Macromolecules **1992,** *25,* 3137–3142

Static and Dynamic Properties of Polyacrylamide Gels and Solutions in Mixtures of Water and Glycerol: A Comparison of the Application of Mean-Field and Scaling Theories

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Received November 7, 1991; Revised Manuscript Received February 13, 1992

ABSTRACT: The role of solvent in determining the static and dynamic behavior of polyacrylamide gels and solutions ($c_{PAA} = 5\%$, $c_{bis} = 2.5\%$) in mixtures of water and glycerol has been examined using light scattering methods. Increasing the glycerol content decreases the solvent quality for polyacrylamide and results in a lower second virial coefficient: $10^4 A_2$ (mol·mL·g^{-2}) = 13.98 – 13.52Φ, where Φ is the volume fraction of glycerol. Solutions and gels show closely similar behavior as regards dependence on solvent quality. The radius of gyration and hydrodynamic radius are experimentally related to the reduced temperature $\tau = (T - \Theta)/T$ by $R_g \sim \tau^{-0.08}$ and $R_h \sim \tau^{-0.10}$, where Θ is the Flory temperature, whereas scaling theory predicts an exponent of –0.2. It was found that the dependence of the longitudinal osmotic modulus on the reduced temperature can be expressed $M_{os} \sim \tau^{0.58}$ for polyacrylamide solutions and gels, compared with the theoretical scaling exponent of 0.75 and a value of unity from mean-field theory. The friction coefficient between network and solvent increases strongly with increasing glycerol content in the solvent. The ratio of the friction coefficient to the viscosity of the solvent scaled as $f/\eta_0 \sim \tau^{0.45}$, which is close to the predicted scaling exponent of 0.5.

Introduction

There are relatively few light scattering studies on gels in mixed solvents. Those particularly relevant to the present topic are those of Tanaka,[1-3] who used acetone–water mixtures for polyacrylamide (PAA), and Geissler et al.,[4] who used a 3:1 mixture of methanol and water to obtain Θ-conditions for the same polymer. The dynamic and static properties of aqueous PAA gels and solutions have been reported in a previous paper.[5]

The static and dynamic properties of polymer gels (and solutions) depend on polymer molecular weight, composition, and temperature and are sensitive to the quality of the solvent. This work was directed to examine the influence of the solvent quality on the static and dynamic properties of PAA gels and solutions in mixtures of water and glycerol by changing the composition of the solvent. Since a change in the composition of the solvent produces an analogous effect to a change in temperature, the principles describing the temperature dependence of gel properties can be also applied to a change in composition of the solvent.

Theoretical Background

Critical behavior may occur either on lowering the temperature or changing the composition of the solvent. The temperature dependence of the intensity and the correlation time of the scattered light from gels has been investigated theoretically and experimentally by Tanaka and co-workers.[1-3] It was found that both the intensity and the correlation time of the scattered light from a PAA gel ($c_{polymer} = 2.5\%$) in water increased as the temperature was decreased with a significant divergence at about –17 °C.[1] The latter was considered to be the spinodal temperature. PAA gels swollen in a mixture of acetone and water showed a discrete transition at an acetone concentration of about 41%.[4] Tanaka interpreted these data using mean-field theory, which is based on an extension of Flory's formula for the free energy of the polymer network. He used a continuum model[3] for the relationship between the scattered light intensity (I) and the longitudinal osmotic modulus (M_{os}) and mode-coupling theory[2] for the correlation length (ξ). The temperature dependence of M_{os} is given in Tanaka's theory[1] by

$$M_{os} = K + 4G/3 = a(T - T_s) \tag{1}$$

where K and G are, respectively, the compressional and shear moduli and T_s is the spinodal temperature. An expression for the coefficient a is given in ref 1. The inverse intensity of the scattered light is given by

$$1/I \sim (T - T_s)/T \tag{2}$$

The correlation length, ξ, is expressed[2b] by

$$\xi \sim \xi_0[(T - T_s)/T]^{-1/2} \tag{3}$$

On the other hand, scaling theory[6] gives

$$\Pi \sim c^{9/4}(^1/_2 - \chi)^{3/4} \tag{4}$$

where Π is the osmotic pressure, c concentration, and χ the Flory–Huggins interaction parameter. The following predictions[7] for the temperature dependence of the static and dynamic properties of polymer semidilute solutions in a good solvent ($\nu = {}^3/_5$ in $R_g \sim M^{\nu}$) may be derived: (a) The longitudinal osmotic modulus scales as

$$M_{os}/kT = c(\partial\Pi/\partial c)/kT \sim c^{9/4}(^1/_2 - \chi)^{3/4} \sim \tau^{3/4} \tag{5}$$

(b) The static correlation length evaluated from M_{os} scales as

$$\xi_s = (3kT/4\pi M_{os})^{1/3} \sim \tau^{-1/4} \tag{6}$$

where τ is the reduced temperature $\tau = (T - \Theta)/T$, with Θ the Flory temperature.

