Swelling Equilibria and Volume Phase Transition in Hydrogels with Strongly Dissociating Electrolytes

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ABSTRACT: Several sulfonic acid copolymer gels were prepared by radical copolymerization of *N,N*-dimethylacrylamide (DMAA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) using *N,N'*-methylenebisacrylamide (BIS) as the cross-linker. The concentration of pregel solutions and BIS content in dried gels were held constant at 0.75 mol/L and 1.3 mol %, respectively, while the mole fraction f of AMPS in dried gels determined by elemental analysis varied from 0 to 0.608. Swelling ratios for our sample of $f = 0.468$ were compared with those for an acrylic acid copolymer gel of $f = 0.494$ and 25 °C in aqueous buffers from pH = 2 to pH = 10 at 0.01 M ionic strength, and the results indicated that even in the gel state the sulfonic acid group could dissociate completely in the whole pH range. Therefore, f in this work can be designated to represent the charge density in the swollen gels. The swelling capacity observed in pure water at 25 °C increases monotonically with increasing f, showing a higher increasing rate when $f > 0.3$ without any sign of counterion condensation. The experimental swelling curve was interpreted with the Flory-Huggins theory and with the Hasa-Ilavsky-Dusek (HID) theory, but both theories failed to provide a reasonable approach to the swelling equilibria in our gels with a large amount of strongly dissociating electrolytes. The reciprocal of polymer volume fraction in a swollen gel, $1/\phi$, predicted with the Flory-Huggins theory was much higher than that observed when $f > 0.2$, while the calculated results given by the HID theory using the experimental nominal value of chain density were considerably lower than measured data in the entire f range. A volume phase transition occurred in these gels when $f > 0$ when the acetone volume fraction V_a in the acetone/water mixture was beyond a certain value, and this transition could be attributed to the weakening of electrostatic repulsion during increasing V_a in the mixture.

Introduction

A polymer gel is a multicomponent system consisting of at least a synthesized network and a swelling agent. The swelling behavior of hydrogels has been studied for more than four decades[1] for its significance in fundamental science and application. The first observation of a volume phase transition in hydrolyzed polyacrylamide gels in acetone/water mixtures by Tanaka[2] greatly prompted research in this field.

In the case of a polyelectrolyte gel (i.e., a polymer network with ionizable groups on the chain which swells in water) the situation of electrostatic interaction in the swollen gel is similar to that in a polyelectrolyte solution without added salts, except that the chains in the gel are cross-linked. On the other hand, the polyelectrolyte gel acts like a membrane through which the counterion cannot freely permeate into the surrounding water as required by the condition of electric neutrality in the gel.[1,3]

In the early 1950s, Katchalsky and colleagues reported the swelling behavior of poly(methacrylic acid) gels with different neutralization degrees in several aqueous salt solutions and argued that the Donnan distribution could not give even a rough approximation.[4] They proposed a random coil model[5] to describe titration curves[6] and swelling equilibria[4] of polyelectrolyte gels swollen in salt solutions. The feature of this theory lies in that the charge interaction along a chain is calculated by means of the Debye-Hückel theory and that the displacement probability between any two arbitrary charges in the chain is known with a random coil distribution. Along this thought, Dusek's group modified the elasticity theory for polyelectrolyte gels by considering the influence of charges on deformation[7] and published many experimental results on poly(methacrylic acid) gels and related copolymer gels concerning their swelling and elasticity behavior.[8-11] This theory was also applied by Konak and Bansil to poly(methacrylic acid) gels swollen in water without any added salt.[12] In recent years, observations for volume phase transition were carried out intensively on polyelectrolyte gels with carboxylate groups swollen in various solutions.[13-21]

However, all polyelectrolyte gels used above are weakly ionizable, and the change in ionization degree was realized by changing the degree of neutralization for a given sample. It is, therefore, impossible to keep the polymer concentration constant when altering the ionization degree. Meanwhile, the ionization degree would be easily affected by experimental conditions such as pH value, temperature, and so on.

