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Translational Diffusion Coefficient of Sodium Poly(2-acrylamido-2-methylpropanesulfonate) in Aqueous Sodium Chloride

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Summary

Dynamic light scattering measurements have been made on 9 samples of sodium poly(2-acrylamido-2-methylpropanesulfonate), an intrinsically flexible, linear polyelectrolyte, ranging in weight-average molecular weight from 2.9×10^4 to 1.5×10^6 with 0.05 and 0.5 M aqueous NaCl at 25°C as the solvents. The measured translational diffusion coefficients or hydrodynamic radii R_H are analyzed on the basis of the wormlike chain with excluded volume. The quasi-two-parameter theory for the hydrodynamic-radius expansion factor with the known expression for the translational friction coefficient of an unperturbed wormlike chain describes the molecular weight dependence of R_H in the aqueous salts with a degree of accuracy very similar to that known for nonionic flexible polymers in good solvents.

Introduction

Electrostatic repulsions between neighboring charged groups of a linear polyelectrolyte in aqueous solution cause the backbone stiffness to increase [1-4]. When the polymer is modeled by the wormlike chain [5], this stiffening effect manifests itself in an increase in the electrostatic persistence length. For flexible polyelectrolytes, electrostatic excluded-volume interactions between charged groups distant along the chain contour also lead to chain expansion, and the stiffness and excluded-volume effects similarly affecting the chain dimensions can hardly be separated by experiment without resort to a relevant excluded-volume theory.

In previous studies [6-9], we estimated these effects in aqueous NaCl solutions of sodium poly(styrenesulfonate) (Na PSS) (at NaCl concentrations $C_\mathrm{s} \geq 0.05$M) and sodium poly(2-acrylamido-2-methylpropanesulfonate) (Na PAMPS) (at $C_\mathrm{s} = 0.05$ and 0.5 M) with the aid of the quasi-two-parameter (QTP) theory (i.e., the Yamakawa-Stockmayer-Shimada theory [10-12]) for the wormlike chain (or more generally, the helical wormlike chain [12]). This theory combined with known expressions [12-15] for unperturbed wormlike chains was capable of consistently describing three physical properties (the mean-square radius of gyration $\langle S^2 \rangle$, the intrinsic viscosity $[\eta]$, and the translational diffusion coefficient D) for Na PSS and two of them ($<S^2>$ and $[\eta]$) for Na PAMPS at C_s = 0.05 and 0.5 M if the currently known errors in the transport theories for Gaussian chains were permitted [12,16]. In other words, the dilute-solution behavior of these charged polymers may be understood at a level as high as that established for nonionic flexible chains in good solvents [12].

In the present work, we made dynamic light scattering measurements on 9 samples of Na PAMPS with molecular weights of 2.9×10^4 – 1.5×10^6 in 0.05 and 0.5 M aqueous NaCl at 25°C to see whether the QTP scheme indeed allows a quantitative explanation of D for the polyelectrolyte. As far as we know, no systematic D data for this polymer are available in the literature (see ref. 17 for early characterization work on PAPMS). The experimental results and their analysis are presented below.

Experimental

Samples

Na PAMPS samples f-1 – f-8 [9] with known weight-average molecular weights M_w were used for the present study. They had been prepared by the radical polymerization of the acid form monomer, followed by extensive fractionation and purification. The z-average to weight-average molecular weight ratios determined by sedimentation equilibrium for low molecular weight fractions were about 1.1 [9]. One fraction, designated below as f-y9, was added to the eight samples, but it was investigated only for 0.05 M aqueous NaCl because of the limited quantity. The molecular weight of this fraction was determined by static light scattering (in 0.05 M aqueous NaCl at 25°C) on a Fica 50-light scattering photometer (see ref. 9 for the experimental procedures). Optical anisotropy correction was made though it was small (2% for M_w).

Dynamic Light Scattering

Normalized autocorrelation functions $g^{(2)}(t)$ at time t were obtained for 0.05 and 0.5 M aqueous NaCl solutions of Na PAMPS at 25°C in an angular range from 30 to 90° using an ALV/DLS/SLS light scattering photometer equipped with an ALV-5000E WIN correlator. A YAG laser of 532 nm in wavelength λ_0 (DPSS model 532, Coherent) was used as the light source. Test solutions were optically clarified by filtration through 0.45-μm Millipore filters, followed by 4-h centrifugation at 2.5×10^4 g (Sorvall RC 5C).

