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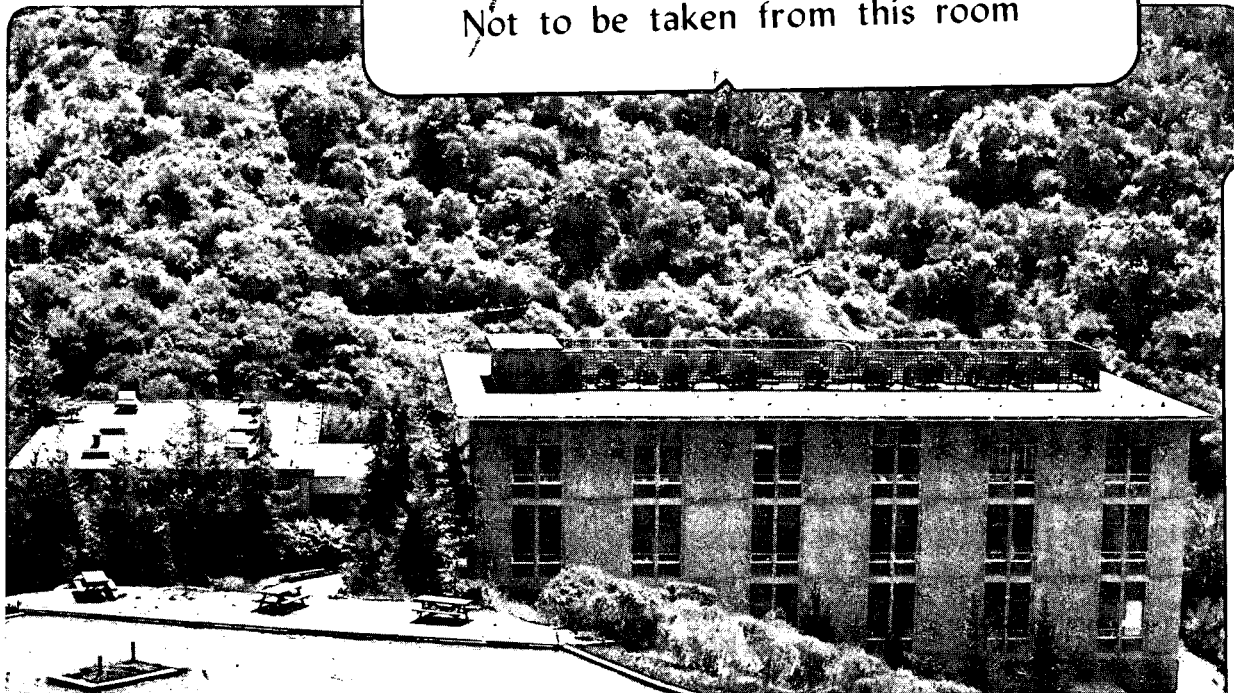### Swelling Equilibria for Acrylamide-Based Polyampholyte Hydrogels

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DISCLAIMER

Swelling Equilibria for Acrylamide-Based Polyampholyte Hydrogels

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Abstract

Polyampholyte hydrogels show promise for use in applications that require the material to maintain appreciable swelling capacity in high-ionic-strength aqueous media. Polyampholyte hydrogels were synthesized by copolymerizing acrylamide (AAm) with the cationic monomer methacrylamidopropyl trimethylammonium chloride (MAPTAC) and the anionic monomer sodium styrene sulfonate (SSS). The total nominal charge density of the hydrogels was held constant at 4.7±0.1 mole percent (dry basis), while the molar ratio of anionic to cationic moieties within the hydrogels was varied. Swelling equilibria were measured in water and in aqueous sodium chloride solutions ranging in ionic strength from 10^{-5} to 1.0 M. The hydrogels show increasing insensitivity to ionic strength as the molar ratio of anionic to cationic moieties in the hydrogel approached unity. At ionic strengths of 0.1 M and above, all hydrogels prepared show an increase in water content with rising NaCl concentration.

