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Molecular Weight Scaling of the Transport Properties of Polyacrylamide in Water

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ABSTRACT: Measurements of single-chain z-average translational diffusion coefficients, $D_{t,z}{}^0$, and radii of gyration, $R_{g,z}$, by photon correlation spectroscopy and intrinsic viscosities, $[\eta]$, of several polyacrylamide (PAAm) fractions in 0.1 M NaCl with 0.02 wt % NaN_3 are reported. Intrinsic viscosity data are insensitive to NaCl concentration up to 0.5 M, suggesting that the chain expansion of PAAm is independent of ionic strength. Our results are compared with recent literature data in which a variety of anomalous excluded-volume exponents for these quantities have been reported. We find good agreement between our data for $[\eta]$ and $R_{g,z}$ with the earlier results but significant discrepancies when comparing our $D_{t,z}{}^0$ results with the weight-average values, $D_{t,w}{}^0$, in the literature. The effect of polydispersity on the experimental data is discussed in terms of the Schulz–Zimm distribution. In agreement with our observations, z-average diffusion coefficients are expected to be numerically consistent with the intrinsic viscosity data and, to a lesser extent, with experimental measurements of $R_{g,z}$, provided the weight-average molecular weight $\bar{M}_w$ is used as a scaling parameter. Substantial discrepancies in scaling exponents are liable to occur from the comparison of $D_{t,w}{}^0$ against $\bar{M}_w$ for polydisperse systems. Within experimental uncertainties our data $D_{t,z}$ and $[\eta]$ data for the PAAm–0.1 M NaCl system are consistent with typical literature data for flexible-chain molecules in good solvents.

Introduction

Modern theories of chain statistics[1] lead to a variety of simple scaling laws for the molecular weight, temperature, and concentration dependence of the structural and dynamic properties of chain molecules in dilute[2,3] and semidilute solutions.[4-6] In the present paper, we are interested in the prediction of statistical theories for single-chain properties. The relevant experimental quantities are the radius of gyration, R_G, and the Stokes hydrodynamic radius, R_H, the latter being derived from the limiting translational diffusion coefficient, $D_t{}^0$, the limiting sedimentation coefficient, S^0, or the intrinsic viscosity, $[\eta]$. Scaling laws for these properties are expressed in terms of characteristic excluded-volume exponents:

$$R_G \sim N^{\nu_G} \tag{1}$$

$$R_H \sim N^{\nu_H} \tag{2}$$

and

$$[\eta] \sim N^a \tag{3}$$

For polymers in good solvents, $\nu_G = 0.6$, while, for Θ solvents, $\nu_G = 0.5$. For marginal conditions, ν_G may exhibit apparent values intermediate between 0.5 and 0.6, corresponding to crossover from ideal statistics at short distances to excluded-volume contribution at large distances (higher molecular weight).

Experimentally, for polymers in the asymptotic regimes of good and Θ conditions, the predicted behavior of ν_G has been confirmed[7] in the molecular weight range $250\,000 < \bar{M}_w < 10^6$. On the other hand, flexible-chain molecules of comparable molecular weights in very good solvents[8,9] exhibit values of $\nu_H \sim 0.56$, rather than the anticipated value of 0.6. Similarly, the experimental Mark–Houwink exponent a is usually smaller than 0.8 for flexible coils in good solvents. Physically, these observations have been interpreted[2,3] to indicate that the crossover regime in chain statistics occurs more gradually in R_H and $[\eta]$ than in R_G. Weill and des Cloizeaux[3] have proposed that the exponent a should be related to both ν_G and ν_H. Thus, they suggest

$$M[\eta] \sim R_G{}^2 R_H \tag{4}$$

and hence

$$1 + a = 2\nu_G + \nu_H \tag{5}$$

This result contrasts with the earlier expression of Flory and Fox[10]

$$M[\eta] \sim R_G{}^3 \tag{6}$$

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and

$$1 + a = 3\nu_G \tag{7}$$

A third relationship may be deduced from the Mandelkern–Flory equation,[11] which we write in the form

$$M[\eta] = \beta\left(\frac{D_t^0\eta_0}{T}\right)^{-3} \tag{8}$$

where β is a constant predicted to be weakly dependent on the polymer solvent interaction. Equation 8 implies that the hydrodynamic radius deduced from the intrinsic viscosity $R_{H,\eta}$ and that deduced from a frictional coefficient $R_{H,f}$ exhibit the same scaling exponent ν_H, and hence

$$1 + a = 3\nu_H \tag{9}$$

Experimental data consistent with all three equations can be found in the literature.[2,8,12,13]

Recently, Francois and co-workers[14-18] have measured R_G, D_t^0, and $[\eta]$ for a series of polyacrylamide (PAAm) fractions in 0.1 M NaCl with 0.2% NaN_3 at 20 °C. They found results for the scaling exponents

$$R_G = 7.49 \times 10^{-2}\bar{M}_w^{0.64} \quad (\text{Å}) \tag{10}$$

$$D_t^0 = 1.24 \times 10^{-4}\bar{M}_w^{-0.53} \quad (\text{cm}^2/\text{s}) \tag{11}$$

$$[\eta] = 9.33 \times 10^{-3}\bar{M}_w^{0.75} \quad (\text{mL/g}) \tag{12}$$

These exponents are in agreement with eq 4 and 5, but not with eq 8 and 9. A novel explanation for the unusually large value of ν_G and anomalously small ν_H was offered based on the notion that the solvent is a marginal one. The value of ν_G as shown to assume values larger than 0.6 by imposing an appropriate functionality on the crossover regime from Gaussian to excluded-volume behavior in chain statistics.

