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Effect of Charge Density and Simple Salts on the Diffusion of Polyelectrolytes in Aqueous Solution

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ABSTRACT: Translational diffusion coefficients of the sodium salts of acrylamide/acrylic acid copolymers of different charge densities and identical degrees of polymerization have been determined at 25 °C in 0.1 and 0.5 M NaBr by quasi-elastic light scattering. At a fixed concentration of NaBr, the limiting diffusion coefficients, obtained by extrapolation of concentration-dependent diffusion coefficients to zero polyelectrolyte concentration, decrease linearly with the square root of the polyelectrolyte charge density. The lower the simple salt concentration, the larger is the rate of decrease with increasing charge density. A "critical" polyelectrolyte concentration has been observed, at which the diffusion coefficients are independent of both the polyelectrolyte charge density and the concentration of simple electrolyte. Above the critical concentration the polyelectrolyte diffusion coefficients increase with increasing charge density; below the critical concentration the diffusion coefficients decrease with increasing charge density, approaching the limiting values. The Mandelkern–Flory constant $\Phi_0^{1/3}P_0^{-1}$ is shown to be constant over the wide range of charge densities investigated and independent of the simple salt concentration.

Introduction

While studies dealing with the diffusion of counterions and coions in polyelectrolyte solutions have provided important information regarding the interactions of small ions with polyelectrolytes,[1-5] the measurement of polyelectrolyte diffusion coefficients has been problematic and few studies dealing with this subject have been reported. The development of quasi-elastic light scattering techniques[6-8] has given impetus to this area of investigation, since it allows for the determination of polymer diffusion coefficients more rapidly and accurately than previously possible. Quasi-elastic light scattering techniques have been utilized to study the effects of salts on the diffusion coefficients of polyelectrolytes in aqueous solution.[9-14] However, no systematic study of the effects of polyelectrolyte charge density on diffusion coefficients has been reported, even though it is well recognized that the charge density of ionic polymers is the most important structural variable which affects their solution properties. It was therefore the purpose of the present investigation to explore this area.

To focus upon the effect of charge density on the diffusion of a polyelectrolyte while minimizing specific nonelectrostatic effects, it is necessary to keep the primary structure and degree of polymerization of the polyelectrolyte constant, while varying the degree of ionic character. Acrylamide/acrylic acid copolymers are excellent model polyelectrolytes for this purpose, since their charge density may be varied by changing the ratio of acrylamide to acrylic acid, and they may be prepared readily by hydrolyzing nonionic polyacrylamide (PAM) to any desired extent without altering the degree of polymerization.

Presently, we report the diffusion coefficients of the sodium salts of fully neutralized acrylamide/acrylic acid copolymers of four different charge densities whose acrylic acid content ranged from 0.6 to 65 mol %. Intrinsic viscosities and counterion activity coefficients for the same series of polyelectrolytes have previously been reported.[15-17] The effect of NaBr concentration on the diffusion coefficients of each of these polyelectrolytes in aqueous solution has been investigated, and the effects of charge density on the measured diffusion coefficients are discussed in terms of the dimensionless charge density parameter ξ that is frequently used to characterize polyelectrolytes when a line charge model is employed

$$\xi = e^2/DkTb \qquad (1)$$

where e is the protonic charge, k is the Boltzmann constant, T is the absolute temperature, D is the bulk dielectric constant, and b is the spacing between ionic groups along the contour length of the polyelectrolyte. The importance of ξ in governing the solution properties of polyelectrolytes has been proposed in theoretical treatments,[18,19] particularly that of Manning.[20,21] Empirical relationships between ξ and counterion activity coefficients[15,16] and intrinsic viscosities[17] of polyelectrolyte so-

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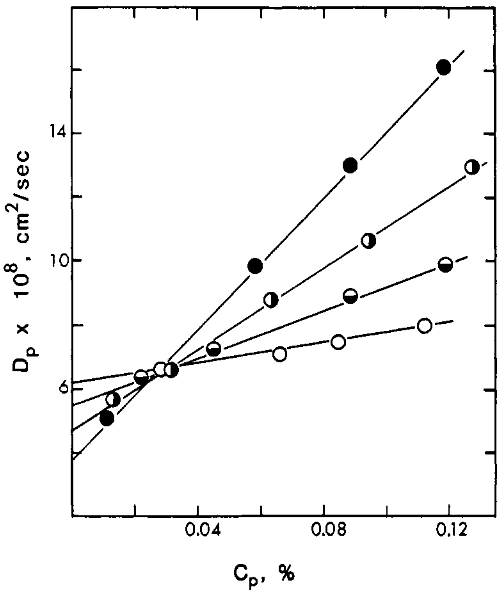

Figure 1. Dependence of D_p on polyelectrolyte concentration for sodium acrylamide/acrylate copolymers of different charge densities in 0.1 M NaBr: (●) $\xi = 1.85$; (◑) $\xi = 0.63$; (◒) $\xi = 0.31$; (○) $\xi = 0.02$.

lutions have also been demonstrated.