Introduction

In recent years years, hydrogels have received attention for potential use as extraction solvents[1], for use in medical therapeutics and diagnostics,[2] and for use in drug-delivery devices.[3,4] The medical and pharmaceutical applications of hydrogels have been extensively reviewed.[5] Many potential applications of hydrogels require maintenance of hydrogel swelling capacity at high ionic strengths; for this reason we have investigated some properties of polyampholyte hydrogels. Possible applications for such materials include use in enhanced-oil-recovery techniques (brine solutions) and in biomedical devices for implantation in the body (the ionic strength of biological fluid is approximately 0.15 M). For these applications,

hydrogels must maintain significant swelling capacity in aqueous solutions of elevated ionic strength (> 0.1 M).

The hydrodynamic radius of a polyelectrolyte decreases as the ionic strength of its solution rises; this decrease is the polyelectrolyte effect. Fixed-charge repulsions that tend to elongate the chain are screened as the Debye length in the solution declines. This decrease in hydrodynamic radius can be detected, for example, through intrinsic-viscosity measurements of polyelectrolyte solutions.[6] Cross-linked hydrophilic polymers (hydrogels) containing fixed charges may exhibit analogous behavior in aqueous solution. The swollen hydrogels collapse as the ionic strength of the solution rises because the electrostatic forces of repulsion between fixed, ionized groups are drastically reduced at high ionic strength. Hooper et al.[7] found that acrylamide-based polyelectrolyte hydrogels collapse with increasing ionic strength, and that swelling remains at a constant, low level for ionic strengths of 0.1 M and above.

To our best knowledge, no attention has been given previously to polyampholyte hydrogels. However, attention has been given previously to polyampholytes, i.e. polymers containing both cationic and anionic fixed charges.[8-11] Peiffer and Lundberg[10] studied hydrophilic polyampholytes formed by copolymerizing acrylamide (AAm) with methacrylamidopropyl trimethylammonium chloride (MAPTAC) (cationic monomer) and sodium styrene sulfonate (SSS) (anionic monomer). They found that AAm-based polyampholytes (containing moderate charge densities) retain their viscosity-enhancing properties in high ionic-strength solutions. Peiffer and Lundberg observed that, while the dilute-solution viscosity in pure water was relatively low, the viscosity *markedly increased* with rising solution ionic strength. Viscosity enhancement has been attributed to the

breaking of intramolecular ionic linkages that form at low ionic strength between the oppositely charged moieties on the polymer chains. Increasing the ionic strength of the solution disrupts the ionic linkages, allowing the polymer chains to become more fully extended in solution, thus increasing the hydrodynamic radius of the polymer. The increased hydrodynamic radius of the polymer is reflected by rising solution viscosity.

The increase in end-to-end distance of a polyampholyte as the ionic strength of the solution rises may be called the *polyampholyte effect*, analogous to the *polyelectrolyte effect*.

In this work, we prepared hydrogels similar in composition to linear polymers studied by Peiffer and Lundberg[10], viz. acrylamide (AAm) copolymerized with the cationic methacrylamidopropyl trimethyl-ammonium chloride (MAPTAC) and the anionic sodium styrene sulfonate (SSS); we added a cross-linking agent, N,N'-methylenebisacrylamide (BIS), to form loose networks. Swelling equilibria for the polyampholyte hydrogels were measured as a function of ionic composition and solution ionic strength.

Experimental Methods

Materials. Acrylamide (AAm), N,N'-methylenebisacrylamide (BIS), and ammonium persulfate (APS) were supplied by Eastman Kodak. Methacrylamidopropyl trimethylammonium chloride (MAPTAC) (50% by weight in aqueous solution) and sodium styrene sulfonate (SSS) were obtained from Aldridge, and sodium chloride (NaCl) from Fisher. All reagents were used as received. All water used in synthesis and swelling measurements was distilled, and then purified and filtered through a Barnstead Nanopure II system.

Synthesis. Free-radical aqueous copolymerization of AAm, MAPTAC, and SSS was employed to prepare the hydrogels. BIS was used as the cross-linking agent. Polymerization was initiated by APS, and occurred in 10 x 75-mm test tubes.