Several potential problems arise, however, in regard to molecular weight scaling of experimental quantities from PAAm solutions. First, the PAAm samples studied are invariably more polydisperse, even after fractionation, than, for example, the anionically polymerized polystyrenes used for comparable studies. Comparison of data for samples of different polydispersities may lead to apparent discrepancies in molecular weight scaling parameters. Also, when one is comparing, for the same samples, experimental quantities which reflect different averages over the molecular weight distributions, variations in polydispersity may lead to discrepancies when comparing excluded-volume exponents for these quantities. Second, numerous reports indicate PAAm samples may exhibit structural heterogeneities (e.g., imide formation, partial hydrolysis, and conformational changes) which could lead to variations in chain statistics. Thus these are considerable deviations in experimental scaling laws reported for the transport properties of PAAm in aqueous media from different laboratories[19-23] which can be assigned to the above factors or in some cases to limitation of the experimental study to a relatively narrow range of molecular weights. A further complication is the existence of aging effects[23b] which may be due to either slow disentanglement of molecules or the slow relaxation of metastable hydrogen-bonded conformations. A recent very comprehensive review of the literature has been given by Kulicke et al.[23b] The latter authors note that a second relation for $R_{g,z}$ of PAAm samples in H_2O has been reported[23a] with a smaller exponent

$$R_g = 0.147\bar{M}_w^{0.59} \tag{13}$$

We note here that the R_g data of Klein and Conrad[23a] are actually quite consistent with those of Francois et al. (eq 10), and, for $\bar{M}_w > 10^6$, tend to average about 10% larger than the latter. Kulicke et al.[23b] also note that a large body of viscometric data for PAAm in water is accurately correlated by the relation

$$[\eta] = 0.01\bar{M}_w^{0.755} \tag{14}$$

Equation 14 is again very consistent with that of Francois et al. (eq 12).

Finally, the diffusion data of eq 11 were generated by the comparatively imprecise method of ultracentrifugation and are weight-average values. These results are in substantial disagreement with the earlier ultracentrifuge studies of Scholtan[19] which reported an exponent $\nu_H = 0.69$. Thus there appears to be reasonable concordance between literature data for R_g and $[\eta]$ for PAAm in H_2O and in 0.1 M NaCl, but a large discrepancy in D_t^0 values.

In this paper, we report measurements of the *z*-average translational diffusion coefficients of polyacrylamide in 0.1 M NaCl containing biocide, 0.02 wt % NaN_3, at 20 °C, using the photon correlation spectroscopy method.[24] These data are compared with intrinsic viscosity and *z*-average radius of gyration values on the same samples and with the previous experimental values in the literature. The numerical influence of sample polydispersity on the experimental results for excluded-volume exponents is discussed. A well-specified sample preparation history is followed as described below.

Experimental Section

Methodology. The photon correlation spectrometer used has been described elsewhere.[24] A wavelength of 6328 Å is produced by a 10-mW He–Ne ion laser. The scattered light is detected by an ITT FW-130 photomultiplier tube and the time autocorrelation function $C(\tau)$ of the intensity fluctuations of the scattered light is performed by using a Saicor Model 42A autocorrelator. Mean intensity measurements are determined by using an Ortec photon counter. All measurements were made at 20 ± 0.1 °C.

The *z*-average translational diffusion coefficients were determined by using a computer program written by Dr. J. Southwick. This program applies the method of moment analysis[25] to characterize the distribution of relaxation time constants $G(\Gamma)$ in the correlation function

$$C(\tau) = \int_0^\infty G(\Gamma)\exp(-\Gamma\tau)\,d\tau \tag{15}$$

where $\Gamma = \int_0^\infty G(\Gamma)\Gamma\,d\Gamma$ is the mean relaxation rate. Expansion of the correlation function by a Taylor series leads to a polynomial expansion

$$\ln C(\tau) = \Gamma\tau + \frac{1}{2!}\frac{\mu_2}{\bar{\Gamma}^2}(\bar{\Gamma}\tau)^2 - \frac{1}{3!}\frac{\mu_3}{\bar{\Gamma}^3}(\bar{\Gamma}\tau)^3 + \ldots \tag{16}$$

where the first moment, $\bar{\Gamma}$ can be related to the *z*-average translational diffusion coefficient $\langle D_t\rangle_z$:

$$\bar{\Gamma} = \langle D_t\rangle_z K^2 \tag{17}$$

where $K = 4\pi\bar{n}/\lambda_0 \sin\theta/2$, $\lambda_0 = 6328$ Å, $\bar{n}$ is the solution refractive index and θ is the scattering angle. The second moment μ_2 is the variance in Γ

$$\mu_2 = \langle\Gamma^2\rangle - \bar{\Gamma}^2 \tag{18}$$

and is a measure of the width of the distribution $G(\Gamma)$. It is noted that, to permit application of eq 17, correlation data must be obtained in the small-angle limit, $KR_g < 1.0$. The data were analyzed as follows: The moments are determined by least-squares fit of the data to the first two terms in eq 16 as shown in Figure 1. Since systematic errors occur in these fits for large data sets, accurate values of the first and second moment are estimated by extrapolation to zero of plots of these quantities vs. the number of time increments in the data set as shown in Figure 2. For all samples, the normalized variance $\mu_2/(\bar{\Gamma})^2$ had values in the range 0.4 ± 0.1, indicating the degree of polydispersity to be similar for