Assuming that the dynamic correlation length (ξ_h) is approximately equal to the static correlation length (ξ_s), then the cooperative diffusion coefficient (D_c), corrected by the viscosity of the solvent and absolute temperature

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T, scales as

$$\eta_0 D_c/T \sim 1/\xi \sim \tau^{1/4} \tag{7}$$

The friction per unit volume (f) may also be calculated from M_{os} and D_c and, when corrected by the viscosity of the solvent, scales as

$$f/\eta_0 = M_{os}/\eta_0 D_c \sim \tau^{1/2} \tag{8}$$

For dilute solutions of chains containing N monomer units in good solvents the radius of gyration (R_g) scales as

$$R_g = N^{3/5}(^1/_2 - \chi)^{1/5} \sim \tau^{1/5} \tag{9}$$

Under Θ-conditions, all the above quantities are independent of the reduced temperature, τ.

Compared with Tanaka's mean-field theory, scaling theory predicts smaller exponents for the reduced temperature dependence of M_{os} and ξ. Although the Θ-temperature differs from the spinodal temperature by definition, the two quantities are similar. The Θ-temperature was estimated by Geissler[8] to be −20 °C for PAA in water.

The experimental data in this work will be compared with the predictions of these two theories for the temperature dependence of M_{os}, ξ, and frictional properties.

Experimental Section

Preparation of PAA Gels and Solutions. Gels were prepared by standard procedures (e.g., ref 9), using synthesis-grade acrylamide and N,N'-methylenebisacrylamide from Merck, FRG. The relative amounts of reagents used to prepare the 5% PAA gel containing 2.5% w/w bisacrylamide (based on acrylamide plus bisacrylamide) were as follows: 2.45 mL of 10% w/w acrylamide; 1.25 mL of 0.5% w/w bisacrylamide; 1.35 mL of water/glycerol; 0.1 mL of 1% w/w ammonium persulfate [$(NH_4)S_2O_8$]; 4 μL of TEMED (tetramethylethylenediamide). In all cases the appropriate water/glycerol mixture was used to make up the stock solutions. Prior to addition of initiator, the solutions were degassed under reduced pressure, and flushed with nitrogen, filtered through 0.22-μm Millipore filters, and allowed to stand for 1 h in crushed ice. No salt or buffer was present, and the ionic strength was close to zero. PAA solutions were prepared under precisely parallel conditions, except that no bisacrylamide was added. The samples were prepared directly in 10-mL cylindrical light scattering cells, flushed with dry nitrogen, and sealed. The weight-average molecular weight from static light scattering on the PAA solutions was 9 × 10^4.

Glycerol was 99% from Sigma, St. Louis, MO. Glycerol solutions were prepared gravimetrically.

Dynamic light scattering measurements were made using the apparatus and techniques described earlier.[10] The laser was a 35-mW He–Ne (633 nm) Spectra Physics model. The autocorrelator was a multi-τ Model ALV-3000 from ALV-Langen, FRG, allowing 23 simultaneous sampling times and thus a monitoring of very widely spaced decays (up to 9 decades in time) in the same experiment. Laplace inversion, to obtain the distribution of decay times, was made using REPES,[11] which directly minimizes the sum of the squared difference between the experimental and calculated autocorrelation functions $g^2(t) - 1$ using nonlinear programming. With data of low noise, REPES can handle data of unusual decay time width without giving spurious peaks. The "smoothing" parameter P (probability to reject)—which takes values from 0 to unity, corresponding to zero and complete smoothing—was given the value 0.5. In each solution, the moments of peaks are given in the output, yielding the relative amplitude and frequency of each resolved component. For a system exhibiting a distribution of relaxation times, the field correlation function $g^1(t)$ is given through ILT by a continuous function of the relaxation time τ:

$$g^1(t) = \int_{-\infty}^{\infty} \tau A(\tau) e^{-t/\tau}\, d(\ln \tau)$$

Thus, relaxation time distributions are given, for example in Figures 6 and 7, in the form of $\tau A(\tau)$ versus $\log \tau$ plots, with $\tau A(\tau)$ in arbitrary units. This provides an equal-area representation. The distributions were found to be closely similar to those obtained using, for example, CONTIN[12] and the maximum entropy method, MAXENT.[13] It is important that the gels prepared as above contain negligible static heterogeneities. Thus measurements could be made in the homodyne mode, and no significant baseline was observed in the correlation functions. Moreover, the amplitudes for gels and solutions were similar.

Table I
Viscosity and Density of the Mixed Solvents at 25 °C (Measured (*) or Interpolated Values)

glycerol %	$\eta/10^{-3}$ Pa·s	ρ/g·mL^{-1}
0	0.8904*	0.9971
30	1.364	1.0736
50	4.7*	1.1274
70	14.8*	1.1831
80	47.8	1.2085
90	145	1.2373
99	454*	1.2585
100	945	1.2611

Intensity light scattering measurements were made using a photocounting device supplied by Hamamatsu. The light source was a 3-mW He–Ne laser (λ = 633 nm). The optical constant for vertically polarized light is $K = 4\pi n_0(\mathrm{d}n/\mathrm{d}c)^2/N_A\lambda^4$, where n_0 is the solvent refractive index, dn/dc is the refractive index increment which was measured using a specially constructed differential refractometer with Rayleigh interference optics, and N_A is Avogadro's number. Due to the difficulty of measurement at high glycerol content, the refractive index increments for PAA in Φ = 0.80 and 0.90 glycerol mixtures were obtained by extrapolation according to the equation $\mathrm{d}n/\mathrm{d}c = 0.150 - 0.130\Phi$, where Φ is the volume fraction glycerol. The reduced scattering intensity, Kc/R_θ, was measured on the same solutions and gels as used for dynamic light scattering. R_θ is the Rayleigh ratio obtained by calibration measurements with benzene: $R_{90} = 8.51 \times 10^{-6}$ at 25 °C.[14] There was no significant angular dependence of Kc/R_θ in the range 45–135° for the gels; at smaller angles Kc/R_θ was lower, however, indicating a small degree of excess scattering.

All measurements were made in concentration ranges in which multiple scattering effects could be neglected. Since the gels contained negligible static heterogeneities, the longitudinal osmotic modulus could be evaluated directly from $M_{os} = (KC/R_{90})RTc$, where R is the gas constant.

Viscosities of mixtures of water and glycerol were measured using a Rheometrics RFS 8500 instrument with a fluid bath temperature control and a 100 g·cm transducer. Couette geometry was used for the measurements: inner bob, 16 mm; bob height, 32 mm; radius of outer cylinder, 17 mm. Thermal equilibration was for 30 min. The loss modulus G'' was determined from oscillatory shear measurements over the angular frequency range 0.1–100 rad/s. All mixtures behaved as Newtonian liquids and $G'' \gg G'$. The solvent viscosities (η_0) were calculated as (G''/ω) as an average over the angular frequency range. The measured values at 25 °C are similar to those given in ref 15 and are listed in Table I.

Results and Discussion

Solutions of 5% PAA in solvents of various water/glycerol mixtures were diluted with the same solvent mixtures and measured as a function of angle by static light scattering. The second virial coefficients and radii of gyration of the polymer in the different mixtures were obtained from the Zimm plots. The second virial coefficient is plotted as a function of glycerol content in Figure 1. The following equation applies: $10^4 A_2$ (mol·mL·g^{-2}) = 13.98 − 13.52Φ, where Φ is the volume fraction of glycerol. Qualitatively the same behavior is found on addition of methanol to PAA solutions.[4]

To determine the temperature dependence of the various parameters from the second virial coefficient dependence, we have used a scaling relationship[16] between the reduced temperature and the second virial coefficient in a good

