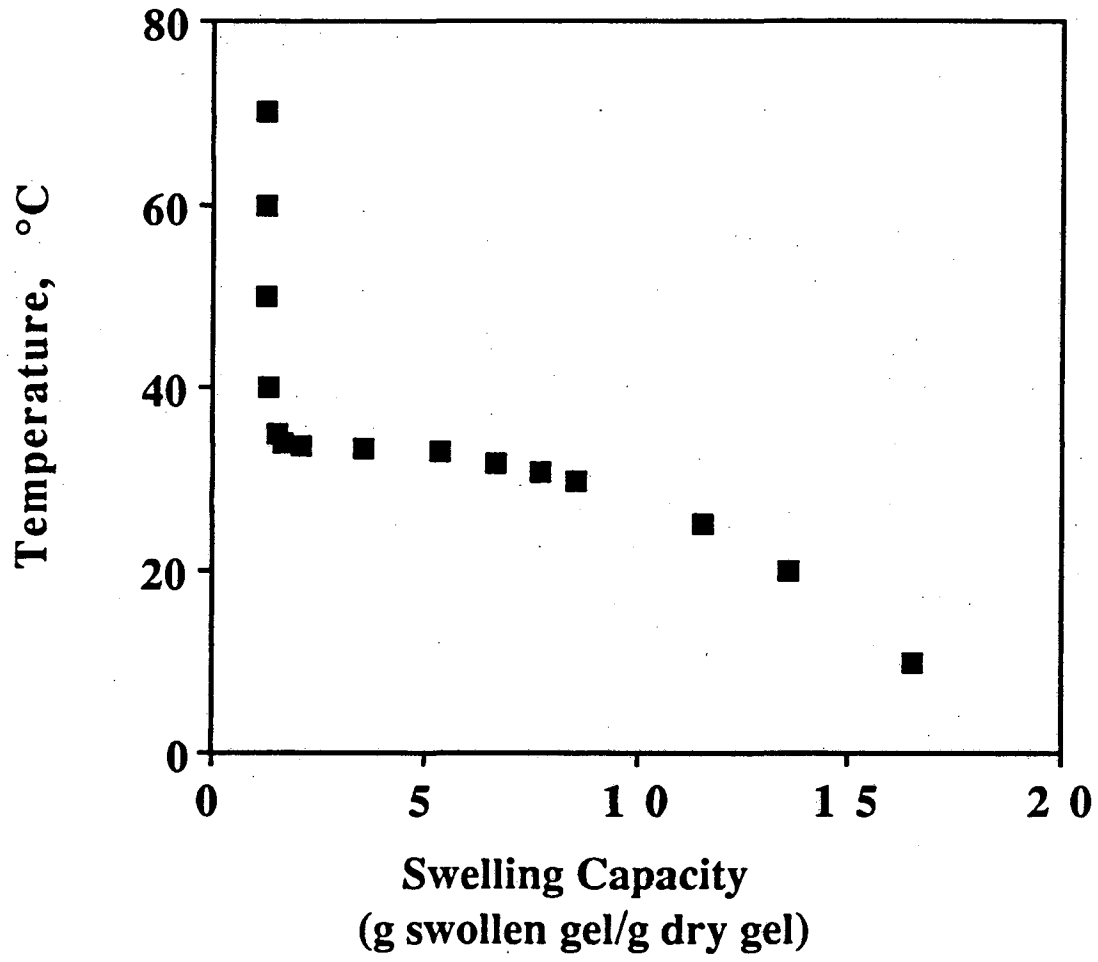


Figure 1

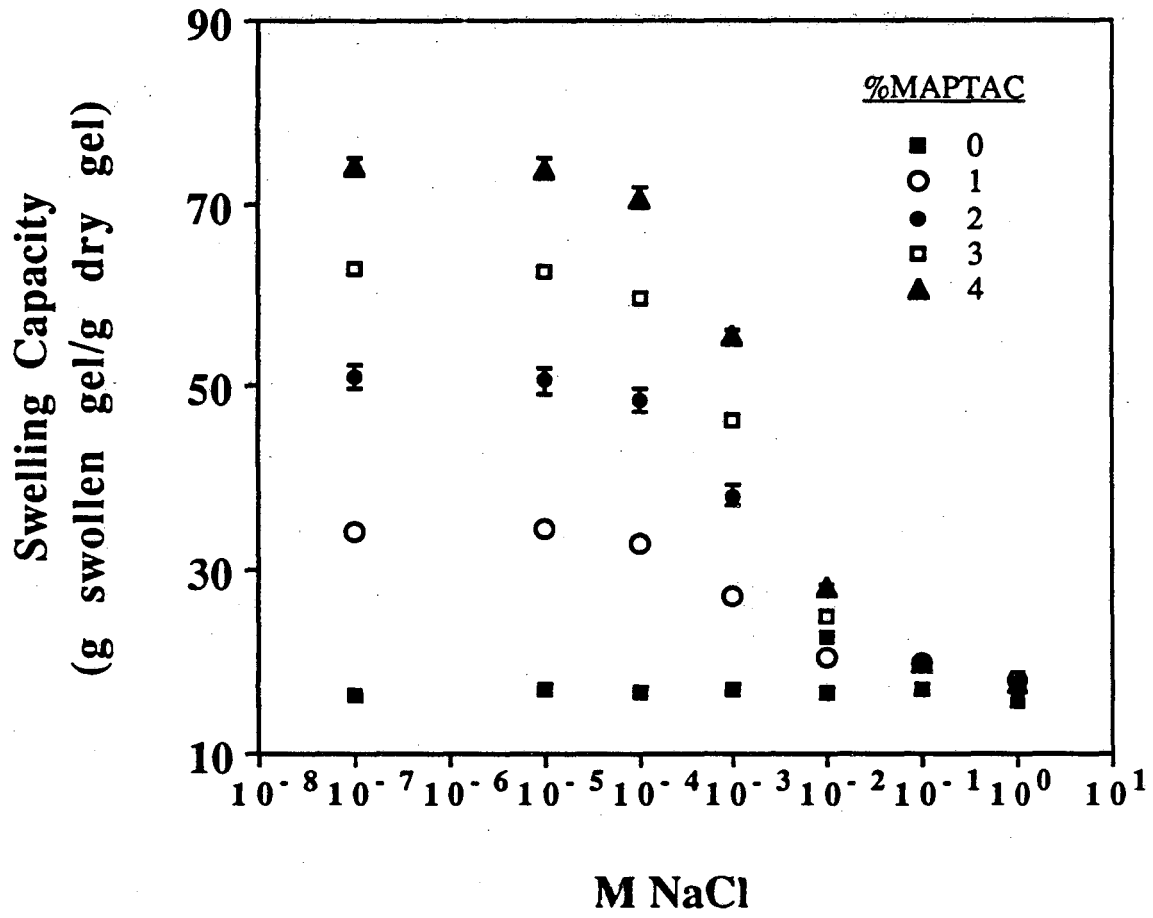


Figure 2.