The composition of the various hydrogels was determined by the nominal amounts of reagents present in the hydrogel-feed solution. Four parameters were used to define this composition:

$$\%T = \frac{\text{mass of all monomers (g)}}{\text{volume of water (ml)}} * 100 \tag{1}$$

$$\%C = \frac{\text{moles of BIS in feed solution}}{\text{total moles of monomer in feed solution}} * 100 \tag{2}$$

$$\%MAPTAC = \frac{\text{moles of MAPTAC in feed solution}}{\text{total moles of monomer in feed solution}} * 100 \tag{3}$$

$$\%SSS = \frac{\text{moles of SSS in feed solution}}{\text{total moles of monomer in feed solution}} * 100 \tag{4}$$

Seven hydrogels were prepared (I - VII). %T and %C were held constant (at 16% and 0.4% respectively), while %MAPTAC and %SSS were varied. The total nominal charge density of the hydrogels was held nearly constant; the sum of %MAPTAC and %SSS was 4.7% ±0.1. Table 1 shows the composition parameters for the seven hydrogels.

To illustrate the synthetic procedure, we give details for the preparation of hydrogel I (16%T, 0.4%C, 4.2%MAPTAC, 0.6%SSS). Added to 37.6 ml water were 6.684 g AAm, 0.056 g BIS, 1.83 ml MAPTAC solution, and 0.816 g SSS. The solution was stirred with a magnetic stirrer until well-mixed, then degassed under 27-in Hg. An initiator solution of 0.075 g APS in 15 ml water was degassed at the same

time as the monomer solution. After 1 hr, both solutions were transferred to a nitrogen atmosphere. Under nitrogen, 5 ml of the initiator solution was added to the monomer solution. The mixture was stirred until well-mixed and poured into the test tubes for reaction. The test tubes were placed in a thermostatted bath at 50°C. After 24 hr, the hydrogels were removed from the test tubes, and then sliced into disks approximately 5 mm thick. The hydrogel disks were soaked in water which was refreshed periodically to leach away the soluble fraction and initiator residues.

Swelling Studies. Hydrogels were swollen to equilibrium in water at 8°C. Equilibrium was attained in one week; the approach to equilibrium was monitored by measurement of the mass of the swollen hydrogels. Once equilibrium was attained, the swelling capacity in water was determined for each hydrogel in the series. Equilibrated disks were weighed, dried at room conditions, and re-weighed. The swelling capacity in water is defined as the mass ratio of swollen to dry hydrogel.

Aqueous solutions of NaCl were prepared ranging in concentration from 10^{-5} to 1.0 M. Hydrogel disks were transferred from water to each of the salt solutions and allowed to equilibrate. To compensate for possible solvent exchange between hydrogel and external solution, NaCl solutions bathing the hydrogels were changed every other day. Mass measurements of the hydrogels were taken to monitor attainment of equilibrium. After two weeks, mass measurements did not change; the swelling capacities were then determined by:

$$\text{Swelling capacity} = \frac{\text{mass gel in water}}{\text{mass dry gel}} \times \frac{\text{mass gel in salt solutions}}{\text{mass gel in water}} \qquad (5)$$

All swelling studies were performed in triplicate. Table 2 provides mean values and deviations of the measured swelling behavior.

Results and Discussion

The overall nominal charge density of seven hydrogels was fixed at 4.7 ±0.1 mole percent (%MAPTAC + %SSS), while the cationic-to-anionic balance of the hydrogels was varied. Figure 1 shows swelling equilibria for seven hydrogels in water. A minimum in swelling capacity is observed with hydrogel IV (nearly equimolar amounts of SSS and MAPTAC). Swelling increases with rising prevalence of the MAPTAC comonomer (hydrogels I - III), or SSS comonomer (hydrogels V - VII).

The ability of a hydrogel to neutralize itself by forming ionic linkages (the polyampholyte character) is enhanced as the molar ratio of MAPTAC to SSS approaches unity. Conversely, as the MAPTAC-to-SSS ratio departs from unity, polyelectrolyte character is enhanced. Swelling increases as polyampholyte character declines and polyelectrolyte behavior rises.

Comparing hydrogels with similar amounts of "excess" charge in Figure 1, the hydrogel containing excess cationic character consistently swelled to greater capacity than the hydrogel containing excess anionic character. The "asymmetry" in swelling behavior is dramatic: hydrogel I (4.2%MAPTAC, 0.6%SSS) swelled 71% more in water than hydrogel VII (0.6, 4.0); hydrogel II (3.6, 1.1) swelled 77% more than hydrogel VI (1.2, 3.4); and hydrogel III (3.0, 1.7) swelled 112% more than hydrogel V (1.8, 2.8).