Experimental Section

Acrylamide/acrylic acid copolymers of differing acrylic acid content and identical degree of polymerization were prepared by alkaline hydrolysis of polyacrylamide (PAM) purchased from Polysciences. Prior to hydrolysis, the PAM was sheared in a Waring blender to reduce its molecular weight. The viscosity-average molecular weight of the resulting PAM sample was determined to be 1.5×10^6, using the appropriate Mark–Houwink relationship.[22] The hydrolysis was carried out in the presence of NaOH at 60 °C, as described in ref 17. Following hydrolysis, the solutions were acidified to pH <1 and then purified by exhaustive dialysis against doubly distilled water. Concentrations of the resulting polyacid stock solutions were determined by drying several aliquots of the stock to constant weight in a vacuum oven at 60 °C. Equivalent weights (degree of hydrolysis) were determined by potentiometric titration of the purified polyacids with NaOH. The polyacids were converted to their sodium salts with sodium hydroxide and were labeled NaPAM-*y*, where *y* denotes the degree of hydrolysis (i.e., mole percent acrylic acid content of the copolymer).

Diffusion coefficients of the NaPAM-*y* polyelectrolytes were determined at 25 °C in aqueous solutions containing different concentrations of NaBr. Analytical grade NaBr was used, and all solutions were prepared by volumetric dilution of the appropriate simple salt and polyelectrolyte stock solutions. The solutions were filtered through 0.45-μm Millipore filters directly into the light scattering cell.

Quasi-elastic light scattering measurements were carried out with a Malvern photon correlation spectrometer equipped with a 64-channel digital correlator and a 15-mW Spectra-Physics 120 He–Ne laser source at a wavelength of 6328 Å. Measurements were performed at 25 °C at scattering angles ranging between 30 and 90°. No angular dependence was observed in the measured diffusion coefficients. The reported values are the averages of those obtained at three different angles and at several time-delay intervals, with the average standard deviation of the reported values being less than 3%.

Results and Discussion

Diffusion coefficients D_p of the sodium polyelectrolytes listed in Table I were determined at 25 °C in 0.1 and 0.5 M NaBr by quasi-elastic light scattering. The dependence of the measured diffusion coefficients in 0.1 M NaBr on polyelectrolyte concentration C_p is illustrated in Figure 1. For each of the polyelectrolytes investigated, the diffusion coefficients increase linearly with polyelectrolyte concentration, with the highest charge density polyelectrolyte ($\xi = 1.85$) having the steepest slope and the nearly nonionic polymer ($\xi = 0.02$) showing only a small increase in D_p with concentration. In 0.5 M NaBr the same trends are observed, as illustrated in Figure 2; however, the slopes are much smaller than for the 0.1 M NaBr solutions of the corresponding polyelectrolytes.

Table I
Properties of Sodium Acrylamide/Acrylic Acid Copolymers Employed in This Study

sample	mol % hydrolyzed	b,[a] Å	ξ
NaPAM-0.6	0.6	417	0.02
NaPAM-11	11	23	0.31
NaPAM-22	22	11	0.63
NaPAM-65	65	3.8	1.85

[a] Based on a spacing of 2.5 Å for vinyl groups.

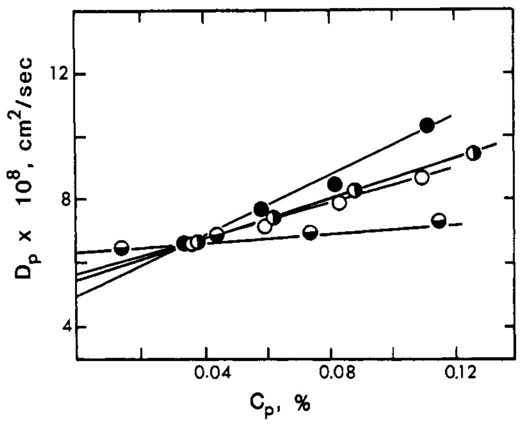

Figure 2. Dependence of D_p on polyelectrolyte concentration for sodium acrylamide/acrylate copolymers of different charge densities in 0.5 M NaBr: (●) $\xi = 1.85$; (◑) ξ 0.63; (○) $\xi = 0.31$; (◒) $\xi = 0.02$.