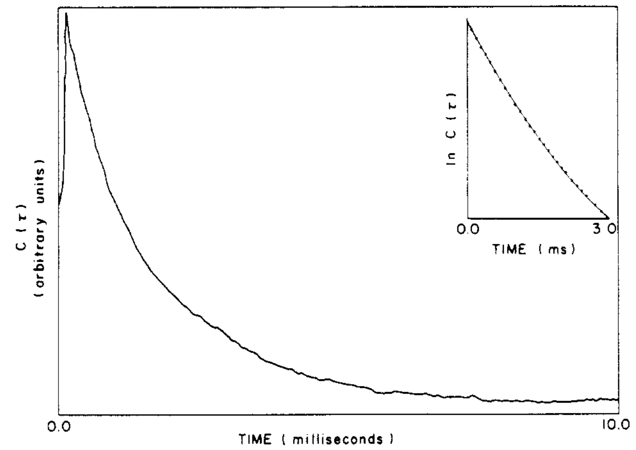

Figure 1. Typical photon correlation function for PAAm in 0.1 M NaCl ($\bar{M}_w = 1.42 \times 10^6$; $c = 1.03$ mg/mL). Abscissa is 10 ms full scale. Inset shown. A cumulant fit to the first 30 data points of correlation function.

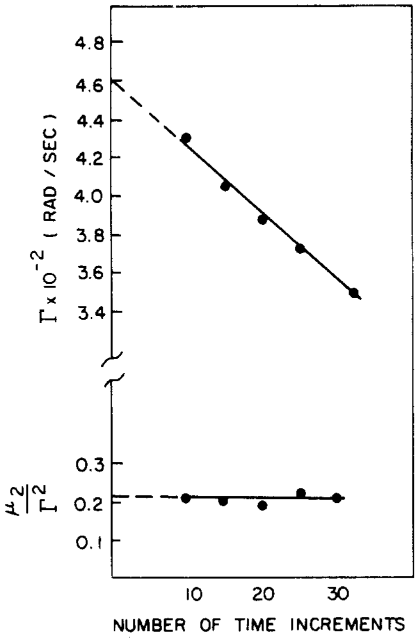

Figure 2. First moment ($\bar{\Gamma}_{app}$) and second moment ($\mu_{2,app}/\bar{\Gamma}_{app}^2$) vs. number of sampling time increments for the PAAm sample in Figure 1.

each sample. We also remark here that in our studies, no evidence of solution instability[23b] was observed during our experiments.

The weight-average molecular weights, $\bar{M}_w$, and second virial coefficients, A_2, were determined from excess light scattering intensity measurements at $T = 20$ °C, using benzene as a reference liquid. A plot of Kc/R_θ vs. concentration gives an apparent molecular weight from the intercept and the initial slope gives the second osmotic virial coefficient, A_2:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_{w_{app}}} + 2A_2c + 3A_2c + \ldots \qquad (19)$$

The true molecular weight $\bar{M}_w$ is then related to $\bar{M}_{w_{app}}$ through the Debye particle scattering factor $P^{-1}(\theta)$ and the scattering volume change, ΔV_s by

$$\bar{M}_w = \bar{M}_{w_{app}} P^{-1}(\theta) \Delta V_s \qquad (20)$$

The scattering volume change $\Delta V_s = \bar{n}^2$ (polymer solution)/n^2(benzene) = 0.81 for the polyacrylamide–0.1 M NaCl system. For samples of lowest molecular weight the scattered intensities were measured at a single scattering angle $\theta = 40°$, small enough that the $P^{-1}(40°)$ correction is close to unity and can be safely estimated from the published R_G data in the literature.[14,23] The largest correction is for sample PS-8251, $P^{-1}(40°) = 0.1 \pm 0.1$. The uncertainties quoted in $\bar{M}_w$ in Table I reflect these small corrections. It is relevant to note that the accuracy of the $\bar{M}_w$ determinations by light scattering for these samples are confirmed by the good agreement of the measured [η] values with literature values as described below. For the two samples of highest $\bar{M}_w$, light scattering intensities were investigated over the angular range $30° < \theta < 90°$ and were analyzed by Zimm plots to determine $\bar{M}_w$ and $R_{g,z}$, as described elsewhere.[26]

Table I
Excess Intensity Light Scattering from Polyacrylamide in Aqueous 0.1 M NaCl-0.03 M NaN$_3$

sample	$\bar{M}_w \times 10^{-6}$	$A_2 \times 10^4$, cm^3/(g^2/mol)	$R_{g,z}$, Å
PS-8247[a]	0.10 ± 0.01	6.4 ± 1.5	
PS-8249[a]	0.48 ± 0.03	3.7 ± 1.0	
PS-8250[a]	0.95 ± 0.07	2.3 ± 0.5	
PS-8251[a]	1.42 ± 0.15	2.0 ± 0.5	
DS-2[b]	5.26 ± 0.25	2.5 ± 0.5	1510 ± 150
DS-1	6.45 ± 0.5	1.9 ± 0.5	2300 ± 200

[a] $\bar{M}_w$ reflects small correction for $P(40°)$, calculated from $R_{g,z}$, using eq 10. [b] Measured in pure water as solvent.

Relative viscosity values were determined by using capillary viscometry. The viscosities were measured in a no. 50 Cannon Ubbelohde viscometer at 20 ± 0.05 °C. Flow times were long enough to ensure that the kinetic energy correction is negligible. The intrinsic viscosity is determined by extrapolation of the reduced specific viscosity to zero concentration by the Huggins equation

$$\eta_{sp}/c = [\eta] + K_1'[\eta]^2c + \ldots \qquad (21)$$

The refractive index increment at constant chemical potential was determined to be 0.170 ± 0.005 mL/g, using a C. N. Wood differential refractometer Model RF-600 at a wavelength of 546 nm by comparing exhaustively dialyzed solutions of polyacrylamide vs. dialysate.[27] For comparison, the value at constant molarity of solvent species was found to be 0.165 ± 0.005 mL/g.