Three mechanisms, possibly working in concert, may account for the asymmetry in swelling bracketing hydrogel IV: (1) Differences in cross-

link density caused by different rates of copolymerization. Due to the difficulties associated with copolymerizing four monomers, the cross-linking reaction may be enhanced in the net anionic hydrogels, or it may be impeded in the net cationic hydrogels. This possible explanation could be ruled out by a thorough analysis of the copolymerization. However, such analysis was beyond the scope of this preliminary study. (2) Hydrophobicity imparted to the net anionic hydrogels by styrenic moieties. Hydrophobic interactions between the styrenic moieties of SSS may tend to reduce chain expansion inside the network, depressing the swelling of the hydrogel. The net anionic hydrogels should be less solvophilic than the net cationic hydrogels, and should thus swell less. (3) Differences in the activities of the counterions to the charged groups. Since a quaternary amine group is bulkier than a sulfonate group, the electric field near the interface between the quaternary amine group and water will be weaker than the corresponding field at the sulfonate-water interface. Because of the difference in electric-field strength surrounding the two functional groups, the attraction between counterion and functional group will be weaker for MAPTAC than for SSS. Thus the counterions for MAPTAC are more osmotically active than the counterions for SSS, resulting in higher swelling capacities for the net cationic hydrogels.

Figures 2 and 3 show swelling equilibria in aqueous NaCl solutions for the net cationic hydrogels (I - III) and for the net anionic hydrogels (V - VII), respectively. The same coordinate axes are used in both plots to facilitate qualitative comparisons. All hydrogels exhibit polyelectrolyte behavior at relatively low ionic strengths (10^{-5} M to 0.01 M). As observed in the swelling experiments in water, swelling of the net anionic hydrogels was found to be depressed relative to that of the net cationic hydrogels.

This asymmetry in swelling behavior is shown in Figure 4; here, we show swelling equilibria in NaCl solutions for hydrogels III, IV, and V. Hydrogel III swells 117% more than hydrogel V in 10^{-5} M NaCl; III swells 33% more than V in 0.01 M NaCl. While the swelling of hydrogel IV is relatively insensitive to ionic strength at concentrations less than 0.01 M NaCl, hydrogels III and V exhibit marked polyelectrolyte behavior in this concentration range. An increase with rising NaCl concentration was observed for all three hydrogels at ionic strengths of 0.01 M or greater; hydrogel IV swelled most in the highest ionic-strength solution used in this study, 1.0 M. This increase in swelling may be analogous to the increase in solution viscosity for linear polyampholytes, and thus may reflect a polyampholyte effect for hydrogels.

Conclusions

Acrylamide-based polyampholyte hydrogels were synthesized; their swelling properties were observed in water and in aqueous NaCl solutions. The hydrogels with excess cationic character (hydrogels I - III) consistently reached higher swelling capacities in aqueous media than those with similar amounts of excess anionic character (hydrogels V - VII). Methacrylamidopropyl trimethylammonium chloride (MAPTAC) and Sodium styrene sulfonate (SSS) were, respectively, the cationic and anionic monomers chosen for this study. The structure of SSS appears to be more hydrophobic compared to that of MAPTAC; the hydrogels with excess anionic character may be relatively less solvophilic because of styrenic moieties within them. Structural distictions between the two charged monomers, which may also lead to the observed "asymmetric" swelling behavior, may be reflected in differences in cross-link density and

differences in counterion activity between the net anionic and net cationic hydrogels

Polyelectrolyte hydrogels show *extreme sensitivity* to ionic strength at NaCl concentrations below 0.01 M, and show *insensitivity* to ionic strength at NaCl concentrations of 0.1 M and above. The hydrogels prepared for this study showed *decreasing sensitivity* to ionic strength (increasing polyampholyte behavior) as the molar ratio of anionic to cationic moieties in the hydrogel approached unity. At ionic strengths of 0.1 M and above, all polyampholyte hydrogels showed an *increase* in swelling capacity with rising NaCl concentration. Hydrogels that are insensitive to changes in ionic strength, or that swell with rising ionic strength, may be useful for applications requiring materials that can maintain appreciable swelling capacity in high-ionic-strength environments.

Acknowledgements

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Table 1 Composition parameters for the seven hydrogels prepared for this work. The total nominal charge content of the hydrogels was held nearly constant; the sum of %MAPTAC and %SSS was 4.7% ±0.1. The hydrogels were 16% T and 0.4% C.