The experimental first cumulant Γ at a scattering angle θ for a given solution was evaluated according to the equation

$$\ln [g^{(2)}(t) - 1] = -2\Gamma t + \text{constant} \qquad \mathbf{(1)}$$

This cumulant associated with D is defined for such large t that all the internal motions of polymer chains have relaxed away [12]. The desired D is equal to the zero-angle value of Γ/k^2 at infinite dilution, where k denotes the magnitude of the scattering vector defined by $k = (4\pi n_0/\lambda_0) \sin (\theta/2)$ with n_0 being the solvent refractive index.

Results and Discussion

Molecular Weight Dependence of D

Figure 1 shows plots of ln $[g^{(2)}(t) - 1]$ against k^2t at different scattering angles for a 0.5 M aqueous NaCl solution of Na PAMPS sample f-2 with a polymer mass concentration c of 0.001402 g cm^{-3}. The plotted points at the respective θ follow straight lines in the indicated k^2t range except a very small k^2t region, in which data points exhibit certain fast relaxation modes. These straight lines are parallel with one another, indicating that the Γ/k^2 values are essentially independent of θ as expected. Figure 2 illustrates the concentration dependence of $(\Gamma/k^2)_{k=0}$ (i.e., Γ/k^2 at $\theta = 0$) for samples f-1, f-3, f-5, and f-7 in 0.05 and 0.5 M aqueous NaCl (the data for the other fractions are omitted for clarity). The values of D obtained from the intercepts of the indicated straight lines and similar straight lines for the other samples are summarized in Table I, along with those of M_w.

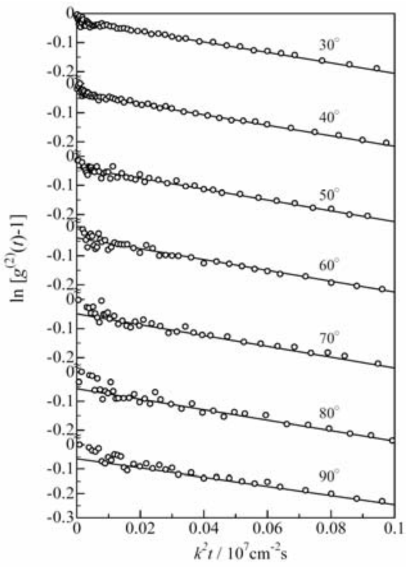

Figure 1. Plots of ln $[g^{(2)}(t) - 1]$ vs. k^2t for a 0.5 M aqueous NaCl solution of Na PAMPS sample f-2 with c = 0.001402 g cm^{-3} at 25°C.

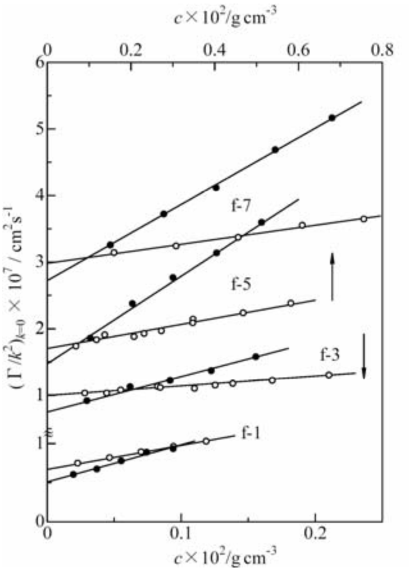

Figure 2. Concentration dependence of $(\Gamma/k^2)_{k=0}$ for the indicated samples in 0.05 M (filled circles) and 0.5 M (unfilled circles) aqueous NaCl at 25°C.

The molecular weight dependence of D in the two aqueous salts is shown in Figure 3, in which the data points are fitted by straight lines with slopes –0.58 and –0.62 for C_s = 0.5 and 0.05 M, respectively. The latter negative slope slightly exceeds the limiting value –0.60 for nonionic flexible polymers in good solvents [12]. The previously determined exponents 1.27 for $\langle S^2\rangle_z$ (the z-average $\langle S^2\rangle$) and 0.89 for $[\eta]$ in 0.05 M aqueous NaCl [9] are also higher than the limiting values (1.2 and 0.8, respectively) for nonionic chains. Interestingly, all these exponents at C_s = 0.05 M are quite close to those (–0.63, 1.26, and 0.88 for D, $\langle S^2\rangle_z$, and [η], respectively) for Na PSS in the same solvent [8].