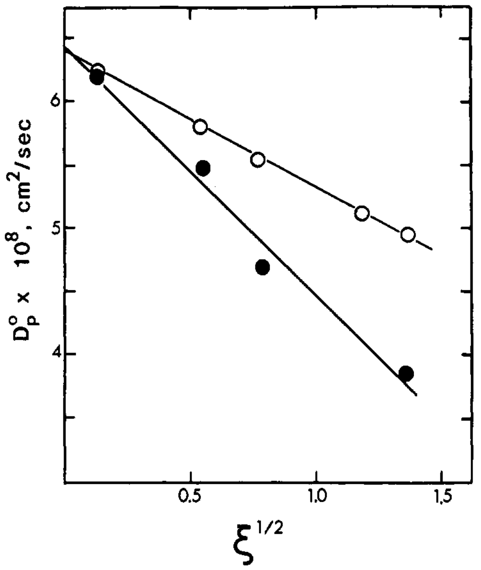

Figure 3. Relationship between limiting diffusion coefficients and polyelectrolyte charge density in 0.1 M (●) and 0.5 M (○) NaBr.

The limiting polyelectrolyte diffusion coefficients $D_p{}^0$, obtained as the intercepts at zero polymer concentration of the plots in Figures 1 and 2, differ markedly with charge density and with ionic strength. The relationship between $D_p{}^0$ and ξ is illustrated in Figure 3. At a fixed simple salt concentration $D_p{}^0$ decreases linearly with the square root

Table II
Values of $\Phi_0^{1/3}P_0^{-1}$ Calculated[a] for Four NaPAM Polyelectrolytes of Different Charge Densities in 0.1 and 0.5 M NaBr

ξ	$[\eta]$,[b] dL/g	$D_p^0 \times 10^8$, cm²/s	$\Phi_0^{1/3}P_0^{-1} \times 10^{-6}$
		0.1 M NaBr	
0.02	4.15	6.21	2.5
0.31	7.61	5.48	2.7
0.63	11.2	4.66	2.6
1.85	16.3	3.83	2.4
		av	2.5 ± 0.1
		0.5 M NaBr	
0.02	4.24	6.28	2.5
0.31	5.67	5.79	2.6
0.63	6.40	5.53	2.5
1.85	7.66	4.95	2.4
		av	2.5 ± 0.1

[a] Calculated from eq 2. [b] Data from ref 12.

of the polyelectrolyte charge density, the slope being determined by the concentration of the simple electrolyte. (It is noteworthy that counterion activity coefficients for the same series of polyelectrolytes[15,16] were also found to decrease linearly with $\xi^{1/2}$.) At the lower simple salt concentration, the slope of the D_p^0 vs. $\xi^{1/2}$ plot is greater than at the higher concentration. The lower the charge density of the polyelectrolyte, the smaller is the difference in the limiting diffusion coefficients between 0.1 and 0.5 M NaBr, with D_p^0 for nonionic polyacrylamide, obtained as the intercept at $\xi = 0$, being identical in the two different salts, with a value of 6.4×10^{-8} cm²/s. The observed trends in D_p^0 with charge density and with ionic strength are quite understandable in view of the expansion of a polyelectrolyte with increasing charge density and with decreasing ionic strength.

It is well established that the molecular weight M of a polymer may be calculated from a knowledge of D_p^0 and the intrinsic viscosity, $[\eta]$, by the Mandelkern–Flory[23-25] equation

$$M^{1/3} = \Phi_0^{1/3}P_0^{-1}kT/\eta_0 D_p^0[\eta]^{1/3} \qquad (2)$$

where η_0 is the solvent viscosity, k is the Boltzmann constant, T is the absolute temperature, and $\Phi_0^{1/3}P_0^{-1}$ is a constant. For nonionic polymers, $\Phi_0^{1/3}P_0^{-1}$ has experimentally been demonstrated to be constant and independent of solvent and temperature, with a commonly accepted value of 2.5×10^6. The validity of eq 2 for polyelectrolytes, however, has not been thoroughly investigated. Although Nagasawa et al.[26] have demonstrated from diffusion studies on sodium poly(styrenesulfonate) (NaPSS, $\xi = 2.85$) that $\Phi_0^{1/3}P_0^{-1}$ is constant over a wide range of ionic strengths, the effect of polyelectrolyte charge density on $\Phi_0^{1/3}P_0^{-1}$ has not been established thus far.