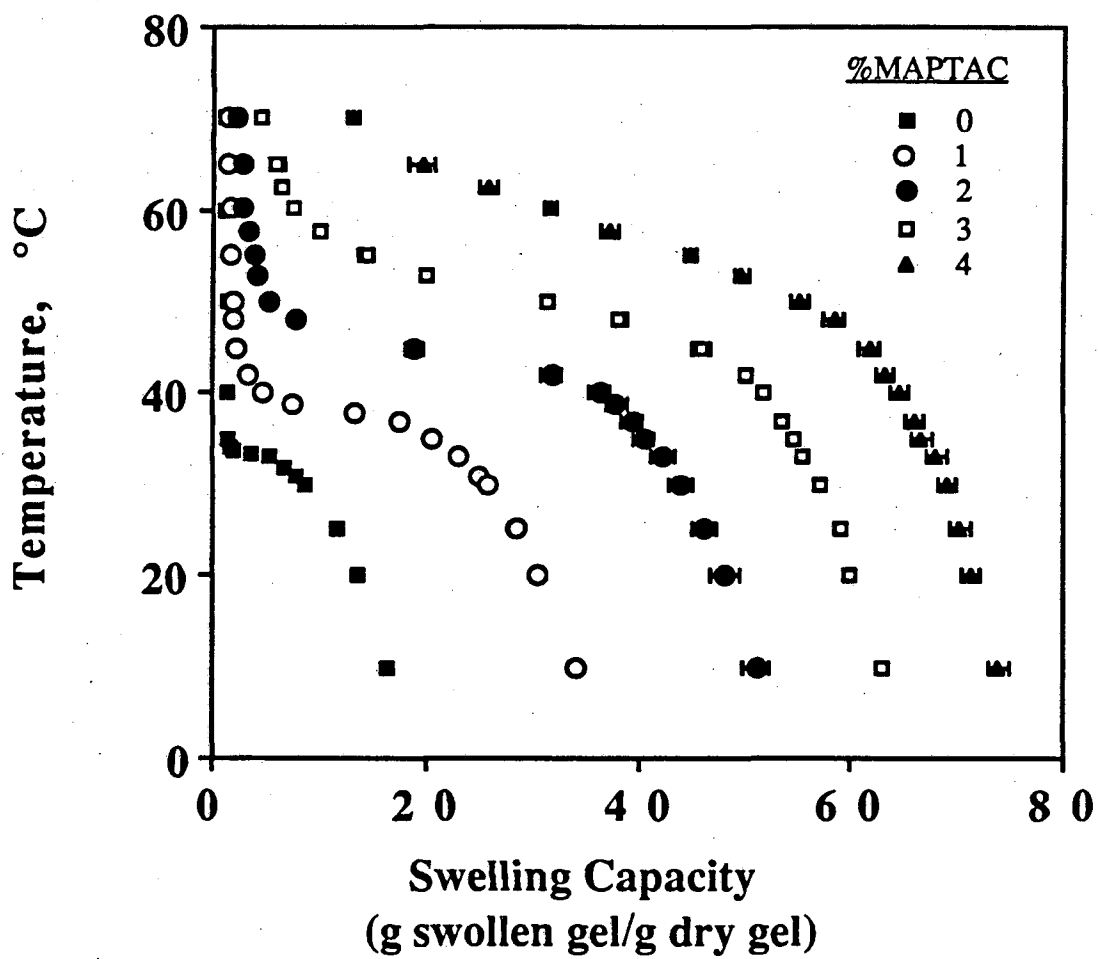


Figure 3

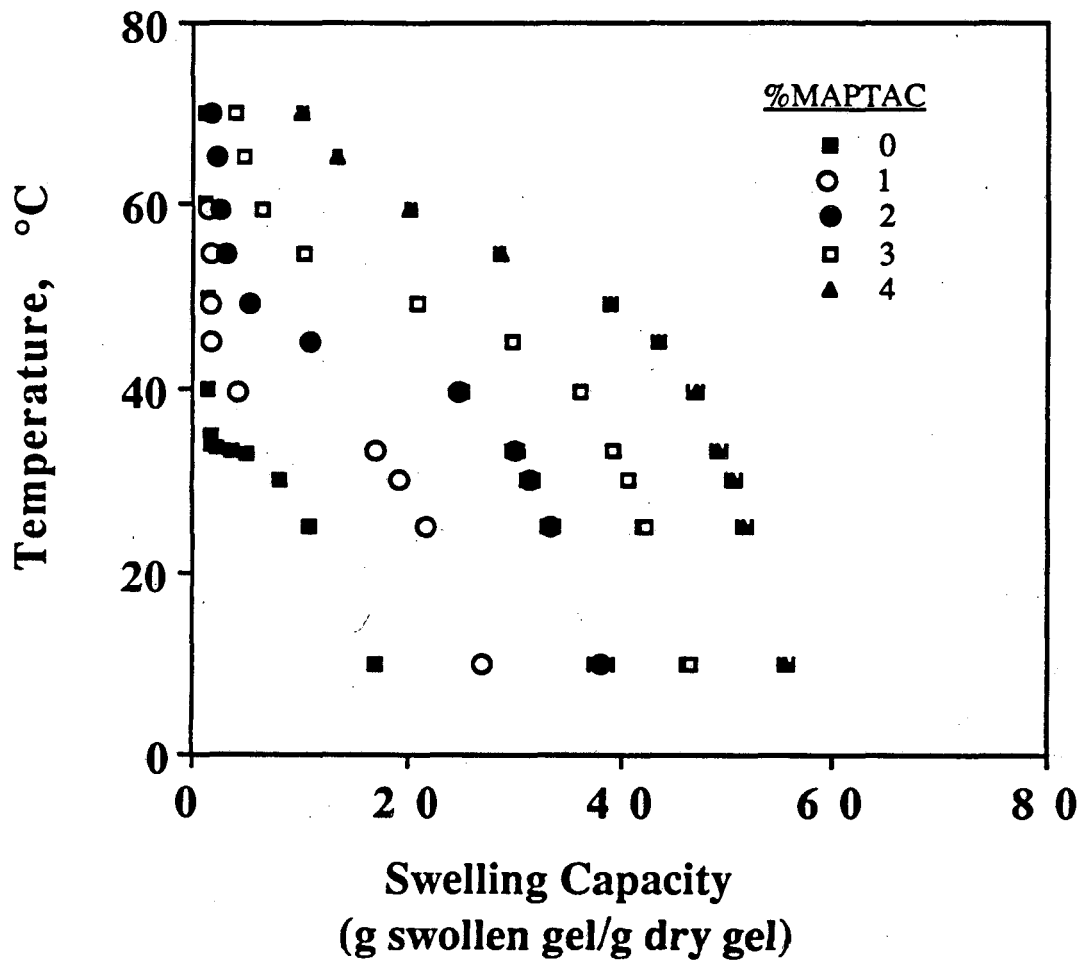


Figure 4

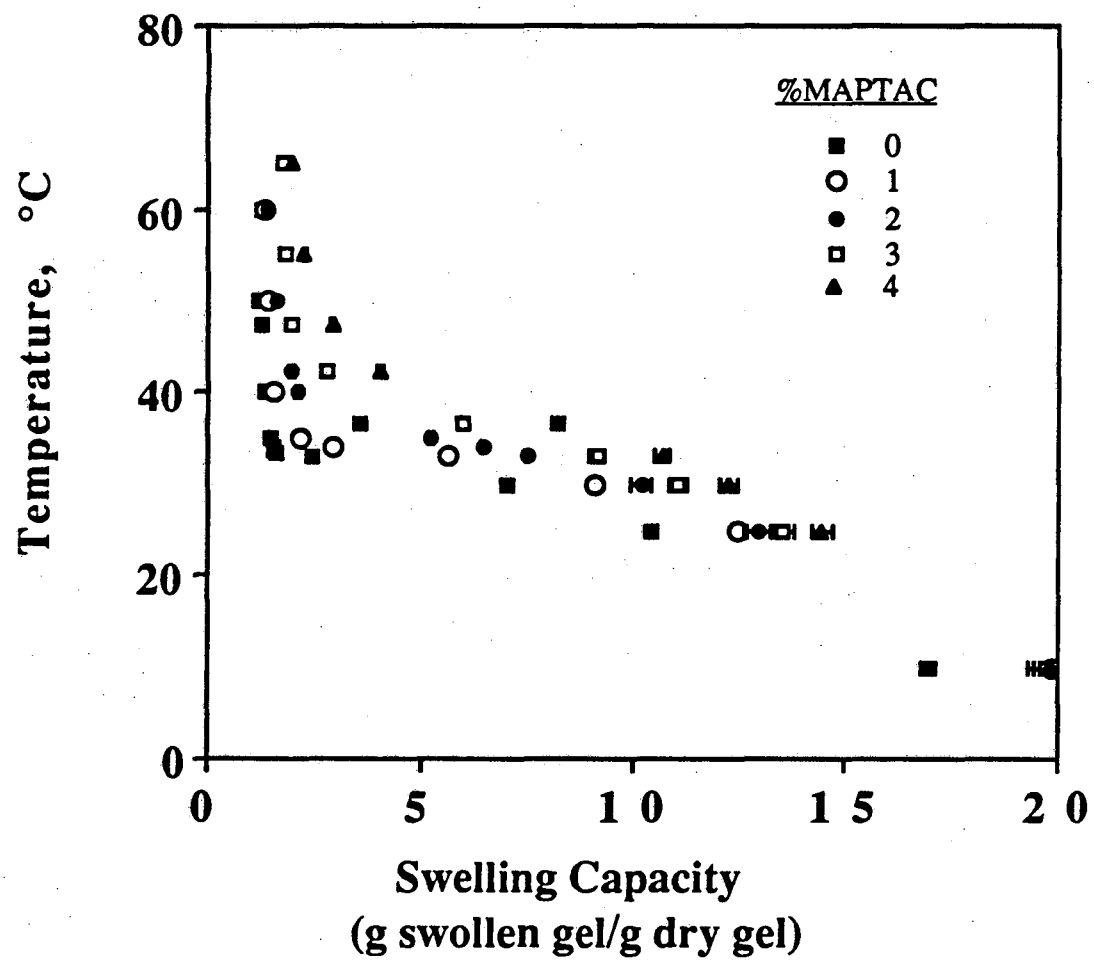


Figure 5