Hydrogel	%MAPTAC	%SSS
I	4.2	0.6
II	3.6	1.1
III	3.0	1.7
IV	2.4	2.3
V	1.8	2.8
VI	1.2	3.4
VII	0.6	4.0

Table 2 Swelling capacity in NaCl solutions for ampholytic hydrogels prepared with different % MAPTAC to % SSS ratios. The values in parentheses represent 95% confidence intervals.

Hydrogel	Swelling capacity (g swollen gel/g dry gel) for specified NaCl concentration						
	1.0 M NaCl	10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M	10^{-5} M	0 M*
I	16.6 (0.2)	15.1 (0.2)	28.1 (0.9)	67.8 (1.0)	95.4 (1.8)	100.2 (0.7)	100.0 (3.5)
II	16.4 (0.2)	14.1 (0.4)	21.3 (0.3)	47.9 (0.3)	64.9 (1.4)	68.6 (1.1)	68.1 (1.1)
III	16.2 (0.2)	13.4 (0.2)	15.4 (0.3)	28.3 (0.4)	36.0 (0.7)	37.4 (1.1)	37.5 (0.6)
IV	15.7 (0.4)	12.9 (0.2)	11.2 (0.2)	12.2 (0.1)	12.8 (0.6)	13.0 (0.2)	13.2 (0.2)
V	15.1 (0.2)	12.6 (0.4)	11.5 (0.7)	14.6 (0.1)	17.0 (0.5)	17.3 (0.2)	17.7 (0.2)
VI	14.8 (0.2)	12.6 (0.2)	15.0 (0.2)	27.4 (0.5)	36.4 (0.5)	37.9 (1.1)	38.4 (0.1)
VII	14.4 (0.2)	13.2 (0.2)	19.7 (0.2)	41.0 (0.1)	55.7 (0.2)	57.7 (0.6)	58.6 (1.9)

* Swelling equilibria in salt-free water.

Figure Captions

Figure 1 Swelling equilibria in water for ampholytic hydrogels with 16% T and 0.4% C. The amount of charged comonomer present in the hydrogel-feed solution was fixed at 4.7%±0.1 (molar basis). There is pronounced asymmetry in swelling behavior between the net anionic hydrogels and the net cationic hydrogels.

Figure 2 Swelling equilibria for net cationic ampholytic hydrogels. Swelling was measured as a function of NaCl concentration.·

Figure 3 Swelling equilibria for net anionic ampholytic hydrogels. Swelling was measured as a function of NaCl concentration. Data are plotted on the same axes as those of Figure 2 to facilitate qualitative comparison.