Polyacrylamide standards of four different molecular weights were obtained from Polysciences, Inc. (Warrington, PA) (catalog no. 8247, 8249, 8250, and 8251). The reported molecular weights for these polymers, determined by GPC were reported to be, respectively, 7.4×10^4, 5×10^5, 1×10^6, and 2×10^6. Two high molecular weight fractions, designated DS-1, and DS-2, were prepared by Millipore filtration of a polyacrylamide obtained from Diamond Shamrock Corp. through 0.45- and 0.8-μm filters, respectively. The polymers were placed in an oven at 60 ± 2 °C for a minimum of 24 h to remove residual water. Under these conditions, residual water content should be less than 3%.[23a] The polymers were allowed to dissolve in 0.1 M NaCl containing 0.02 wt % NaN$_3$ for periods of from 24 h to 3 weeks depending on the molecular weight and concentration, without violent agitation. The solutions were then gravity filtered through Millipore filters (pore sizes 0.2, 0.45, or 0.80 μm depending on concentration and molecular weight). After filtration, the polymer concentrations were determined by using differential refractometry. For higher concentrations, clean, dilute samples were concentrated in an oven at 60 ± 2 °C to the desired concentration. The Polysciences polymers were subjected to an exclusion chromatographic examination by elution down a glass column (height 19 in., diameter 1.1 in.) containing Sepharose 2B and using UV detection at 230-nm wavelength. From the chromatograms, it was noted that these polymers had narrow unimodal distributions and we concluded that further fractionation was not feasible. It is pertinent to note that, in these and previous experiments,[26] we find the exclusion limit of Sepharose 2B corresponds to $R_{H,f} \sim 550$ Å. For this reason it is not possible to fractionate polyacrylamides of molecular weight greater than around 3×10^6 on this column material. Polyacrylamide DS-2, of highest molecular weight, was examined by elution through 1400 Å glyceryl-CPG (Electronucleonics, Inc.) in 0.05 M aqueous Na$_2$SO$_4$ containing 0.01 wt % sodium azide. This analysis was carried out using Waters Associates GPC instrumentation by ModChrom, Inc., Mentor, OH. The chromatogram, was found to consist of a single peak with a low molecular weight tail, similar to those observed for the Polysciences polymers in our work and elsewhere.[28] From the chromatography data, a

Table II
Transport Properties of Polyacrylamide in Aqueous 0.1 M NaCl–0.03 M NaN_3

	$\bar{M}_w \times 10^{-6}$	$D_{t,z}{}^0 \times 10^8$, cm²/s	$\mu_2/\bar{\Gamma}^2$	$R_{H,f}$, Å	[η], cm³/g	$R_{H,\eta}/R_{H,f}$	$R_{H,f}/R_G$
				This Work			
PS-8247	0.10	24.40 ± 1.2	0.40 ± 0.1	89 ± 4	60 ± 3	1.12 ± 0.08	0.72 ± 0.05
PS-8249	0.48	9.86 ± 0.50	0.4 ± 0.1	221 ± 11	192 ± 15	1.12 ± 0.08	0.60 ± 0.04
PS-8250	0.95	7.01 ± 0.35	0.4 ± 0.1	311 ± 15	273 ± 25	1.12 ± 0.08	0.67 ± 0.05
PS-8251	1.42	4.62 ± 0.24	0.4 ± 0.1	472 ± 24	480 ± 40	1.02 ± 0.07	0.73 ± 0.05
DS-2[a]	5.26	2.50 ± 0.12	0.4 ± 0.1	850 ± 40	(1208 ± 100)	(1.18 ± 0.09)	0.56 ± 0.05
DS-1	6.72	2.05 ± 0.1	0.4 ± 0.1	1064 ± 55	(1451 ± 120)	(1.10 ± 0.08)	0.46 ± 0.06
				Francois et al.			
	0.13	23.24		92	52.6	1.12	0.66
	0.92	8.31		258	263	1.31	0.53
	6.70	2.75		780	1258	1.41	0.46

[a] Measured in pure water. Parentheses indicate $R_{H,\eta}$ and [η] calculated from eq 21.

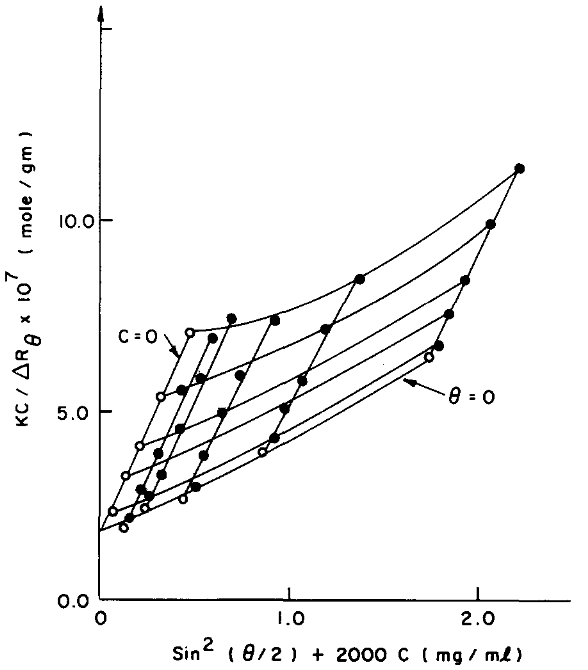

Figure 3. Zimm plot for PAAm sample DS-2 in water at 20 °C.

polydispersity index of $\bar{M}_w/\bar{M}_n = 1.8$ was estimated, by extrapolation of a calibration curve based on the Polysciences polymers. This value is similar to those reported elsewhere for Polysciences samples[28] and consistent[28] with our measured values of $\mu_2/\bar{\Gamma}^2 \sim 0.4$.