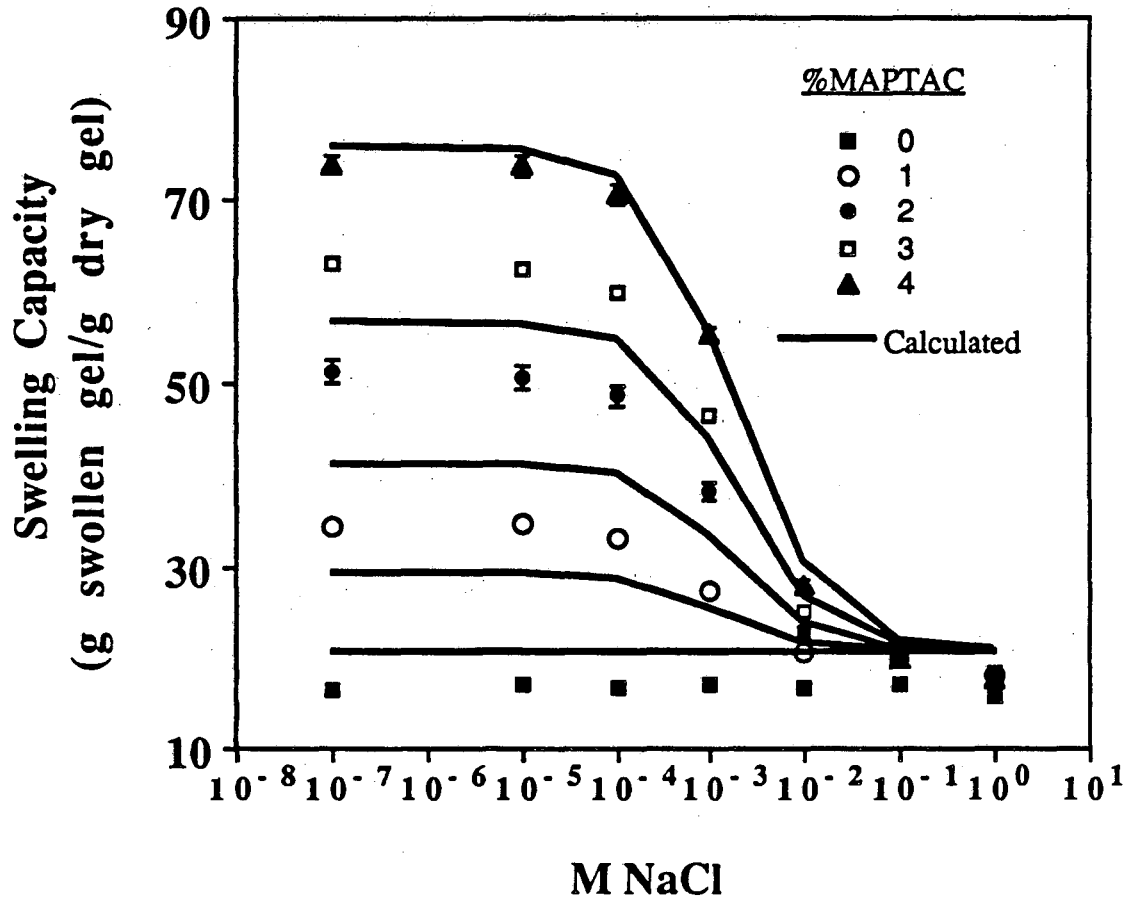


Figure 6

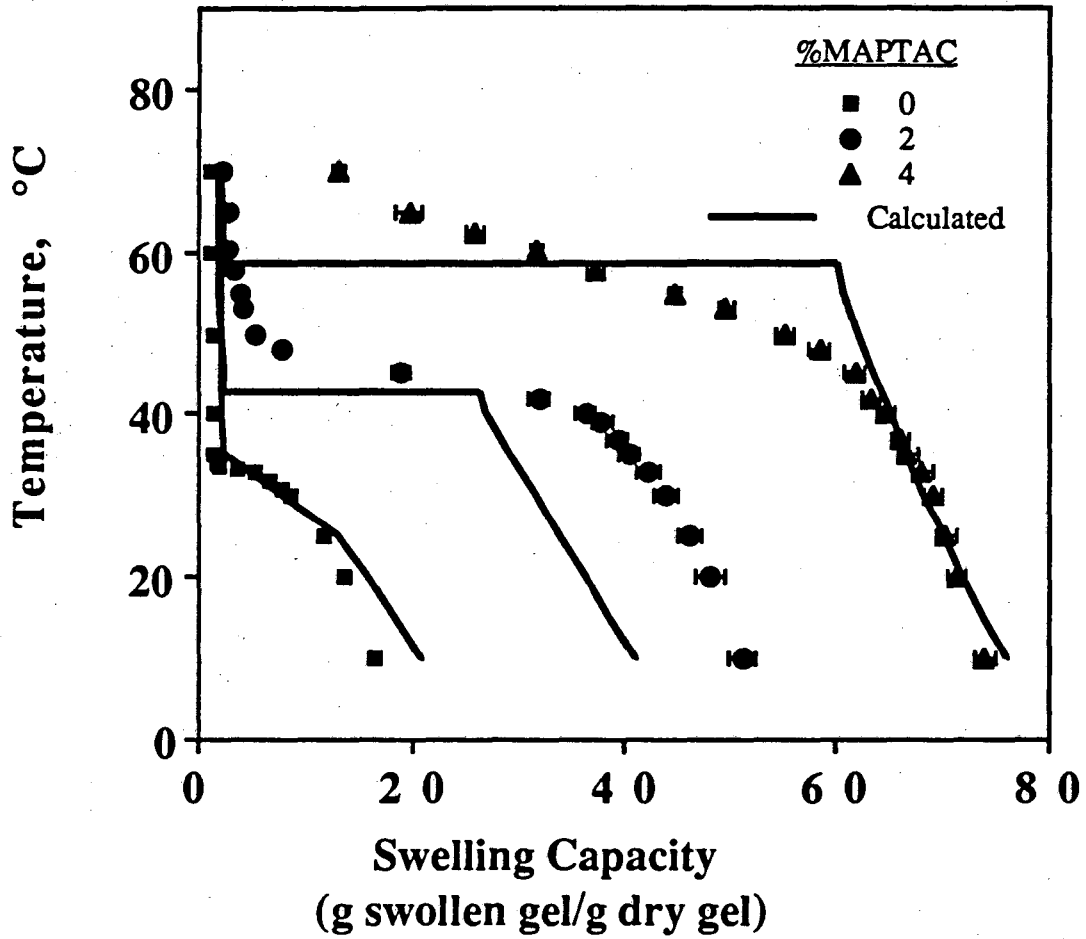


Figure 7

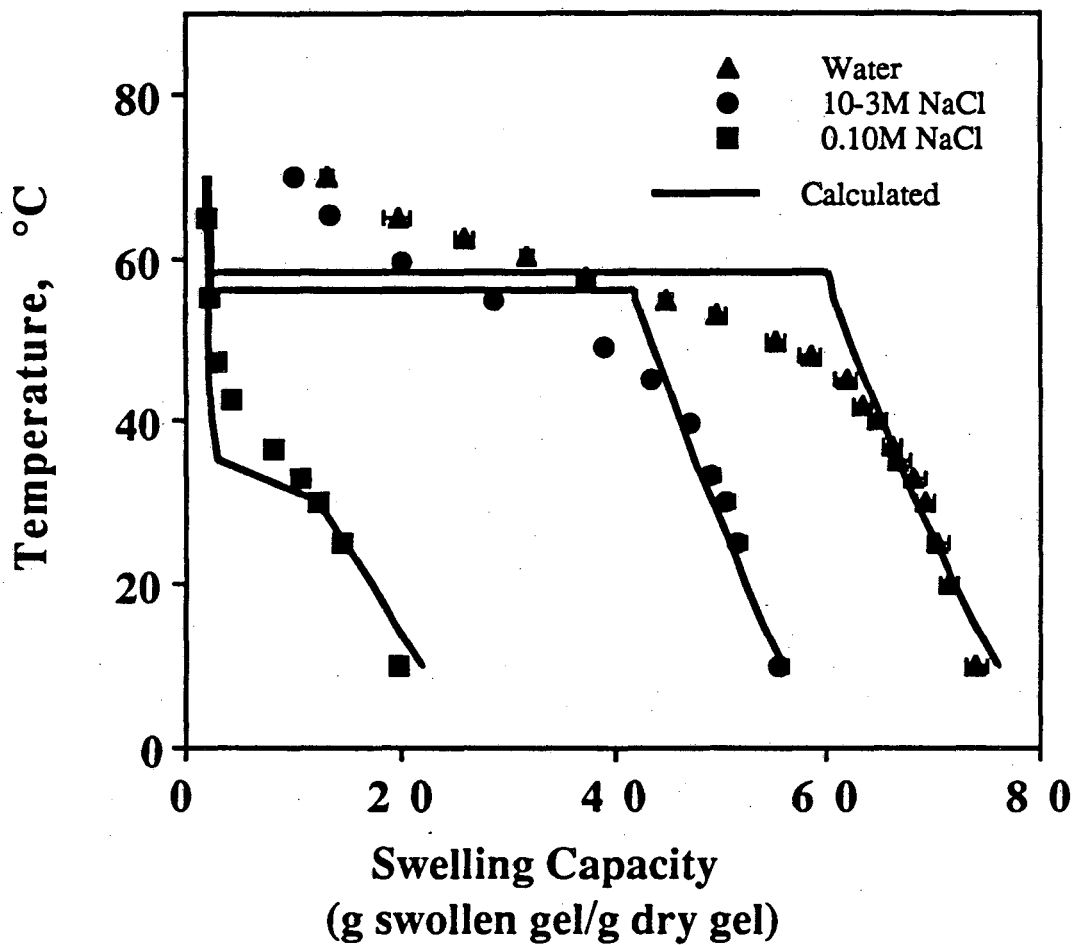


Figure 8



**SUPPLEMENTARY MATERIAL FOR:**

**Swelling Equilibria for Ionized Temperature-Sensitive Gels in Water and in Aqueous Salt Solutions**

*Sagrario Beltran, Herbert H. Hooper, Harvey W. Blanch, and John M. Prausnitz*

Chemical Engineering Department, University of California, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720

Tables 1-4 give experimental swelling data presented in graphical form in the manuscript. Standard deviations are indicated for measurements performed in triplicate.