Hooper et al. presented the swelling equilibria in copolymerized gels containing a strongly dissociating electrolyte of quaternized ammonium groups swelling in aqueous salt solutions and in pure water.[22,23] Their study was conducted with the purpose of testing their lattice models accounting for the hydrogen-bonding system, so the charge density of their gel samples was limited below 5 mol %. To our knowledge, very few studies[24,25] on volume phase transition have been reported for synthesized gels with strongly dissociating electrolyte.

To observe the effect of charge density on elasticity, swelling equilibrium, and phase transition, we have prepared highly charged copolymer gels of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and *N,N*-dimethylacrylamide (DMAA) with a cross-linker in which the AMPS can completely dissociate when swollen in water. Their dynamic response to deformation has been discussed elsewhere with the so-call HID theory.[26] In this paper we report the swelling capacity for these gels in pure water and the volume phase transition occurring in acetone/water mixtures.

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Table 1. Characteristics of the DS Series of Gel Samples[a]

code	F_{AMPS}	f	M_0	$\rho_{25°C}$/(g cm^{-3})	$\phi_0 \times 10^2$
DS0	0	0	99.9	1.213[b]	5.492
DS10	0.10	0.0899	109.6	1.199	6.207
DS20	0.20	0.1819	119.5	1.238	8.220
DS30	0.30	0.2674	128.8	1.243	8.731
DS50	0.50	0.4318	146.5	1.323	9.377
DS50a	0.493	0.4683	150.5	1.37	9.894
DS70	0.70	0.6076	165.5	1.376[c]	9.749

[a] In the pregel solution, $C_t = 0.75$ mol/L and $C = 0.013$, so that the nominal chain density is $\nu = 1.95 \times 10^{-5}$ mol/cm^3. [b] Reference 27. [c] Interpolated value.

Two typical theories are adopted in our work to interpret the swelling equilibrium: One is the Flory–Huggins theory[1] in which the electrostatic energy is ignored; the other is the HID theory[7] where the charge interaction is taken into account using the Debye–Hückel model. One of our goals is to test the ability of existing models to predict swelling equilibria for highly ionized gels as a function of charge density; thus the content of ionizable monomer AMPS in our samples is required to be as high as possible.

Experimental Section

Preparation of Gel Samples. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS), *N,N'*-methylenebisacrylamide (BIS), and ammonium persulfate (APS) were purchased from Wako Chemicals Co., while *N,N*-dimethylacrylamide (DMAA) was kindly provided by Kohjin Co. All reagents were used without further purification. The water used in the synthesis and swelling equilibria was doubly distilled and bubbled with nitrogen before use. The gel samples, designated as the DS series, were prepared by free-radical copolymerization of AMPS and DMAA with BIS in an aqueous pregel solution. The procedure was similar to that described previously,[26] but in this work the gel samples were formed in a glass capillary with an internal diameter of ca. 2.8 mm.

After reaction completion, the gels were removed from the capillary and cut into disks. The disks were soaked in excess pure water, which was replaced daily for ca. 1 week. These gel disks thoroughly washed with water served as starting samples for the remaining experiments.

For our gel samples, the total molar concentration C_t of all monomers, including BIS, in a pregel solution and the mole fraction C of BIS on a water-free basis were held constant at 0.75 mol/L and 0.013, respectively, while the stoichiometric mole fraction F_{AMPS} of AMPS monomer on a dry basis was varied from 0 to 0.7. We refer to these gels by their respective nominal mole percent of AMPS and show the composition parameters of this DS series of samples in Table 1.

A sodium acrylate (SA; acrylic acid delivered by Wako Chemicals Co. was neutralized with an aqueous NaOH solution) and DMAA copolymerized gel DA50 was prepared for comparison in which either C_t or C was identical to the corresponding values of the DS series, and the mole fraction of SA in all monomers was 0.494.