Results

Excess Light Scattering Intensities. Light scattering intensity measurements were applied to determine the weight-average molecular weights of the polymers, using eq 19 and 20. For the high molecular weight fractions DS-1 and DS-2, it was also possible to determine $R_{g,z}$ from Zimm plot analysis (see, e.g., Figure 3). Sample DS-1 was obtained dissolved in 0.1 M NaCl after a single passage through a 0.8-μm Millipore filter and we determined $\bar{M}_w = (6.72 \pm 0.5) \times 10^6$ and $R_{g,z} = 2300 \pm 200$ Å. Sample DS-2 was derived, dissolved in deionized water, after single passage through a 0.45-μm Millipore filter, and was found to have $\bar{M}_w = (5.26 \pm 0.25) \times 10^6$ and $R_{g,z} = 1510 \pm 150$ Å. Figure 4 shows Debye plots of the excess scattering intensities, extrapolated to zero angle vs. polymer concentration for each sample. Table I summarizes the experimental $\bar{M}_w$, $R_{g,z}$, and second osmotic virial coefficients, A_2. It is satisfying to note that our results are comparable with values deduced from the study of Francois et al.[14], and that of Klein and Conrad.[23a]

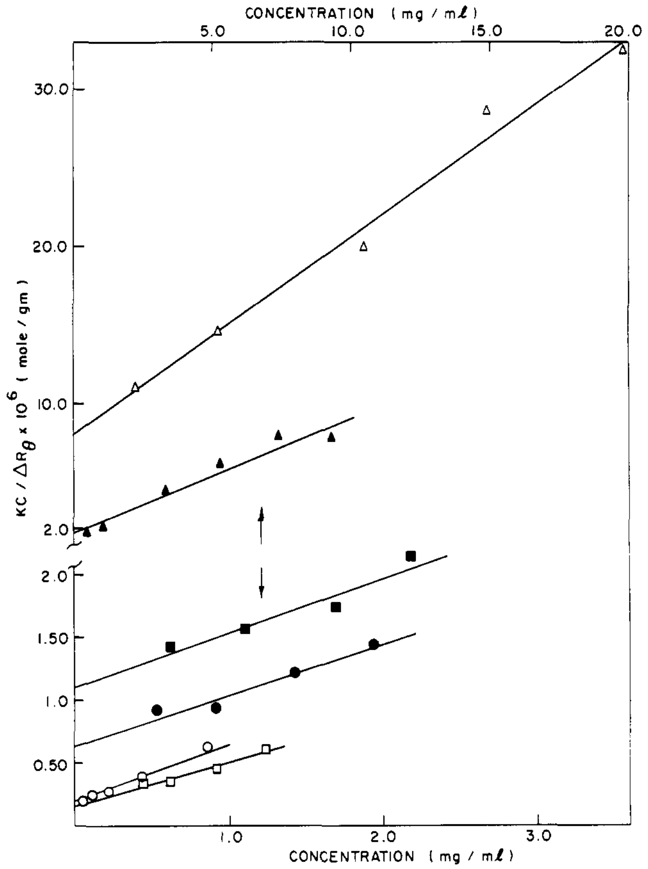

Figure 4. Concentration dependence of $Kc/\Delta R_0$ of PAAm in 0.1 M NaCl at 20 °C: PS-8247 (△); PS-8249 (▲); PS-8250 (■); PS-8251 (●); DS-1 (○); DS-2 (□).

Dynamic Light Scattering. Plots of translational diffusion coefficient vs. concentration for each of the polymers studied are shown in Figure 5. A least-squares fit to the limiting translational diffusion coefficients ($D_{t,z}{}^0$) leads to the relationship

$$D_{t,z}{}^0 = 2.74 \times 10^{-4} \bar{M}_w{}^{-0.61 \pm 0.02} \tag{22}$$

This result disagrees with the result of Francois et al. (eq 11) and with that deduced by Scholtan.[19] The comparison of our $D_{t,z}{}^0$ values with the power law of Francois et al.[14] is amplified in the plot of log $D_t{}^0$ vs. log $\bar{M}_w$ (Figure 6). The value of ν_H from our work is 0.61 ± 0.02 which is significantly larger than Francois[14] (i.e., 0.53) and somewhat smaller than that of Scholtan[19] (i.e., 0.69). Table II lists our measured $D_{t,z}{}^0$ values and also values of the normalized variance $\mu_2/\bar{\Gamma}^2$. The latter are comparable to literature values for polyacrylamides of $\bar{M}_w/\bar{M}_n \sim 2.0$.[28] On the basis of these data each fraction seems to be similar in degree of polydispersity within the experimental error (±25%).

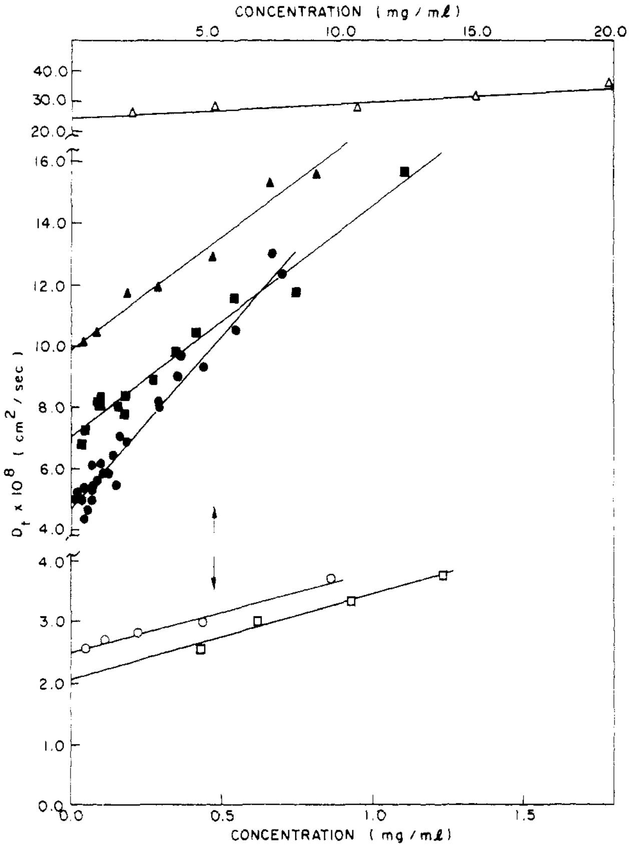

Figure 5. Translational diffusion coefficient vs. concentration for PAAm in 0.1 M NaCl at 20 °C. Symbols as in Figure 4.