Figure 4 Comparison of swelling equilibria for the 3.0% MAPTAC - 1.7% SSS hydrogel with the 1.8% MAPTAC - 2.8% SSS hydrogel. The swelling equilibria for the 2.4% MAPTAC - 2.3% SSS hydrogel are shown here to facilitate comparison.
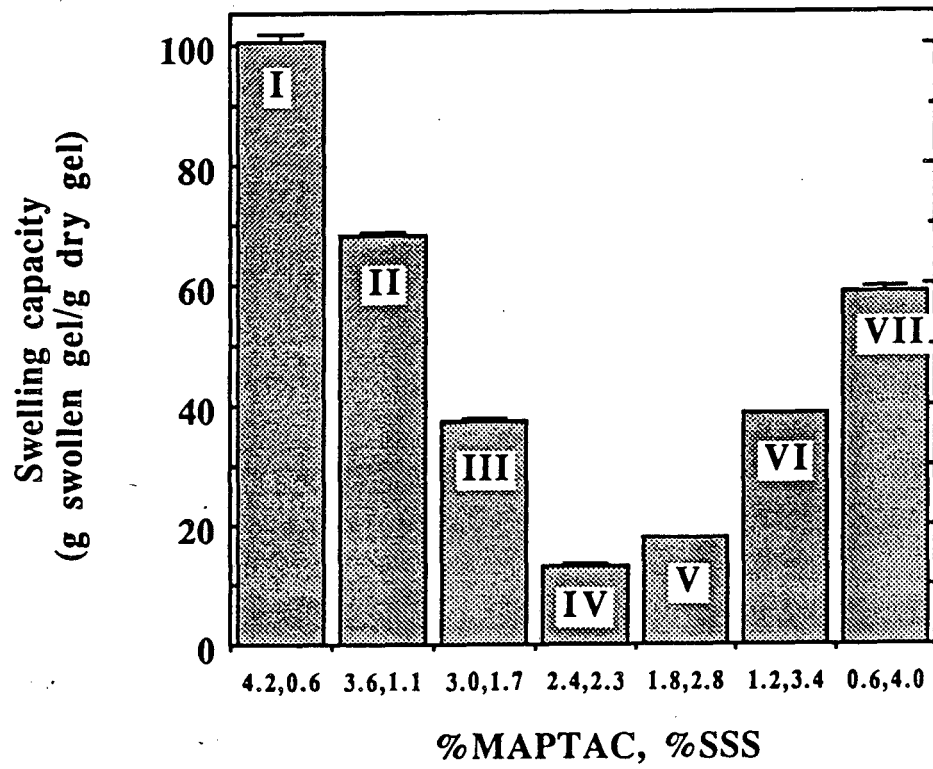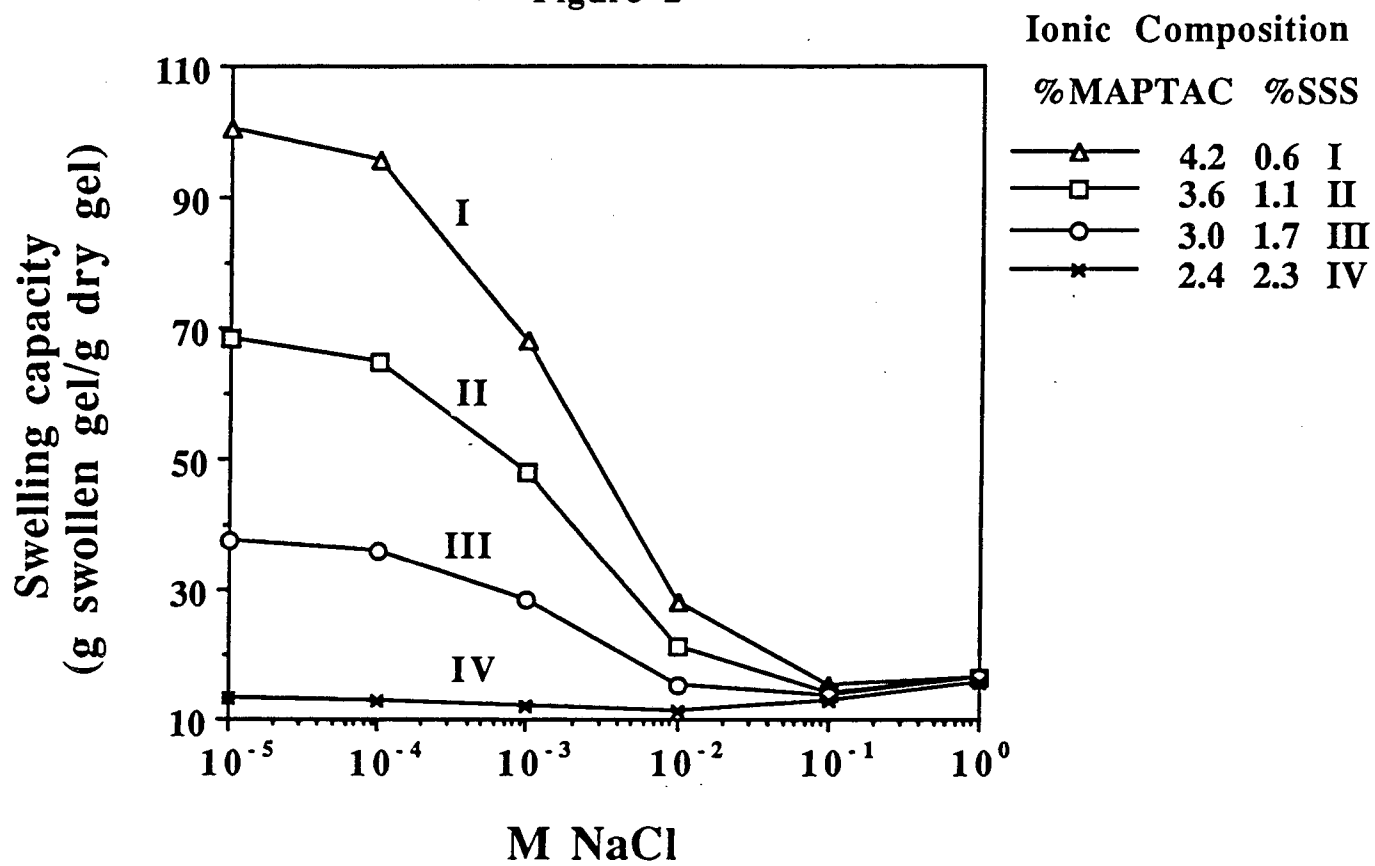
Figure 1