Measurement of Swelling Ratio. After the washing process, the gel disks were allowed to swell in pure water at 25 °C. The approach to swelling equilibrium was followed by monitoring the diameter of the sample with a slide caliper; the diameter ceased to change when equilibrium was reached. Then the samples were allowed to swell in acetone/water mixtures of various compositions at 25 °C. The latter process usually took a week or more to reach equilibrium, and the mixture was replaced every 3 days during this period.

The swelling experiment for the samples DS50a and DA50 was also carried out at 25 °C in several buffer solutions with different pH values at a fixed ionic strength of $I = 0.01$ M. The equilibrated pH values and gel diameter were recorded.

The swelling capacity is expressed in terms of swelling ratio, which is defined as the gel volume V at swelling equilibrium related to its original volume V_0 at polymerization.[18] Assuming isotropic swelling of the sample, we calculated the swelling ratio V/V_0 by

$$V/V_0 = (d/d_0)^3 \tag{1}$$

where d and d_0 denote the corresponding diameters of the gel disks.

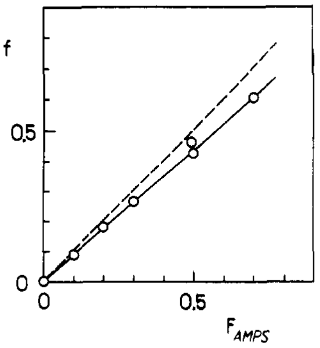

Figure 1. Copolymer composition curve of mole fraction for AMPS in dried gel f with that in feed monomers F_{AMPS}. Dashed line, azeotropic copolymerization.

Determination of Density and Sulfur Content of Dried Gel. The gel sample equilibrated in water was thoroughly dried by heating at 60 °C. The density ρ of the dried gel was determined using a pycnometer with toluene at 25 °C. The literature values of ρ for poly(*N,N*-dimethylacrylamides) gel[27] of 1.213 g/cm^3 and for poly(2-acrylamido-2-methylpropanesulfonamide)[28] of 1.443 g/cm^3 were adopted here; the latter was chosen as the approximate ρ value for the gel of $f = 1$. ρ for DS70 was evaluated by interpolating. The measured ρ data can be well fitted by

$$\rho^2 - 2.039\rho + 1.0249 - 0.1806f = 0 \tag{2}$$

which will be used in the following numerical simulation. In eq 2, f is the real mole fraction of AMPS in the gel network, which was evaluated from the weight fraction of elemental sulfur in the dried gel determined by elemental analysis. The molecular weights of AMPS, DMAA, and BIS were used in the calculation for f with $C = 0.013$. ρ and f values so obtained for our samples are listed in Table 1.

Results and Discussion

Gel Composition. The real mole fraction f of AMPS in the copolymerized network is plotted in Figure 1 as a function of F_{AMPS} in pregel solutions. A straight line gives a good fit with the data but the slope is smaller than unity, indicating that a part of the AMPS monomer molecules are not combined into network chains. When AMPS and DMAA are respectively taken as components 1 and 2, the monomer reactivity ratios r_1 and r_2 estimated with the Fineman–Ross method[29] are 0.53 and 1.03. Of course, these values only have qualitative significance since the monomer conversion in the gel formation is rather high and there exists BIS as the third component. However, these r_1 and r_2 values seem to imply that AMPS monomer is less active in this synthesis reaction and that the microstructure concerning the composition of the network chains may be heterogeneous.