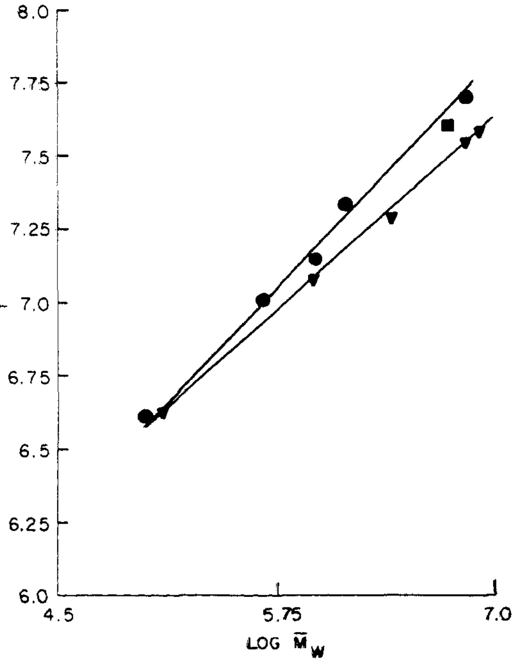

Figure 6. log D_t^0 vs. log M for PAAm in 0.1 M NaCl at 20 °C: (●) this work; (▲) Francois et al. (1980); (■) DS-2 in deionized water.

Viscometry. Figure 7 shows a plot of reduced specific viscosity vs. concentration for the four molecular weights studied. The intrinsic viscosity data lead to a Mark–Houwink equation

$$[\eta] = 11.23 \times 10^{-4} \bar{M}_w^{0.75\pm0.02} \qquad (23)$$

This result is compared as a plot of log [η] vs. log $\bar{M}_w$ with the results of Francois et al.[13] in Figure 8. It can be seen that, although there is a small numerical disagreement, the slopes are the same. It is also noted that eq 23 correlates very well with eq 14 of Kulicke et al.[23b]

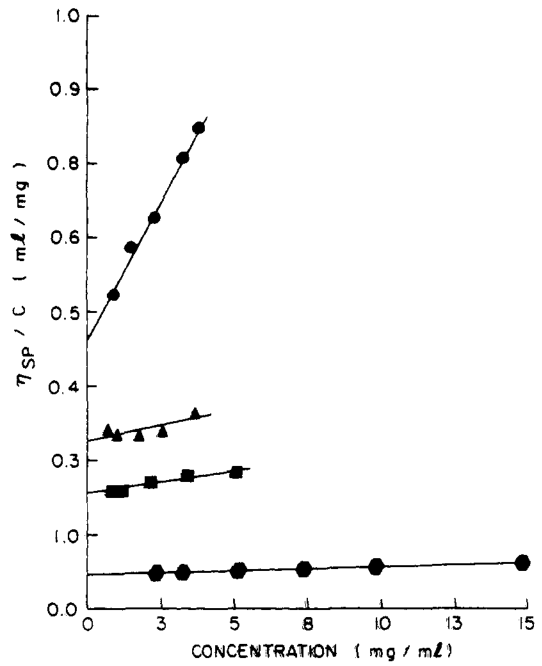

Figure 7. Reduced specific viscosity vs. concentration for PAAm in 0.1 M NaCl at 20 °C: PS-8247 (●); PS-8249 (■); PS-8250 (▲); PS-8251 (●).

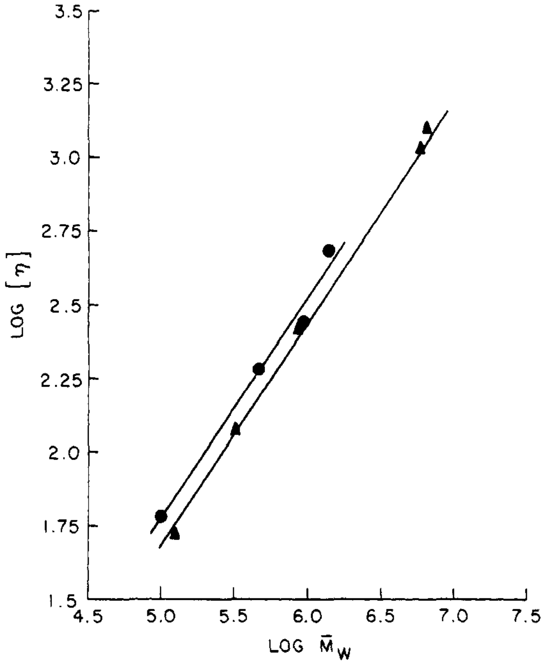

Figure 8. log [η] vs. log $\bar{M}_w$ for PAAm in 0.1 M NaCl at 20 °C: (●) this work; (▲) Francois et al. (1979).