Using the presently determined values of D_p^0 along with the values of $[\eta]$ previously reported[12] for the same series of polyelectrolytes, we calculated values of $\Phi_0^{1/3}P_0^{-1}$ for each of the polyelectrolytes in 0.1 and 0.5 M NaBr. These are tabulated in Table II, where it can be seen that $\Phi_0^{1/3}P_0^{-1}$ is not only independent of the concentration of simple electrolyte, as reported by Nagasawa[26] for NaPSS, but independent of the polyelectrolyte charge density as well. The average value of $(2.5 \pm 0.1) \times 10^6$ for $\Phi_0^{1/3}P_0^{-1}$ is in excellent agreement with the accepted value for nonionic polymers.

It must be pointed out that although Nagasawa found $\Phi_0^{1/3}P_0^{-1}$ to be independent of the simple salt concentration, he also found that the calculated value depended on the type of molecular weight average that was used in eq 2. In the present study, a viscosity-average molecular weight of 1.5×10^6 was used in calculating $\Phi_0^{1/3}P_0^{-1}$. This molecular weight was determined by using the Mark–Houwink parameters reported[15] for weight-average samples of unfractionated PAM. The polymers employed in this study were also not fractionated. Therefore, it is not clear with which of Nagasawa's values, which were determined on a carefully fractionated polymer, comparisons should be made. When a weight-average molecular weight was used, the average value of $\Phi_0^{1/3}P_0^{-1}$ reported by Nagasawa was 2.9×10^6; when a sedimentation diffusion molecular weight (Svedberg equation) was used, $\Phi_0^{1/3}P_0^{-1}$ was calculated to be 2.5×10^6. In any event, this does not alter the conclusion that $\Phi_0^{1/3}P_0^{-1}$ is unaffected by the charge density of the polyelectrolyte.

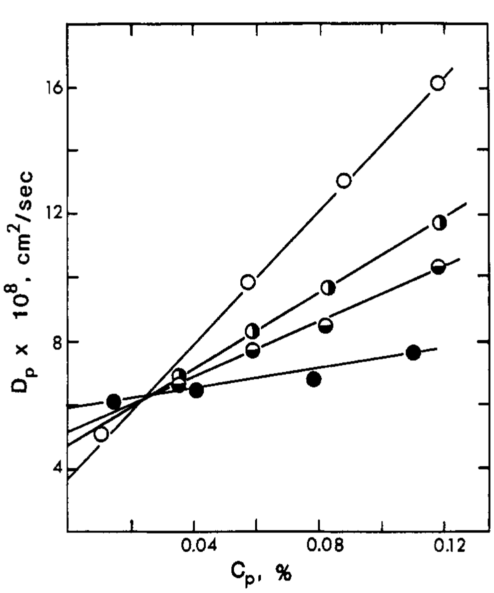

Figure 4. Dependence of D_p on polyelectrolyte concentration for NaPAM-65 in 0.1 M (○), 0.25 M (◑), 0.5 M (◒), and 1.0 M (●) NaBr.

The D_p vs. C_p plots in Figures 1 and 2 warrant some further consideration. It is quite surprising that in both figures the plots for the different charge density polyelectrolytes have a common point of intersection at a polyelectrolyte concentration of 0.03%, where D_p is independent of ξ. Not only is D_p independent of charge density at this "critical" point, it is independent of the NaBr concentration as well; the value of D_p at the critical concentration is 6.4×10^{-8} cm²/s in both 0.1 and 0.5 M NaBr. Further substantiation that D_p is independent of the simple salt concentration is provided in Figure 4, where the values of D_p determined for NaPAM-65 ($\xi = 1.85$) at four different NaBr concentrations show a common point of intersection at $C_p = 0.03\%$.

The fact that D_p is independent of both polyelectrolyte charge density and simple salt concentration at the critical concentration suggests that the diffusion coefficient at this point is that of an effectively uncharged polymer, i.e., that of the parent nonionic PAM. This interpretation of the critical point is further supported by the fact that the diffusion coefficient for nonionic PAM, obtained as the intercept at $\xi = 0$ of both plots in Figure 3, is also found to be 6.4×10^{-8} cm²/s.