The volume fraction ϕ of polymer in a given gel sample swelling equilibrated in water is evaluated from its corresponding weight fraction w as

$$\phi = [1 + \rho/\rho_w(w^{-1} - 1)]^{-1} \tag{3}$$

where ρ_w is the density of water. ϕ_0, the ϕ value for a just-synthesized sample, is obtained from $\phi_0 = (V/V_0)\phi$. ϕ_0 so obtained for our samples is shown in Table 1 and Figure 2, which can be reasonably approached with the following empirical equation

$$\phi_0^2 - 0.1062\phi_0 - 0.003817f + 0.002818 = 0 \tag{4}$$

as presented by the solid line in the figure. This relation

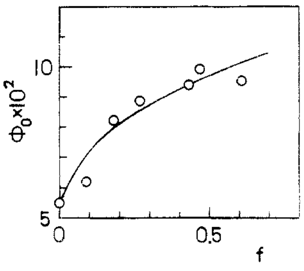

Figure 2. Variation of volume fraction ϕ_0 of polymer as just prepared with its charge density f. Solid line, an empirical fit of eq 4.

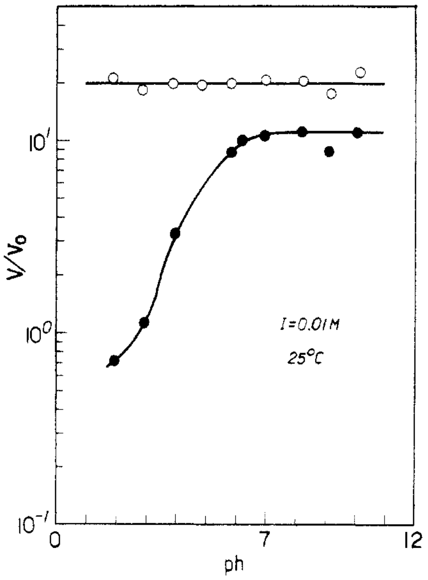

Figure 3. Swelling ratio V/V_0 in various buffers of 0.01 M ionic strength at 25 °C for the sulfonic acid copolymer gel DS50a (○) and acrylic acid copolymer gel DA50 (●).

will be used in the theoretical calculation.

We have measured the dynamic modulus of these gels separately.[26] Unfortunately, the chain density ν in a gel sample just polymerized, however, cannot be unambiguously estimated for the equilibrium shear modulus G_e, since it varies with F_{AMPS}, the stoichiometric mole fraction of AMPS. Therefore, both the nominal value of $\nu = 1.95 \times 10^{-5}$ mol/cm^3 evaluated from BIS concentration C and experimental value of $\nu = 2 \times 10^{-6}$ mol/cm^3 estimated from the order of magnitude of G_e have to be adopted here for calculating the swelling equilibrium.

Swelling Equilibria. Figure 3 presents swelling ratios at 25 °C for DS50a and DA50 gels in aqueous buffers from pH = 2 to pH = 10 at a fixed ionic strength of $I = 0.01$ M. Consistent with expectations, swelling of the poly(acrylic acid) gel DA50 is found to increase with pH when pH < 6, just like the swelling behavior of *N*-isopropylacrylamide/SA copolymer gels observed by Beltran et al.,[30] while the swelling ratio of DS50a gel containing sulfonate groups is found to be a constant about twice as large as that for the DA50 gel at pH > 7. The swelling behavior of DA50 gel at pH < 5 is the macroscopic response to the increase in ionization degree with pH (the pK_a of acrylic acid is 4.3)[31] of the carboxylate groups on the network chains. The constant swelling capacity of the DS50a gel indicates that even in the gel state the sulfonic acid group can completely dissociate in the overall pH range. Therefore, the real mole fraction f of AMPS can be used to represent the charge density in a swollen gel; i.e., the degree of dissociation α for our poly(sulfonic acid) gels would be assumed to be unity.[7]