**Table 1.** Swelling equilibria at 10°C for gels prepared with varying amounts of charged comonomer

% MAPTAC	swelling ratio (g swollen gel/g dry gel) <sup>a</sup> for specified NaCl concentration													
	DI Water <sup>b</sup>		10 <sup>-5</sup> M NaCl		10 <sup>-4</sup> M		10 <sup>-3</sup> M		10 <sup>-2</sup> M		10 <sup>-1</sup> M		1.0 M	
0	16.5	(0.17)	17.0	(0.21)	16.8	(0.17)	16.9	(0.17)	16.7	(0.18)	17.0	(0.17)	15.7	(0.20)
1.0	34.3	(0.20)	34.6	(0.26)	33.1	(0.20)	27.2	(0.17)	20.5	(0.21)	19.9	(0.24)	18.1	(0.15)
2.0	51.2	(1.3)	50.7	(1.4)	48.6	(1.3)	38.2	(1.0)	22.7	(0.59)	19.8	(0.51)	18.3	(0.48)
3.0	63.0	(0.36)	62.6	(0.39)	59.8	(0.56)	46.5	(0.65)	25.0	(0.36)	19.7	(0.38)	18.3	(0.36)
4.0	74.0	(0.92)	73.9	(1.1)	70.7	(1.1)	55.5	(0.71)	28.1	(0.36)	19.8	(0.33)	17.7	(0.24)

<sup>a</sup>Results in parentheses represent standard deviation. <sup>b</sup>Distilled water.

Table 2. Temperature-dependent swelling equilibria in water for NIPA/MAPTAC copolymer gels

T (°C)	swelling ratio (g swollen gel/g dry gel) <sup>a</sup> for specified %MAPTAC									
	0% MAPTAC		1.0%		2.0%		3.0%		4.0%	
10.0	16.5	(0.17)	34.3	(0.20)	51.2	(1.3)	63.0	(0.36)	74.0	(0.92)
20.0	13.6	(0.18)	30.8	(0.23)	48.2	(1.3)	60.0	(0.43)	71.4	(0.89)
25.2	11.6	(0.12)	28.8	(0.25)	46.2	(1.2)	59.2	(0.35)	70.4	(0.96)
30.0	8.54	(0.09)	26.0	(0.19)	44.1	(1.2)	57.1	(0.48)	69.1	(0.86)
31.0	7.70	(0.09)	25.1	(0.16)	-	-	-	-	-	-
32.0	6.68	(0.07)	-	-	-	-	-	-	-	-
33.0	5.37	(0.08)	23.2	(0.15)	42.4	(1.1)	55.5	(0.68)	68.1	(0.86)
33.4	3.52	(0.09)	-	-	-	-	-	-	-	-
33.7	2.08	(0.07)	-	-	-	-	-	-	-	-
34.0	1.66	(0.07)	-	-	-	-	-	-	-	-
35.0	1.52	(0.05)	20.7	(0.16)	40.6	(1.1)	54.6	(0.39)	66.7	(0.96)
37.0	-	-	17.4	(0.27)	39.5	(1.0)	53.6	(0.31)	66.0	(0.89)
38.0	-	-	13.3	(0.37)	-	-	-	-	-	-
39.0	-	-	7.48	(0.18)	38.0	(0.98)	-	-	-	-
40.0	1.34	(0.02)	4.68	(0.15)	36.4	(1.0)	51.8	(0.42)	64.7	(0.85)
42.1	-	-	3.43	(0.21)	31.9	(0.90)	50.1	(0.44)	63.2	(0.78)
45.0	-	-	2.23	(0.14)	18.9	(0.79)	46.0	(0.85)	61.8	(0.94)
48.1	-	-	1.86	(0.08)	7.94	(0.22)	38.2	(0.72)	58.5	(1.0)
50.0	1.26	(0.04)	1.85	(0.20)	5.41	(0.37)	31.5	(0.66)	55.2	(0.90)
53.0	-	-	-	-	4.05	(0.13)	20.1	(0.56)	49.7	(0.73)
55.0	-	-	1.77	(0.12)	4.03	(0.15)	14.4	(0.74)	45.0	(0.56)
57.7	-	-	-	-	3.32	(0.11)	10.1	(0.28)	37.4	(0.76)
60.0	1.24	(0.01)	1.72	(0.14)	2.77	(0.09)	7.41	(0.18)	31.8	(0.66)
62.5	-	-	-	-	-	-	6.30	(0.22)	25.9	(0.82)
65.0	-	-	1.46	(0.02)	2.72	(0.49)	5.93	(0.67)	19.8	(1.2)
70.0	1.23	(0.03)	1.48	(0.05)	2.25	(0.10)	4.38	(0.24)	13.2	(0.56)

<sup>a</sup>Results in parentheses represent standard deviation.