Table III
Intrinsic Viscosity as a Function of NaCl Concentration for Polyacrylamide PS-8251

[NaCl], M	[η], cm³/g
	4.87×10^2
0.1	$4.8 \times 10^2 \pm 0.3$
0.5	4.83×10^2

Our experiments indicate no change in [η] with NaCl concentration up to 0.5 M NaCl (Table III) and our result for PS-8251 in water (Table III) is again in excellent agreement with the value calculated from eq 14 of Kulicke et al.[23b] Also, $R_{g,z}$ and $D_{t,z}^0$ determined for fraction DS-3 in deionized water are consistent with eq 10 and 22, respectively, suggesting that these equations also apply to polyacrylamides in water. Our viscosity and light scattering results indicate therefore that our samples exhibit no polyelectrolyte effect. Also the excellent agreement between our $[\eta]$ data and literature data[23b] serves as confirmation of our $\bar{M}_w$ determinations. It is further relevant to note here that our $D_{t,z}^0$ relation (eq 22) is consistent with the results reported by Dinapoli et al.[28] for polyacrylamide solutions at higher and lower ionic strengths. Table II summarizes our results for $D_{t,z}^0$, μ_2/Γ^2, $[\eta]$, $R_{H,f}$ as well as the radius ratios $R_{H,\eta}/R_{H,f}$ and $R_{H,f}/R_G$. To compute the last ratio for the Polysciences samples, we have used the relationship deduced by Francois (eq 10); our experimental $R_{g,z}$ values are used for the DSC polymers. For comparison, we also list in Table II the experimental data reported by Francois et al.[13-15]

Discussion

First, we must consider how sample polydispersity will influence numerically the characteristic parameters deduced from scaling relations of the form of eq 1–3. We discuss this problem in context of the Schulz–Zimm (S–Z) distribution.[8,12] For any experimental quantity P, it can be shown[8,12] that, when $P_i = kM_i^a$, the S–Z distribution leads to relations of the form

$$\bar{P}_w = k\bar{M}_w^a X(h,a) \tag{24a}$$

and

$$\bar{P}_z = k\bar{M}_w^a Y(h,a) \tag{24b}$$

for the weight and z averages, respectively, where

$$X(h,a) = (h+1)^{-a}\left[\frac{\Gamma(h+1+a)}{\Gamma(h+1)}\right] \tag{25a}$$

and

$$Y(h,a) = (h+1)^{-a}\left[\frac{\Gamma(h+2+a)}{\Gamma(h+2)}\right] \tag{25b}$$

and the polydispersity parameter h is given by $\bar{M}_w/\bar{M}_n = (h+1)/h$. For diffusion data $a = -\gamma$, $0.5 < |\gamma| < 0.6$, $Y(h,a)$ is always close to unity even for high polydispersity (e.g., for $\bar{M}_w/\bar{M}_n = 2.0$, $Y(1.0, -0.6) = 0.94$; for $\bar{M}_w/\bar{M}_n = 9.0$, $Y(0.1, -0.6) = 0.91$). On the other hand, $X(h, -0.6)$ deviates from unity rapidly as polydispersity increases (e.g., ($X(1.0, -0.6) = 1.35$; $X(0.1, -0.6) = 2.0$). For intrinsic viscosity, a is positive, $0.5 < a < 0.8$, and $X(h,a)$ is close to unity for all a, even for very small h (e.g., $X(1, 0.75) = 0.96$; $X(0.1, 0.75) = 0.92$). These considerations tell us that plots of $D_{t,z}^0 = k_D\bar{M}_w^{-\gamma}$ and $[\eta] = k_\eta\bar{M}_w^a$ will be accurate to within 5% for $\bar{M}_w/\bar{M}_n < 2.0$ and to within 10% for $\bar{M}_w/\bar{M}_n < 10.0$. The polymers studied here have unimodal distributions as observed by GPC and, based on light scattering analysis exhibit $\bar{M}_w/\bar{M}_n \sim 2.0$. A further conclusion from the above analysis is that the β-parameter determined for eq 8, using $\bar{M}_w$, $D_{t,z}^0$, and $[\eta]$, will be accurate to within 20% for $\bar{M}_w/\bar{M}_n \lesssim 2.0$. Values of the radius ratio $R_{h,\eta}/R_{h,f}$ should therefore correspond with the monodisperse result to within 7% if we compare $D_{t,z}^0$ vs. $[\eta]^{1/3}\bar{M}_w^{1/3}$. It is also noted that, the z-average radius of gyration is moderately sensitive to sample polydispersity ($Y(1.0, 0.6) = 1.23$; $Y(0.1, 0.6) = 1.39$)). Thus, for $h = 1$, and $\nu_H = \nu_G = 0.6$, eq 24b predicts that the ratio $\langle R_g\rangle_z\langle R_{h,f}^{-1}\rangle_z$ will be 17% larger than the monodisperse result. From the above discussion, it is clear that systematic increases in sample polydispersity as molecular weight increases will lead to anomalously high values of ν_G and a and anomalously small values of ν_H, when P_w or P_z are scaled vs. $\bar{M}_w$.