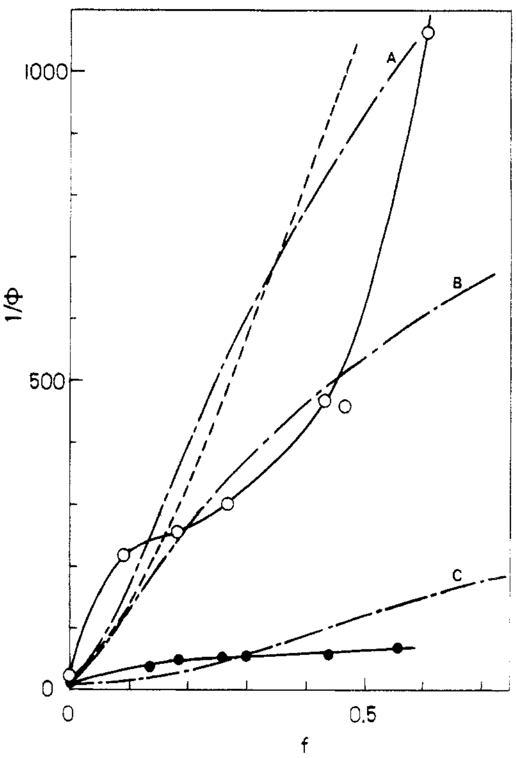

Figure 4. Comparison of calculated and observed f dependence of $1/\phi$ for our gel samples (○) and the partially neutralized poly(acrylic acid) gels (●)[21] equilibrium swollen in pure water at 25 °C. Dashed line, calculated with the Flory–Huggins theory; dot-dash lines, calculated with the HID theory using the following parameters: (A) $\nu = 2 \times 10^{-6}$ mol/cm^3 and $s = 5$; (B) $\nu = 2 \times 10^{-6}$ mol/cm^3 and $s = 8$; (C) $\nu = 1.95 \times 10^{-5}$ mol/cm^3 and $s = 1$.

Figure 4 depicts the charge density f dependence of the swelling ratio for the DS series of samples equilibrated in water at 25 °C as $1/\phi$ is directly proportional to V/V_0. The data for partially neutralized poly(acrylic acid) gels[21] of $C_t = 2.18$ mol/L and $C = 0.036$ are also included in the figure as filled circles, for which f means the real ionization degree. One can see obviously that there exists a considerable difference in swelling capacity for the DS gels of strong polyelectrolyte from the weakly ionizable gels. We have reported elsewhere that the swelling ratio for the poly(acrylic acid) gel only increases slightly with the ionization degree f when $f > 0.25$ as a result of the counterion condensation.[21] In contrast to that, the swelling capacity of these poly(sulfonic acid) gels monotonically increases with increase in f over the entire f range. Moreover, the rate of increase is much higher as $f > 0.3$, exhibiting that there appear two stages in the influence of charge density on swelling capacity. The gel samples with f higher than 0.65 swell to the extent that the polyelectrolyte gel cannot support its own mass, so that the samples with the above C_t and C values available here would contain a net charge density lower than 65 mol %. When the DS70 gel is equilibrated in pure water, the weight fraction w of polymer in the gel becomes 1.291×10^{-3}, just like a dilute polyelectrolyte solution without added salt, so that the repulsive interaction in this system would make the chains of the network take a more expanded conformation. Thus, the higher electrostatic interaction drives the gel to a larger swelling volume macroscopically. It has been reported for linear polymers that the osmotic coefficient of an aqueous solution of sodium poly(styrenesulfonate) increases with polymer concentration[32] and that the counterion binding is stronger for carboxylated polyelectrolytes than for sulfonated polymers.[33] The swelling behavior mentioned above also suggests that the electrostatic repulsion between charged groups on the chain would be much stronger in the poly(sulfonic acid) gel than in the poly(acrylic acid) gel.

Theoretical Simulation. We start with the Flory–Huggins theory[1] for the osmotic pressure of an ionized gel in the Tanaka fashion.[13] At the swelling equilibrium, we have the relation

$$-RT[\ln(1-\phi)+\phi+\chi\phi^2]/v_0+RT\nu[\phi/2\phi_0-(\phi/\phi_0)^{1/3}]+RTf\rho\phi/M_0=0 \quad (5)$$

where R is the gas constant, T the absolute temperature, v_0 the molar volume of the solvent (18 cm^3/mol for water), χ the Flory–Huggins interaction parameter (assuming 0.45 for this system), and M_0 the equivalent molecular weight of the monomer unit varying with the composition of the sample as listed in Table 1.