**Table 3.** Temperature-dependent swelling equilibria in  $10^{-3}$  M aqueous NaCl for NIPA/MAPTAC copolymer gels

T (°C)	swelling ratio (g swollen gel/g dry gel) <sup>a</sup> for specified %MAPTAC									
	0% MAPTAC		1.0%		2.0%		3.0%		4.0%	
10.0	16.9	(0.17)	27.2	(0.17)	38.2	(1.0)	46.5	(0.65)	55.5	(0.71)
25.0	11.0	(0.11)	21.6	(0.13)	33.4	(0.89)	42.2	(0.60)	51.7	(0.72)
30.0	8.14	(0.09)	19.1	(0.12)	31.4	(0.84)	40.6	(0.57)	50.5	(0.68)
33.0	5.03	(0.13)	-	-	-	-	-	-	-	-
33.3	3.68	(0.04)	16.9	(0.11)	30.1	(0.88)	39.2	(0.56)	49.2	(0.67)
33.7	2.16	(0.09)	-	-	-	-	-	-	-	-
34.0	1.69	(0.03)	-	-	-	-	-	-	-	-
35.0	1.55	(0.07)	-	-	-	-	-	-	-	-
40.0	1.31	(0.00)	4.07	(0.05)	24.9	(0.67)	36.2	(0.51)	47.0	(0.64)
45.2	-	-	1.69	(0.06)	10.8	(0.30)	29.8	(0.44)	43.4	(0.57)
50.0	1.28	(0.04)	1.58	(0.05)	5.38	(0.15)	21.0	(0.32)	39.1	(0.52)
54.7	-	-	1.54	(0.14)	3.17	(0.09)	10.2	(0.19)	28.6	(0.49)
60.0	1.25	(0.03)	1.49	(0.08)	2.58	(0.13)	6.51	(0.13)	20.2	(0.36)
65.2	-	-	-	-	2.16	(0.22)	4.77	(0.16)	13.4	(0.26)
70.0	1.23	(0.07)	1.53	(0.11)	1.81	(0.19)	3.88	(0.08)	10.1	(0.39)

<sup>a</sup>Results in parentheses represent standard deviation.

**Table 4.** Temperature-dependent swelling equilibria in 0.1M aqueous NaCl for NIPA/MAPTAC copolymer gels

T (°C)	swelling ratio (g swollen gel/g dry gel) <sup>a</sup> for specified %MAPTAC									
	0% MAPTAC		1.0%		2.0%		3.0%		4.0%	
10.0	17.0	(0.17)	19.9	(0.24)	19.8	(0.51)	19.7	(0.38)	19.8	(0.33)
25.0	10.5	(0.11)	12.5	(0.15)	13.0	(0.34)	13.5	(0.26)	14.4	(0.24)
30.0	7.04	(0.08)	9.13	(0.11)	10.2	(0.26)	11.1	(0.22)	12.2	(0.21)
33.0	2.42	(0.05)	5.64	(0.13)	7.50	(0.05)	9.18	(0.18)	10.7	(0.19)
33.4	1.59	(0.05)	-	-	-	-	-	-	-	-
33.7	1.53	(0.03)	-	-	-	-	-	-	-	-
34.0	1.52	(0.03)	2.96	(0.09)	6.45	(0.06)	-	-	-	-
35.0	1.44	(0.04)	2.15	(0.10)	5.24	(0.09)	-	-	-	-
36.5	-	-	-	-	3.55	(0.11)	5.97	(0.12)	8.19	(0.14)
40.0	1.30	(0.03)	1.56	(0.03)	2.09	(0.05)	-	-	-	-
42.5	-	-	-	-	1.95	(0.07)	2.79	(0.06)	4.06	(0.07)
47.5	1.23	(0.02)	-	-	-	-	1.97	(0.06)	2.90	(0.05)
50.0	1.22	(0.02)	1.39	(0.08)	1.58	(0.02)	-	-	-	-
55.0	-	-	-	-	-	-	1.83	(0.07)	2.25	(0.04)
60.0	1.22	(0.01)	1.34	(0.09)	1.40	(0.03)	-	-	-	-
65.0	-	-	-	-	-	-	1.73	(0.05)	1.93	(0.05)

<sup>a</sup>Results in parentheses represent standard deviation.

LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
1 CYCLOTRON ROAD  
BERKELEY, CALIFORNIA 94720