Table I. Translational diffusion coefficients for Na PAMPS samples in 0.05 and 0.5 M aqueous NaCl at 25°C

sample	$M_w \times 10^{-4}$	$D \times 10^7/\mathrm{cm}^2\ \mathrm{s}^{-1}$ in 0.5 M NaCl	$D \times 10^7/\mathrm{cm}^2\ \mathrm{s}^{-1}$ in 0.05 M NaCl
f-1	147[a]	0.670	0.510
f-2	114[a]	0.755	0.650
f-3	76.8[a]	1.00	0.750
f-4	46.3[a]	1.33	1.07
f-5	27.6[a]	1.70	1.47
f-6	19.6[a]	2.24	1.75
f-7	11.5[a]	2.98	2.72
f-8	5.65[a]	4.33	3.90
f-y9	2.87		6.50

[a] Mean of the previously determined values at C_s = 0.5 and 0.05 M (ref. 9)

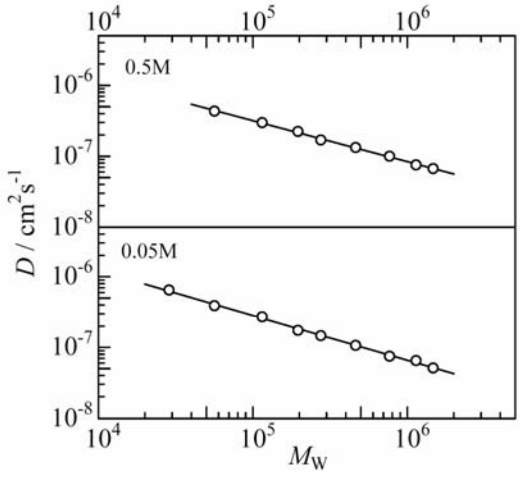

Figure 3. Molecular weight dependence of D for Na PAMPS in 0.5 and 0.05 M aqueous NaCl at 25°C.

We calculated the hydrodynamic factor ρ (= the ratio of $\langle S^2\rangle^{1/2}$ to the hydrodynamic radius R_H) from the previous $\langle S^2\rangle_z$ [9] and present D data using the Einstein-Stokes relation

$$R_H = k_B T/(6\pi\eta_0 D) \tag{2}$$

Here, k_B is the Boltzmann constant, T the absolute temperature, and η_0 the solvent viscosity. The ρ factors at C_s = 0.5 and 0.05 M scattered around 1.5 and 1.6, respectively, being comparable to or slightly larger than those for randomly coiled polymers expanded by large excluded-volume effects [12]. Thus, the present D data confirm that the PAMPS molecule assumes highly expanded coil-like conformations in 0.5 and 0.05 M aqueous NaCl.

Data Analysis and Comparison with Theory

The hydrodynamic radius R_{H0} of an unperturbed wormlike touched-bead chain may be expressed by [12,15]

$$R_{\mathrm{H0}} = L/[2f_{\mathrm{D}}(L/2q, d/2q)] \qquad (\mathbf{3})$$

where L is the contour length of the chain, f_{D} is a known function of $L/2q$ and $d/2q$, q is the (total) persistence length, and d is the bead diameter. The first parameter is related to the molecular weight M by $L = M/M_{\mathrm{L}}$, with M_{L} being the molar mass per unit contour length of the chain. The hydrodynamic-radius expansion factor α_{H} ($\equiv R_{\mathrm{H}}/R_{\mathrm{H0}}$) in the QTP scheme is given by

$$\alpha_{\mathrm{H}} = (1 + 5.93\,\tilde{z} + 3.59\,\tilde{z}^2)^{0.1} h_{\mathrm{H}} \qquad (\mathbf{4})$$

$$h_{\mathrm{H}} = 0.88/(1 - 0.12\alpha_{\mathrm{s}}^{-0.43}) \qquad (\mathbf{5})$$

if the Barrett equation [18] is adopted and if the correction factor h_{H} [19] arising from fluctuating hydrodynamic interactions (HI) is taken into account. In these equations, α_{s} denotes the radius expansion factor and $\tilde{z}$ is the scaled excluded-volume parameter defined by [12]