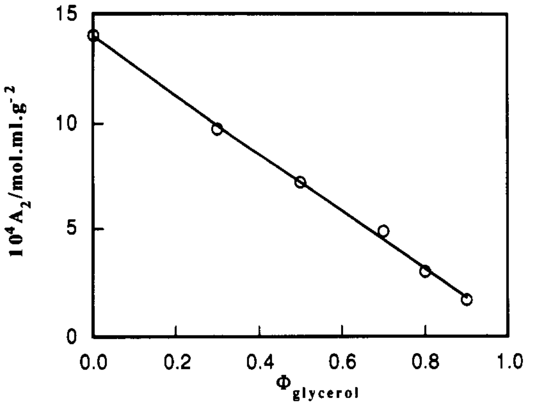

Figure 1. Second virial coefficient in PAA solutions in glycerol/water mixtures as a function of volume fraction of glycerol. (A_2 obtained from the slopes of the plots of the reduced scattered intensity Kc/R_θ versus PAA concentration.)

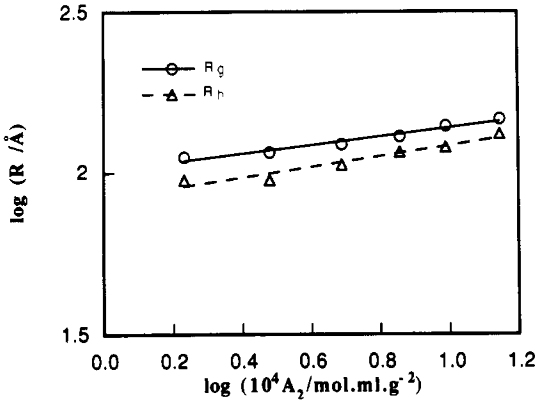

Figure 2. log–log plots of the radius of gyration and the hydrodynamic radius (derived from static and dynamic light scattering measurements in glycerol/water mixtures) in PAA solutions versus the second virial coefficient; temperature 25 °C.

solvent:

$$A_2 \sim R_g^{\ 3} N^{-2} \sim N^{-1/5} a^3 (^1/_2 - \chi)^{3/5} \sim \tau^{3/5} \qquad (10)$$

Using this relationship, the dependence of the different static and dynamic properties on the second virial coefficient can be converted to a dependence on the reduced temperature τ. Our experimental results can then be compared with the results of other authors in a more straightforward way.

Hydrodynamic radii were obtained from $R_h = kT/6\pi\eta_0 D_0$, where D_0 is the diffusion coefficient at infinite dilution obtained by extrapolation of data at low concentrations. Figure 2 shows that the radius of gyration and the hydrodynamic radius become larger as A_2 increases according to expectation. These radii have been fitted as exponential functions of A_2. Using the relationship between A_2 and τ for a good solvent, the exponents of the reduced temperature are found to be −0.08 for R_g and −0.10 for R_h, respectively. The value anticipated from scaling theory is −0.2 in good solvents. Chu and Nose[17] observed a weak positive dependence of R_g and R_h on τ for polystyrene in *trans*-decalin.

The longitudinal osmotic modulus calculated as $M_{os} = (KC/R_{90})RTc$ is plotted as a function of A_2 in Figure 3 and also fitted as an exponential function using the relationship between τ and A_2 for a good solvent. The exponents describing the dependence of M_{os} on τ were estimated as 0.57 and 0.59 for solutions and gels, respectively. These values are smaller than the value 0.75 predicted for the semidilute regime in good solvents using scaling theory[16] and much lower than the value of unity given by Tanaka's theory.[1]

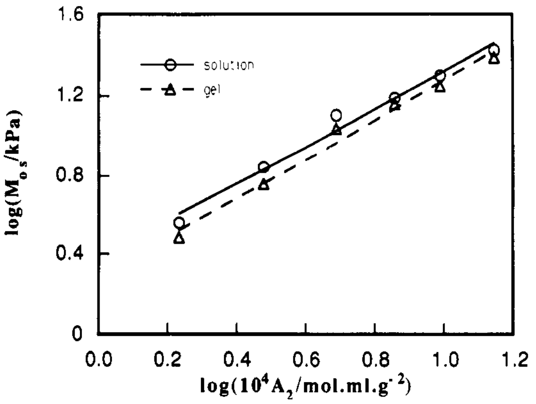

Figure 3. log–log plots of the longitudinal osmotic modulus versus the second virial coefficient for gels and solutions.