Figure 2

Figure 2. Swelling capacity (g swollen gel/g dry gel) versus M NaCl for ionic compositions I–IV.

Figure 3

Figure 3

Swelling capacity (g swollen gel/g dry gel) vs M NaCl

Ionic Composition

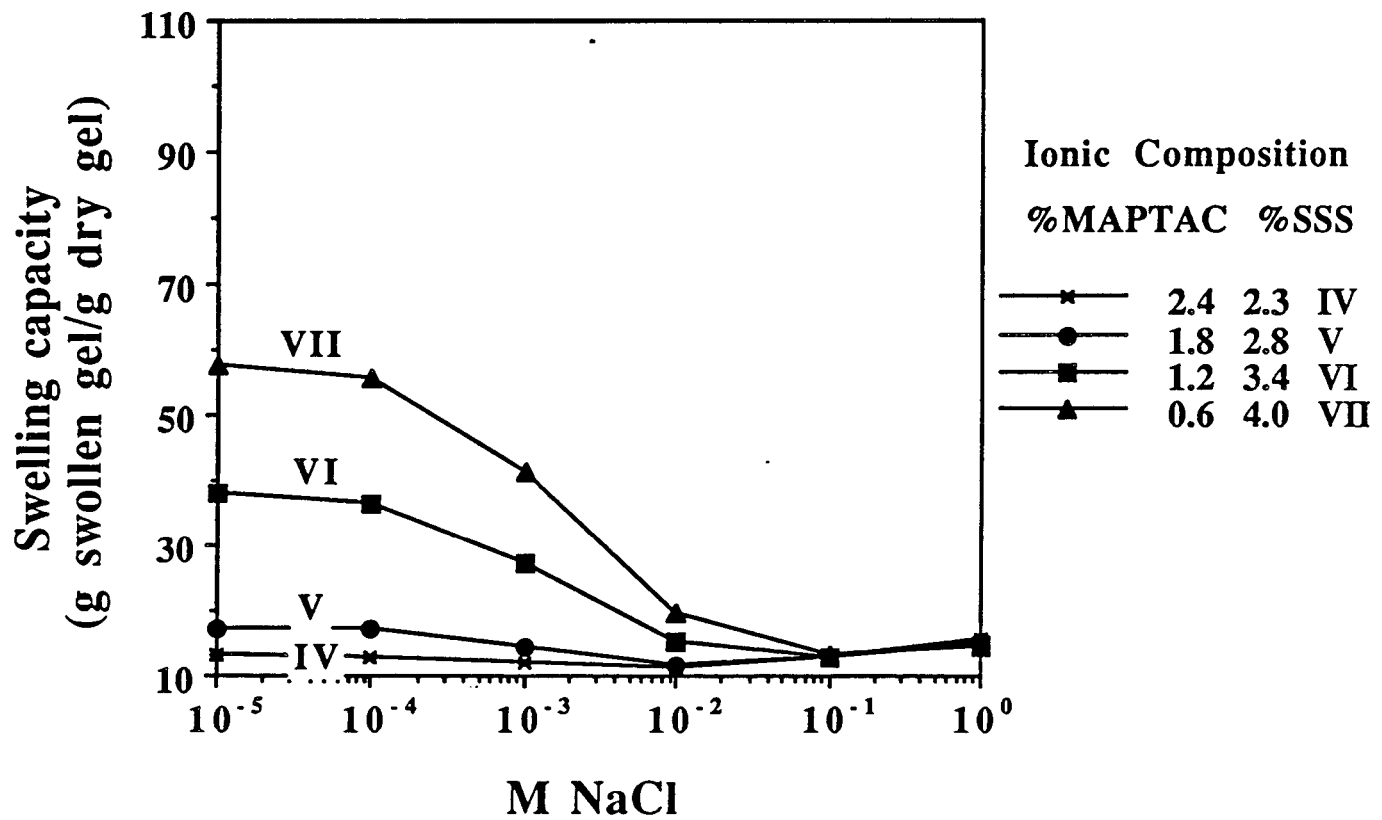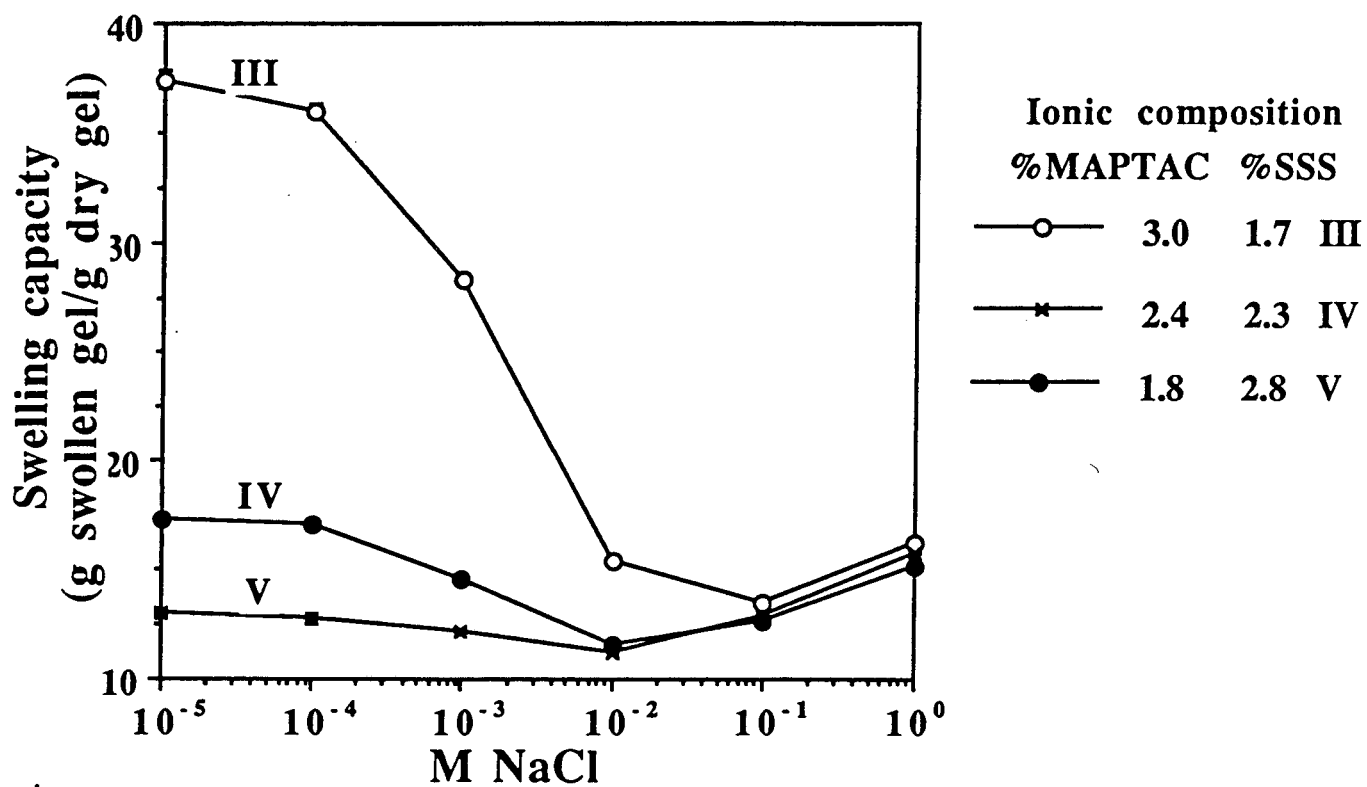|	%MAPTAC	%SSS	
✕	2.4	2.3	IV
●	1.8	2.8	V
■	1.2	3.4	VI
▲	0.6	4.0	VII

Figure 4

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