$$\tilde{z} = (3/4)K(L/2q)z \qquad (\mathbf{6})$$

where $K(L/2q)$ is a known function of $L/2q$ and z (the conventional excluded-volume parameter) is expressed in terms of the wormlike-chain parameters by

$$z = (3/2\pi)^{3/2}(B/2q)(L/2q)^{1/2} \qquad (\mathbf{7})$$

The excluded-volume strength B in this equation is related to the binary cluster integral β by $B = \beta/a^2$ with a being the bead spacing. The radius expansion factor in eq 5 may be calculated from the Domb-Barrett equation [20]

$$\alpha_{\mathrm{s}}^2 = \left[1 + 10\,\tilde{z} + \left(\frac{70\pi}{9} + \frac{10}{3}\right)\tilde{z}^2 + 8\pi^{3/2}\,\tilde{z}^3\right]^{2/15} \qquad (\mathbf{8})$$

$$\times\,[0.933 + 0.067\exp(-0.85\,\tilde{z} - 1.39\,\tilde{z}^2)]$$

As may be seen from the above equations, the molecular weight dependence of R_{H} for Na PAMPS in 0.5 or 0.05 M aqueous NaCl is determined by q, M_{L}, d, and B.

Figure 4 compares the R_{H} data with the theoretical dashed lines, which have been computed from eqs 3 – 8 with the previously estimated parameters (q, M_{L}, and B from

$\langle S^2 \rangle$ and d from $[\eta]$) presented in Table II. These lines appear systematically below the data points at the respective C_s. Their deviations (roughly 10%) should have something to do with eq 3 (basically equivalent to the Kirkwood general theory [21]), which underestimates R_{H0} by about 15% in the coil limit of unperturbed wormlike chains owing primarily to the familiar approximate treatment of fluctuating HI [12,16]. We take this theoretical error into account by multiplying q by a factor of $(1.15)^2$ and keep $\tilde{z}$ essentially unchanged for high molecular weights by adjusting B; note that R_{H0} in the coil limit is proportional to $q^{1/2}$ if M_L is fixed so as to be consistent with our previous data analysis [9] (see Table II), and also that the lowering of R_{H0} (by 15%) at either C_s decreases the coil-limiting ρ in the unperturbed state (from 1.5) to 1.3 in substantial agreement with the theory of Yamakawa and Yoshizaki [16] for D with fluctuating HI.

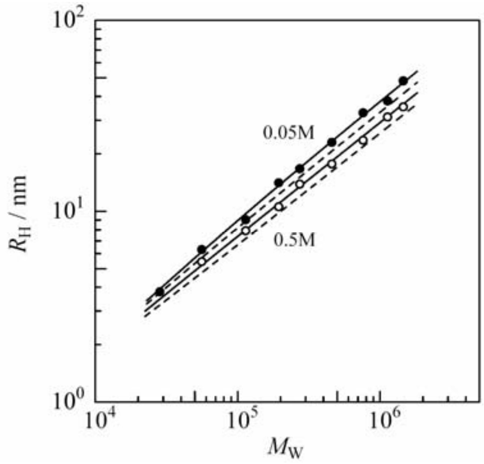

Figure 4. Hydrodynamic radii for Na PAMPS samples in 0.05 M (filled circles) and 0.5 M (unfilled circles) aqueous NaCl at 25°C, compared with the theoretical solid curves for perturbed wormlike chains with the parameters listed in Table II. The dashed lines were calculated with the q, M_L, and B values from $\langle S^2 \rangle$ and the d value from $[\eta]$ in the table.

Table II. Model parameters for Na PAMPS in 0.05 and 0.5 M aqueous NaCl at 25°C

C_s / M	M_L / nm^{-1}	q / nm	B / nm	d / nm	Method
0.5	900[a]	1.4	2.7	1.55	$[\eta]$[c]
	900[a]	1.6	3.0		$\langle S^2 \rangle$[c]
	900[a]	2.1	4.6	1.55[b]	D (or R_H)
0.05	900[a]	3.0	6.2	1.7	$[\eta]$[c]
	900[a]	3.0	6.2		$\langle S^2 \rangle$[c]
	900[a]	4.0	9.8	1.7[b]	D (or R_H)

[a] Estimated by fitting $[\eta]$ data at the two NaCl concentrations [9]; [b] Assumed; [c] ref. 9

The B and q values thus altered (Table II) have been used to compute R_H. The resulting solid curves in Figure 4 come close to the plotted points for the respective C_s (the corresponding theoretical curves for D are indistinguishable from the empirical straight lines in Figure 3). In this connection, we note that, although for $M < 2 \times 10^5$

the new sets of q and B (from D in the table) yield $\tilde{z}$ values appreciably smaller than those given by the parameter sets from $<S^2>$, the difference in α_H is negligible (at most 1.8% for the lowest-M_w sample f-y9 at $C_s = 0.05$ M).