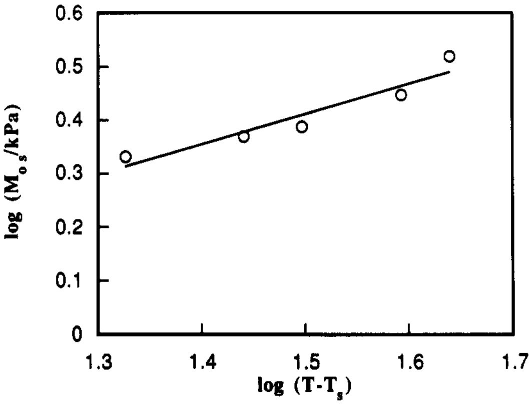

Figure 4. log–log plot of the longitudinal osmotic modulus of aqueous PAA gels (c = 2.5%, c_{bis} = 2.5% (ref 5)) versus the reduced temperature ($T - T_s$), where T_s = −17 °C is the spinodal temperature determined by Tanaka.[1]

The temperature dependence of M_{os} for an aqueous PAA gel of c_{PAA} = 2.5%, c_{bis} = 2.5% is shown in Figure 4; these data are taken from ref 5. The exponent is 0.56 if $T_s \approx$ −17 °C is used according to Tanaka. This value is in good agreement with the value 0.59 obtained by changing the composition of the solvent; this demonstrates that changing the reduced temperature corresponds closely to changing the composition of the solvent since the different solvents will have different Θ-temperatures.

The static correlation length, ξ_s, was derived from intensity light scattering data employing the relationship $M_{os} = 3kT/4\pi\xi_s^{\ 3}$ with the measured M_{os} values and is shown as a function of A_2 in Figure 5a. The exponents describing the dependence on τ are −0.19 and −0.20 for the solutions and gels, respectively. These values compare well with the value −0.25 from scaling theory. Their magnitudes are substantially smaller than −0.5 given by Tanaka's theory.

Chu and Nose[17] investigated the properties of polystyrene in *trans*-decalin. The temperature dependences of the inverse osmotic compressibility ($\partial\Pi/\partial c$) and ξ_s from static light scattering experiments could be expressed as $(\partial\Pi/\partial c)/T \sim \tau^{0.75}$ and $\xi_s \sim \tau^{-0.35}$. These results are close to the predictions of scaling theory. Typical autocorrelation functions and decay time distributions obtained using the inverse Laplace routine REPES are shown in Figure 6 for three solvent compositions: $\Phi_{glycerol}$ = 0, 0.50, and 0.70, respectively. A shift of $1/\eta_0$ has been made on the time axis relative to the water data to facilitate comparison between the different solvent systems. The autocorrelation functions for gels and solutions are almost single-exponential, and there are only small contributions from quasi-static scatterers in the solutions. In light of the

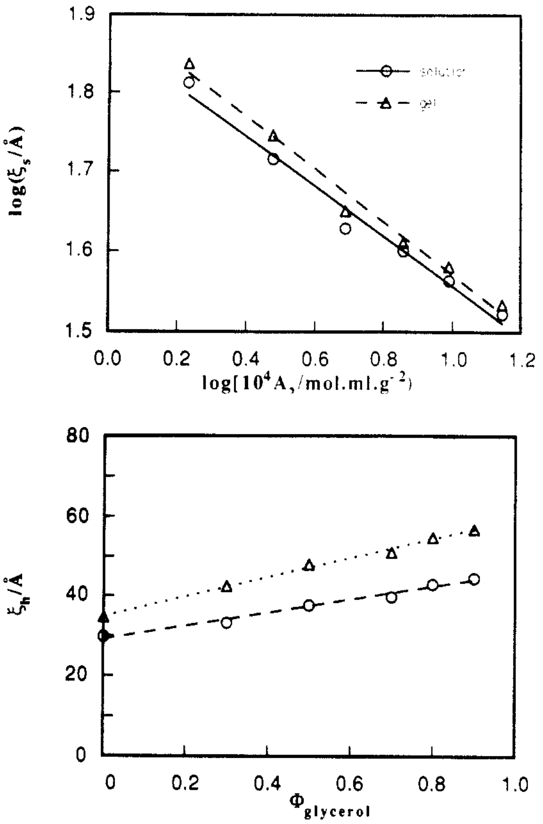

Figure 5. (a, Top) log–log plots of the static correlation length (ξ_s) determined from static light scattering measurements versus the second virial coefficient for PAA gels and solutions in glycerol/water mixtures. (b, Bottom) Dynamic correlation length (ξ_h) determined from dynamic light scattering in PAA solutions and gels as a function of glycerol content. (Δ, gels; O, solutions).