Table IV
Concentration Dependence of $D_{t,z}$

	k_D^{exptl}, mL/g	$k_D(Y)$, mL/g	$k_D(Y^*)$, mL/g
PS-8247	22 ± 3	35 ± 17	33 ± 6
PS-8249	68 ± 10	89 ± 45	102 ± 17
PS-8250	97 ± 15	102 ± 50	117 ± 20
PS-8251	225 ± 34	49 ± 100	260 ± 46
DS-2	533 ± 80	757 ± 300	664 ± 116
DS-1	663 ± 100	503 ± 300	797 ± 144

Comparing our excluded volume exponents for $[\eta]$ and R_H measured in our experiments with those of Francois et al.,[14-16] our value for the Mark–Houwink exponent a is similar to their result, but our value for ν_H is larger, though not as large as that of Scholtan.[19] The reason for the latter discrepancy remains unclear. We point out that the data of Scholtan[19] are confined to $M_w < 5 \times 10^5$, and are approximately weight-average diffusion coefficients, scaled vs. an ill-specified molecular weight average calculated via the Svedberg equation from weight-average sedimentation and diffusion coefficients. Also, the reported diffusion coefficients from all three studies are in reasonable agreement for $10^5 < \bar{M}_w < 5 \times 10^5$. As noted above, the z-average diffusion coefficients reported here when plotted vs. weight-average molecular weights are expected to lead to accurate values of ν_H while the plot of weight-average D_t vs. $\bar{M}_w$ will be more sensitive to polydispersity. However, the systematic deviations between our data and those of Francois et al.[16] as $\bar{M}_w$ increases (see Figure 5) are not consistent with the relatively small polydispersity indices reported for their samples.[14] Thus, we are led to suggest an alternative source of the discrepancy in ν_H is that the hydrostatic pressures imposed in the ultracentrifuge study of Francois et al. lead to a substantial lowering of the solvent quality.

In view of the experimental uncertainties, our results do not enable a clear choice between eq 8 and, when combined with R_g data of Francois or Klein and Conrad,[21] eq 4 or 6. The discrepancies observed in Figure 5 also result in very different molecular-weight dependence of the radius ratios $R_{H,f}/R_G$ and $R_{H,\eta}/R_{H,f}$. Our results for the latter are, within experimental error, independent of molecular weight and are in close accord with previous literature data for flexible chains in both good and bad solvents. As explained above, this is expected since the influence of polydispersity is small when $R_{H,f}$ is derived from $D_{t,z}^0$. In contrast, the results of Francois et al., based on $D_{t,w}^0$, lead to unusually large values of $R_{H,\eta}/R_{H,f}$ at high molecular weights. Further, our $R_{H,f}$ data, for the PS polymers lead to a molecular weight independent ratio $R_{H,f}/R_G = 0.72 \pm 0.05$. For DS-1 and DS-2, a decrease to smaller values is seen. The results of Francois indicate $R_{H,f}/R_G$ varies similarly from a low value 0.46 at high molecular weights to 0.66 at low molecular weights. The original hydrodynamic theory of Kirkwood and Riseman predicts, for monodisperse flexible nondraining coils, $R_{H,f}/R_G = 0.665$. More recent theory,[2] however, predicts $R_H/R_G = 0.537$ in good solvents smoothly increasing to $R_H/R_G = 0.665$ in Θ solvents. The degree to which literature data confirm the latter predictions is uncertain, however. In our view, the decrease in $R_{H,f}/R_G$ seen in our DS-1 and DS-2 experiments most likely reflects an increase in polydispersity with molecular weight.

Finally, in Table IV, we have listed concentration-dependence coefficients k_D for the diffusion coefficient:

$$D_{t,z} = D_{t,z}^0(1 + k_D c) \tag{26}$$

These data are compared with two theoretical estimates.

The first, $k_D(Y)$, is calculated from Yamakawa's modified theory[29]

$$k_D(Y) = 0.8A_2\bar{M}_w - \frac{N_A V_h}{\bar{M}_w} - \bar{v}_2 \tag{27}$$

where $V_h = (4/3)\pi R_{H,f}^3$ and $\bar{v}_2$ is the polymer partial specific volume. Within experimental error, reasonably good concordance between theory and experiment is found. The discrepancies are due primarily to the cumulative errors in $k_D(Y)$ from A_2, M_w, and $R_{H,f}$. This is illustrated in the second theoretical estimate which is again based on Yamakawa's eq 27 but utilizes the approximate result, valid for good solvents[29,30]

$$A_2\bar{M}_w = (1.1 \pm 0.1)[\eta] \tag{28}$$

Since, as noted above, experiment indicates[12] $R_{H,\eta} \sim 1.1R_{H,f}$, we may approximately write

$$\bar{M}_w[\eta] \simeq (3.30 \pm 0.1)N_A V_h \tag{29}$$

Inserting eq 28 and 29 in eq 27, we obtain

$$k_D(Y^*) = [0.58 \pm 0.09][\eta] \tag{30}$$

Comparison of $k_D(Y^*)$ vs. experimental k_D indicates that the latter are in agreement with expectation[29,30] for flexible polymer coils in good solvents.

In summary, we have reported measurements of $D_{t,z}{}^0$, $R_{g,z}$, and $[\eta]$ for PAAm in aqueous 0.1 M NaCl at 20 °C. The results for $R_{g,z}$ and $[\eta]$ are in good agreement with previous observations for this system[14] as well as for PAAm in water.[23] Strong systematic differences are found in the molecular weight dependence of $D_{t,z}{}^0$ compared with the $D_{t,w}{}^0$ values previously studied.[16,19] It is noted that the effect of polydispersity on the scaling of $D_{t,z}$ and $[\eta]$ vs. $\bar{M}$,w is expected to be comparatively small. Substantial deviations are to be anticipated for polydisperse samples when comparing $D_{t,w}$ or $R_{g,z}$ vs. $\bar{M}_w$ with the monodisperse result. Because of the difficulty of precisely characterizing the polydispersity of high molecular weight polyacrylamides, and the sensitivity of aqueous PAAm to sample preparation history, strong caution is indicated in ascribing any undue significance to the high values of ν_H, a, and ν_G deduced in this and in earlier studies. Within the experimental uncertainties our $D_{t,z}$ and $[\eta]$ data for the PAAm–0.1 M NaCl system are consistent with representative literature data for flexible chain molecules in good solvents.

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Registry No. PAAm (homopolymer), 9003-05-8.

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