Excluded-Volume Effects on R_H

While eq 8 for α_s^2 and the Barrett equation (eq 9) for α_η^3 (the cube of the viscosity expansion factor) [22] are known to accurately describe excluded-volume effects on $<S^2>$ and $[\eta]$, respectively, for nonionic flexible polymers, eq 4 with eq 5 for α_H is not always the case [12]. To examine R_H of Na PAMPS in relation to the known behavior of this expansion factor for nonionic chains, we indirectly obtained α_H vs. $\log \tilde{z}$ relations for our samples in the two aqueous salts by estimating R_{H0} with the parameters in Table II ($B = 0$); we note that this polyelectrolyte attains no theta state in aqueous NaCl. The results indicated by circles in Figure 5 show that α_H is a function only of $\tilde{z}$ in a first approximation and thus satisfies the requirement of the QTP theory. The solid curve representing eq 4 (with eqs 5 and 8) appears slightly above many of the circles (this graph may be regarded as a magnification of Figure 4 viewed from a different angle).

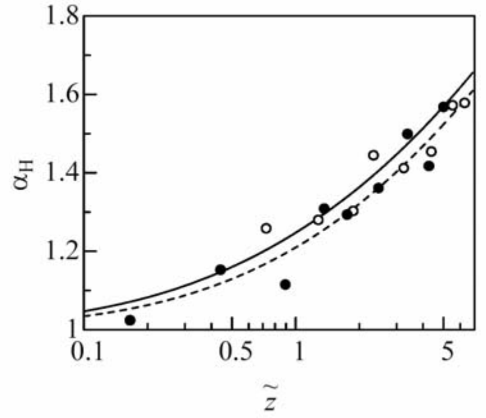

Figure 5. Relation between α_H and log $\tilde{z}$ for Na PAMPS in 0.05 M (filled circles) and 0.5 M (unfilled circles) aqueous NaCl, compared with the theoretical solid (eq 4 with eq 5) and dashed (eq 9 with $\alpha_\eta = \alpha_H$) curves. The parameters are the same as those used for the solid lines in Figure 4.

The dashed line in Figure 5 shows the relation (the Barrett equation [22] in the QTP scheme)

$$\alpha_\eta = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.1} \qquad \textbf{(9)}$$

with $\alpha_\eta = \alpha_H$. It can be seen that this line comes somewhat closer to the plotted points than does the solid line. This is quite similar to what has been found for nonionic flexible polymers (see Fig. 8.17 in Chap. 8 of ref. 12). Thus, we may conclude that excluded-volume effects on R_H or D of Na PAMPS in 0.5 and 0.05 M aqueous NaCl can be explained in the framework of the QTP scheme with essentially the same degree of accuracy as that for those polymers in good solvents. The slightly poor description of eq 4 with eq 5 remains to be seen theoretically [12].

Conclusions

The measured hydrodynamic radii (or translational diffusion coefficients) for sodium PAMPS samples in 0.5 and 0.05 M aqueous NaCl at 25°C are quantitatively described by the available expressions for unperturbed wormlike chains and excluded-volume effects (in the QTP scheme [10-12]) over a range of M_w from 2.9×10^4 to 1.5×10^6 provided that correction is made for the effect of fluctuating hydrodynamic interaction on the unperturbed R_H in the coil limit. Under this condition, the degree of agreement between theory and experiment is comparable to what has been established for typical linear polymers with no charge [12]. As mentioned in the Introduction, this was also the case with $\langle S^2 \rangle$ and $[\eta]$ of Na PAMPS in the aqueous salts [9]. These conclusions together with the similar one drawn earlier for Na PSS [8] strongly suggest that the QTP theory for nonionic chains almost quantitatively describes excluded-volume effects on three important properties, D, $\langle S^2 \rangle$, and $[\eta]$, of flexible polyelectrolytes in aqueous 1-1 salts down to a C_s of about 0.05 M.

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