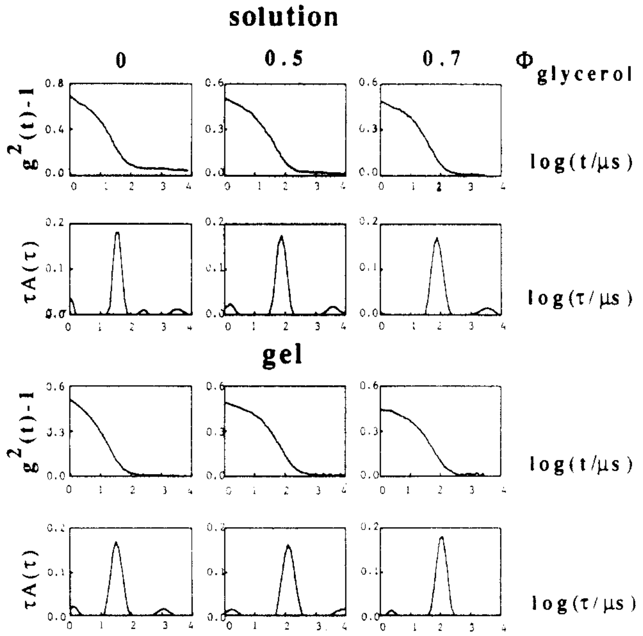

Figure 6. Autocorrelation functions $g^2(t) - 1$ and corresponding relaxation time distributions $\tau A(\tau)$ for solutions and gels in three mixed solvents (Φ = 0, 0.50, and 0.70 glycerol in water, respectively). Polymer concentration is 6%, angle is 90°, and temperature is 25 °C. A shift of $1/\eta_0$ has been made on the time axis relative to the data in pure water for the data in each glycerol/water mixture to facilitate comparison.

recent discussions concerning the nonergodic character of gels,[23,24] it is interesting that for PAA gels in the water/glycerol mixtures this effect is not apparent and that they behave as ergodic media; i.e., the amplitudes of the correlation functions in the gels and equivalent solutions

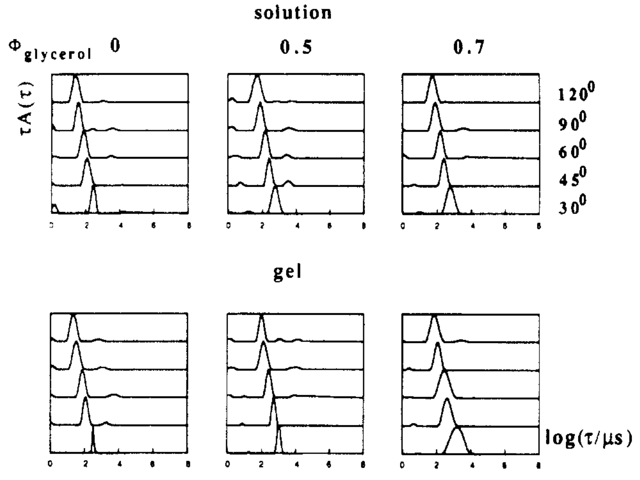

Figure 7. Relaxation time distributions for solutions and gels in the three mixed solvents (Φ = 0, 0.50, and 0.70 glycerol in water, respectively) at the angles shown. Polymer concentration is 5%, and temperature is 25 °C. A shift of $1/\eta_0$ has been made on the time axis at each solvent relative to data in water to facilitate comparison.

are approximately equal. This has also been found to be the case in partially-neutralized poly(acrylic acid) gels.[25] Gels are thus not nonergodic media per se. With PAA gels in pure water, the lower amplitude of the correlation function (see also ref 5) indicates a significant contribution from heterodyning. It has been argued[24] that the possible existence of large-scale inhomogeneities may result from semimicroscopic segregation in the gels if water is a poorer solvent in the presence of cross-links. It is clear, however, that this phenomenon is not particular to gels swollen in pure water.[22] There is also pronounced nonergodic behavior with poly(vinyl acetate) gels swollen in organic media (acetone; methanol).[21] The nonergodicity does not appear to be related to the swelling degree; the highest swelling was observed for PVA gels in acetone and the lowest in water, while the nonergodicity of the samples was of comparable magnitude. We are currently making a more detailed study of ergodicity effects in various types of gel.