By substituting eqs 2 and 4 into eq 5 for ρ and ϕ_0, respectively, we evaluate ϕ for the poly(sulfonic acid) gels swollen in water to equilibrium as a function of f, shown by the dashed line in Figure 4. Although in this theory the electrostatic interaction between charges is simply ignored and the counterions are treated as uncharged particles freely movable in the swollen gel, the predicted ϕ values reflect the steep rise of the observed swelling ratio with increasing f. Perhaps the two defects pointed out above are excessively compensated by the entropy of mixing, so that the prediction can bring about an unexpected result: i.e., the predicted $1/\phi$ values are much larger than experimental data in the range of $f > 0.2$.

To take the electrostatic repulsion into account, we adopt the theory proposed by Hasa et al. (HID theory)[7] for simulation, in which the charge interaction is estimated with the so-called Debye charging method. According to this theory, the condition for swelling equilibrium can be expressed as

$$-RT[\ln(1-\phi)+\phi+\chi\phi^2]/v_0+RTf\rho\phi/M_0-RT[\phi^{1/3}-\phi/2+3/(5\phi^{1/3}n)+99/(175\phi n^2)+513/(875\phi^{5/3}n^3)]\phi_0-N_A\nu Z^2\epsilon^2f^2/(3D\phi_0\langle R_0^2\rangle^{1/2})\phi^{4/3}[2.5A/(1+A)-\ln(1+A)]=0 \quad (6)$$

with

$$A=[9DkTM_0/(\pi N_A\epsilon^2\langle R_0^2\rangle f\rho)]^{1/2}\phi^{-5/6} \quad (7)$$

Here, n is the number of statistical segments in the chain, N_A the Avogadro number, Z the polymerization degree of the chain in the network, ϵ the unit charge, D the dielectric constant of the medium, $\langle R_0^2\rangle$ the mean-square end-to-end distance in the reference state, and k the Boltzmann constant. Here for our poly(sulfonic acid) gels, Z is estimated from $Z=\rho\phi_0/M_0\nu$ and $\langle R_0^2\rangle$ from $\langle R_0^2\rangle = Zsb^2$, where s is the number of monomer units in the statistical segment and $b = 2.55 \times 10^{-8}$ cm is the monomer length.[8]

The calculated values of $1/\phi$ are shown in Figure 4 by dot–dash lines for different ν and s values. One can find that if the stoichiometric value of the chain density $\nu = 1.95 \times 10^{-5}$ mol/cm^3 is used (curve C), the HID theory can only yield $1/\phi$ values much lower than the observed results even for a hypothetical network with the softest chains ($s = 1$). When the experimental ν value of 2×10^{-6} mol/cm^3 estimated from Ge[26] is adopted, the simulation with $s = 5$ (curve A) will predict a magnitude of $1/\phi$ comparable with those given by the Flory theory in the range of $f < 0.40$. However, in the region of higher f, the swelling curve given by the HID theory gradually bends downward apart from the observed tendency. The larger the s, the more evident the curvature appears. For more actual situations, the increase in charge density will cause the network chains to become more rodlike and the swelling capacity to increase to a much higher level. According to the HID theory,[7] this means that s will increase with f, resulting in the predicted increasing rate of swelling ratio going down (curve B), in contrast to the actual data from the DS samples in Figure 4. The difference in the network structure probably induced by the composition difference in the pregel solutions may also affect the swelling behavior. Furthermore, neither the Flory theory nor the HID theory can give a reasonable approach to the swelling equilibrium for polymer gels with strongly dissociating electrolytes swelling in water.