The trends in D_p on either side of the critical point indicate that different interactions dominate above and below this concentration. This is illustrated in Figure 5, where at any fixed concentration of polyelectrolyte D_p varies linearly with $\xi^{1/2}$. (The points were taken from the least-squares fits of the data in Figure 1.) Above the

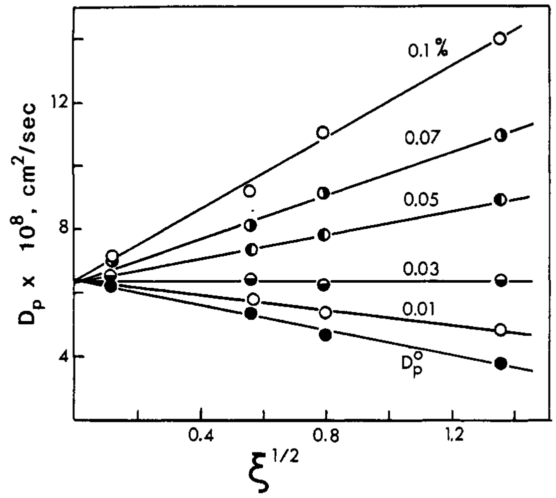

Figure 5. Relationship between D_p and charge density at different polyelectrolyte concentrations above and below the critical concentration (0.03%) in 0.1 M NaBr. The points were taken from the least-squares fits of the data in Figure 1.

critical concentration, which is depicted as a horizontal line, the values of D_p increase with increasing charge density, while below the critical concentration they decrease with increasing charge density, as do the limiting diffusion coefficients depicted in Figure 3. It would appear that below the critical concentration primarily intramolecular interactions dominate, since the trends in the data may be explained in terms of the same arguments that are used at infinite dilution. The reversal in the trends above the critical point may be due to the increased importance of intermolecular interactions with increasing polyelectrolyte concentration, which become dominant above the critical concentration. In view of this behavior, perhaps comparisons of experimental data with limiting laws should be restricted to experiments performed at polyelectrolyte concentrations below 0.03%.

Similar trends to the ones described here may be seen in the diffusion data reported by Nagasawa et al.[26] for NaPSS ($\xi = 2.85$) in aqueous NaBr solutions. The values for D_p for NaPSS increase with increasing polyelectrolyte concentration, with the largest slopes being observed at the lowest concentrations of NaBr. Of particular interest, although not discussed by the authors, the plots of D_p vs. C_p at several NaBr concentrations also exhibit a common point of intersection at 0.03% NaPSS concentration, with the same trends above and below the critical point as with our NaPAM polyelectrolytes. Since both NaPSS and the NaPAM-*y* polyelectrolytes exhibit a critical point at the same concentration, it would appear that, at least for vinylic polyelectrolytes, the critical concentration is independent of the nature of the ionic group. Similar studies with other polyelectrolyte systems should be conducted to verify this.

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Second Virial Coefficient of Polydisperse Polymers

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ABSTRACT: The osmotic and light-scattering second virial coefficients, A_2^{OS} and A_2^{LS}, of polydisperse homopolymers are calculated by using the Padé approximant based on the first three coefficients C_k ($k = 0, 1, 2$) in the cluster series for A_{ij}, the second virial coefficient between two molecules of molecular weights M_i and M_j. The third coefficient C_2 is reevaluated and an error in the earlier result corrected. It is predicted that A_{ij} is always equal to or greater than the arithmetic average of A_{ii} and A_{jj}. In a ternary system, both A_2^{OS} and A_2^{LS} as functions of composition of the mixed homopolymer exhibit a maximum if the ratio of the two molecular weights and the solvent power are high enough. This conclusion is consistent with experimental data. For continuous molecular weight distributions of the Schulz–Zimm and log-normal types, ratios A_2^{OS}/A_2^{LS} are greater than unity, in accord with the hard-sphere theory, but contrary to its results they tend to approach some solvent-dependent limit as the polydispersity increases.

I. Introduction

Extensive studies of the second virial coefficient A_2[1,2] of flexible polymers have been done for many years, experimentally and theoretically.[3] Most of them are limited to monodisperse linear polymers and there is no satisfactory theory of A_2[4-12] for a mixture of two monodisperse linear polymers differing only in molecular weight. The Flory–Krigbaum theory[13] and the hard-sphere model[14] by

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