Decay time distributions at different angles for solutions and gels of concentration 5% are shown in Figure 7. The small peaks in the distribution function are caused by noise due to the weak scattered intensity. The angular dependence of the decay time of the main peak shows that this mode is diffusive. The collective diffusion coefficients D_c of solutions and gels in the different mixtures have been calculated from the corresponding decay rate. The friction coefficient describing the resistance encountered by the solvent as it diffuses through the polymer network can be calculated as

$$f = M_{os}/D_c = 6\pi\eta_0\xi_h/\xi_s^3 \tag{11}$$

It should be noted that this definition differs from that defined by

$$f^* = kT/D_c = 6\pi\eta_0\xi_h \tag{12}$$

The former is the friction coefficient per unit volume, while f^* is the friction coefficient per "blob" of dimension ξ_h. The parameter f, when corrected by the solvent viscosity, should decrease as the correlation length increases, if it is assumed that the hydrodynamic correlation length (ξ_h) is approximately equal to the static correlation length (ξ_s). Experimentally, it was found that $\xi_h \approx \xi_s$ for PAA gels if the cross-linking density is sufficiently high (see ref 5). On the other hand, f^* corrected by the viscosity of the solvent should increase as ξ_h increases.

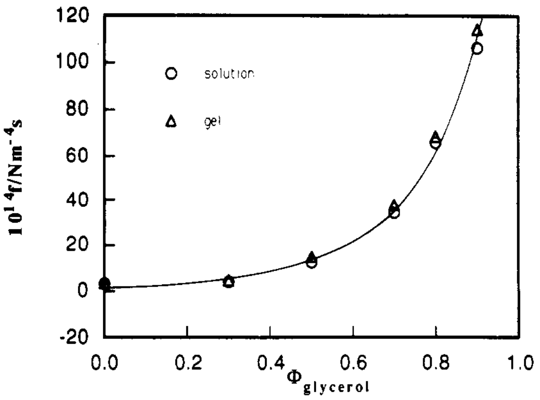

Figure 8. Plot of the friction coefficients of solutions and gels versus the glycerol content.

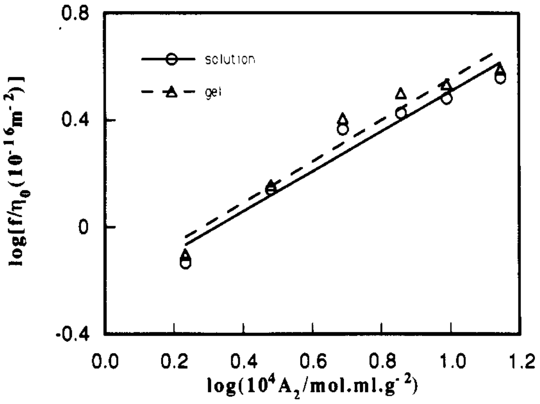

Figure 9. log–log plots of the ratios of the friction coefficients of solutions and gels to the viscosity of solvent versus the second virial coefficient.

It may be noted that $D\eta_0/T$ scales as $\tau^{1/4}$ and M_{os}/T scales as $\tau^{3/4}$. Thus $f/\eta_0 \sim \tau^{1/2}$ instead of $f \sim \tau^{1/2}$. The friction coefficient itself may have a negative temperature dependence if the viscosity of the solvent increases strongly with decreasing temperature.

Figure 8 shows the dependence of f on glycerol content. The friction coefficient increases strongly with increasing glycerol content. According to eq 11, two factors may contribute to a change in the friction since $f \sim \eta_0/\xi^2$. First, f will increase with the viscosity of the solvent as the glycerol content becomes greater. Second, since the correlation length increases as the solvent quality decreases with increasing glycerol content (Figure 5b), this will produce a decrease in f. It seems that the former factor prevails over the latter so that the friction increases strongly with increasing glycerol content.

Konak et al.[18] measured the frictional properties of probe particles in aqueous PAA gels and observed a temperature dependence represented by $f \sim (T - T_s)^{-1.5}$ using Tanaka's spinodal temperature $T_s \approx -17$ °C. However, they did not give an explicit expression for the temperature dependence for PAA itself.