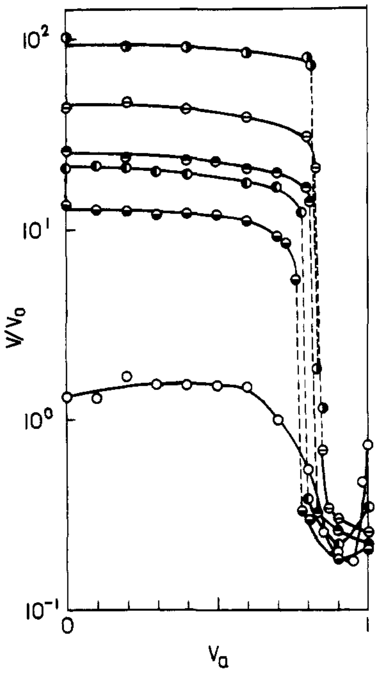

Figure 5. Swelling ratio V/V_0 plotted against the acetone volume fraction V_a in acetone/water mixtures at 25 °C for samples with different f values: (○) DS0; (◒) DS10; (◐) DS20; (◓) DS30; (⊖) DS50; (◑) DS70.

Volume Phase Transition. Figure 5 presents the change in swelling ratio for the DS series of gels swollen in acetone/water mixtures with different volume fractions V_a of acetone at 25 °C. It can be seen that the gel DS0 without any ionizable groups exhibits a continuous change in swelling volume over the entire V_a range, and a minimum appears on the curve when $V_a = 0.95$. On the other hand, all other samples with sulfonic acid groups on the chain undergo a discontinuous volume change as V_a increases over a level of ca. 0.80; i.e., a first-order volume phase transition universally occurs in these gels containing a large amount of strong electrolyte. Before shrinking, the gel sample with a higher charge density will contain a greater amount of solvent mixture to swell to a larger volume regardless of the solvent composition. While in the shrunken state, there appears a minimum on some swelling curves at $V_a \simeq 0.93$. This phenomenon may be correlated with the minimum for the DS0 gel, and a peculiar swelling behavior similar to this has been reported for poly(vinyl alcohol) gel in dimethyl sulfoxide (DMSO)/water mixture with ca. 80 wt % of DMSO.[34] After shrinking, the gel sample becomes a hard and white chip so that the complete equilibrium may be difficult to reach.

The volume fraction, $v_{a,tr}$ of acetone in the mixture at which the volume phase transition takes place is plotted in Figure 6 as a function of f for the DS samples with the results reported on the partially neutralized poly(acrylic acid) gels[21] for comparison. It is obvious for the poly(sulfonic acid) gels that more acetone is needed in the

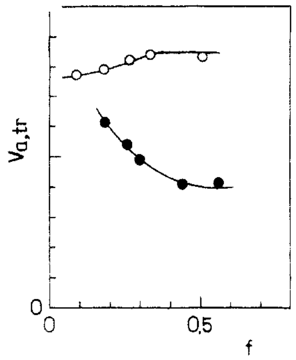

Figure 6. Observed f dependence of $V_{a,tr}$, the acetone volume fraction in acetone/water mixtures at which the phase transition takes place in the gels: (○) this work; (●) partially neutralized poly(acrylic acid) gels.[21]

mixture to induce the phase transition for the sample with a higher charge density, contrary to the abnormal phenomenon observed for the poly(acrylic acid) gels. However, the range for $V_{a,tr}$ variation is very narrow, even less than 10% for the DS samples. This implies that the phase transition must occur regardless of the charge density in the sample provided the V_a is beyond a certain value of 0.85 and $f > 0$.

According to the classification proposed by Ilmain et al.,[35] the volume phase transition of the poly(sulfonic acid) gels in acetone/water mixture may be attributed to ionic repulsion. By adding the organic solvent acetone to water, the dielectric constant D of the mixture is decreased (D of acetone is 20.7 at 25 °C). Once D becomes lower than a certain value, the sulfonic acid group on the chain cannot dissociate into countercations and polyanions, resulting in the collapse transition. Therefore, $V_{a,tr}$ depends mainly on the D value and less on f for gels with a large amount of strongly dissociating electrolytes.

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