Geissler et al.[19] found a negative reduced temperature dependence for the friction coefficient for a polystyrene solution in cyclohexane with mass concentrations in the range 0.18–0.56. Tanaka[2] found the friction coefficient f decreased as $(T - T_s)$ increased for aqueous PAA gels.

To investigate the role of the second virial coefficient, the ratio f/η_0 was calculated using the measured macroscopic viscosity of the solvent and is plotted as function of A_2 in Figure 9. The data do not fit a single-exponential function. However, we can qualitatively discuss the data using scaling arguments. A positive temperature dependence of (f/η_0) suggests that the effective pore size of the network becomes larger as the quality of solvent decreases since this ratio scales as ξ_h/ξ_s^3. This observation is consistent with that made by Chu[17] and Tanaka.[1] The exponents relating (f/η_0) to τ are 0.45 for solutions and 0.46 for gels, respectively, if forced fitting is used. These values are close to the value 0.5 from scaling theory.

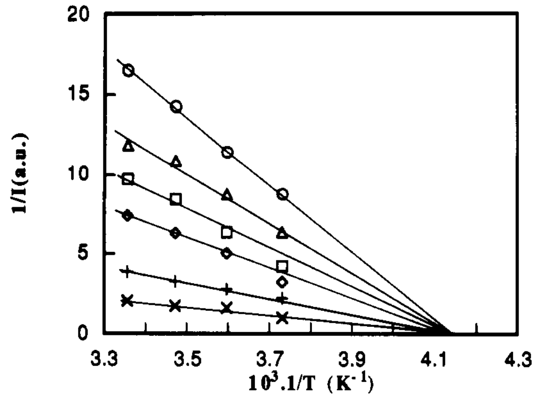

Figure 10. Plots of inverse scattered intensity versus reciprocal absolute temperature, used to estimate critical behavior.

Chu and Nose[17] found that the ratio f/η_0 exhibited a positive temperature dependence. However, it varies less strongly with respect to temperature than does the inverse osmotic compressibility, because f is proportional to $(\partial\Pi/\partial c)/D_c$. Their experimental results agree well with scaling predictions. The temperature dependence varies with the concentration of polymer.

Tanaka[20] recently reported mechanical measurements on aqueous PAA gels of concentration 5% and 8%. Surprisingly, in contrast to the scaling prediction, the ratio of the friction coefficient to the fluid viscosity was found to be constant over the temperature range 0–60 °C and it was concluded that the pore structure at these concentrations is stable. This difference between the experimental results from mechanical measurements and the expected scaling is possibly due to dilation of the pores of the gel under mechanical pressure which reduces the friction (i.e., f/η_0) of the network. Although theoretically the hydrodynamic correlation length should depend on temperature, some experimental results[5] also show that the hydrodynamic correlation length for PAA gels in water is almost independent of temperature. These results are consistent with Tanaka's results.

Recent measurements of the scattered intensity from PAA gels in water and glycerol/water mixtures suggest that the demixing temperature for a 5% PAA gel (2.5% bis) may lie significantly below −17 °C and in the vicinity of −30 °C (Figure 10). Direct observations on the gel in the thermostat at this latter temperature revealed no opacity. The presence of high concentrations of glycerol in some of the gels eliminates the possibility that the increase in scattered intensity results from the formation of ice as discussed by Tanaka.[1]

Conclusions

Solutions and gels exhibit very similar behavior as regards dependence on solvent quality, but the relevant parameters differ in magnitude. Thus M_{os} is somewhat larger for solutions than for gels, and both the friction coefficient and the reduced friction coefficient (f/η_0) for solutions are smaller than the corresponding quantities for gels.

The experimental exponents describing the reduced temperature dependence of M_{os} and ξ_s are closer to the predictions of scaling theory rather than those given by mean-field theory. However, the dynamic properties are more complicated and cannot be expressed as simple scaling laws. The viscosity of the mixed solvents changes strongly with the composition of solvent, complicating the interpretation.

Acknowledgment. This work has been supported by the Swedish National Board for Technical Development (NUTEK) and the Bo Rydin Fund (SCA, Sundsvall, Sweden). Dr. Cestmir Konak, Institute of Macromolecular Chemistry, Prague, is thanked for constructive discussions.

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Registry No. Acrylamide/*N,N'*-methylenebisacrylamide (copolymer), 25034-58-6; glycerol, 56-81-5.