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on the extension of the theory to include the statistical effects of loop entropy[9] and perhaps also of out-of-register structures (which may exist in the transition zone of the thermal denaturation curve). Under the circumstances, it is wise to wait until a completely self-consistent set of data on the various fragments can be fit with a more complete theory.

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Comments on "Effect of Charge Density and Simple Salts on the Diffusion of Polyelectrolytes in Aqueous Solution"[1]

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Kowblansky and Zema recently reported diffusion coefficients (D_p) for acrylamide/acrylic acid copolymers (PAM) of various charge densities (ζ) as a function of the polymer concentration (C_p) and the added NaBr (C_s).[1] These data suggested that D_p was a linear function of C_p and that the slope (S) and intercept (D_p^0) depended on both ζ and C_s. In particular, D_p^0 decreased and S increased as C_s decreased and/or ζ increased. An apparent peculiar feature of these data when presented on the same graph was a common value for D_p at the polymer concentration $C_p = 0.03\%$ (w/w). This common value of $D_p = 6.4 \times 10^{-8}$ cm^2/s led these authors to postulate the existence of a "critical concentration" in which "the trends in D_p on either side of the critical point indicate that different interactions dominate above and below this concentration".[1] It is shown in the present note that these *linear* D_p vs. C_p plots are also consistent with current polyelectrolyte theories without having to propose the existence of a "critical concentration".

Table I
Characterization of the Diffusion Data of Kowblansky and Zema for PAM

C_s, M	$D_p^0 \times 10^8$, cm^2/s	$S \times 10^8$, cm^2/s$C(\%)$	ζ[a]
0.1	6.21	13.9	0.02
0.1	5.48	37.2	0.31
0.1	4.66	63.4	0.63
0.1	3.83	101.7	1.85
0.5	6.28	7.2	0.02
0.5	5.79	26.1	0.31
0.5	5.53	31.7	0.63
0.5	4.95	48.5	1.85

[a] Defined as $e^2/\epsilon kTb$, where the average intercharge spacing b was estimated from potentiometric titration measurements with an assumed value of 2.5 Å between vinyl groups.

For the purpose of quantitative reanalysis of the Kowblansky–Zema data, we employ the expression derived by Schurr et al.[2,3] for D_p

$$D_p = (1/2)[D_p^0(1 - \Omega) + D_s(1 + \Omega)] \tag{1}$$

where D_p and D_p^0 retain their meaning as above, D_s is the average diffusion coefficient for the counterions and the byions (referred to as the small-ion diffusion coefficient), and

$$\Omega = \frac{D_p^0 - D_s[1 + (2C_s/C_p)Z^{-1}]Z^{-1}}{D_p^0 + D_s[1 + (2C_s/C_p)Z^{-1}]Z^{-1}} \tag{2}$$

where Z is the apparent charge on the polyion. In the dual limits $C_s \gg ZC_p$ and $D_s \gg D_p$, eq 1 reduces to the familiar Donnan equilibrium form

$$D_p = D_p^0[1 + (Z^2C_p/2C_s)] \tag{3}$$

There are two additional effects to be included ad hoc to obtain our operational expression: electrolyte dissipation effects and direct polyion–polyion interactions. The effect of an asymmetric distribution of small ions about the polyion is to provide an additional source of dissipation; hence D_p^0 is expressed in terms of the composite friction factor[4]

$$D_p^0 = kT/\{6\pi\eta a + [(Z^2e^2/12a^2\epsilon\kappa D_s) \times (1 - ((1 + 2\kappa a)\exp\{-2\kappa a\}))]\} \tag{4}$$

where η is the solvent viscosity, e is the electron charge, a is the polyion radius, κ is the Debye–Hückel screening parameter, and ϵ is the bulk dielectric constant. The quantity in the square brackets is the additional friction due to electrolyte dissipation. Direct polyion–polyion interactions also result in a dependence of D_p on C_p, which we denote by the parameter A_2. Our final expression for the linear dependence of D_p on C_p is therefore

$$D_p = D_p^0[1 + ((Z^2/2C_s) + 2A_2)C_p] \tag{5}$$

where D_p^0 is defined by eq 4. We represent the data of Kowblansky and Zema[1] by the linear expression

$$D_p = D_p^0 + SC(\%) \tag{6}$$

where $C(\%)$ is the percent weight of PAM and D_p^0 is the

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Table II
Reanalysis[a] of the Diffusion Data of Kowblansky and Zema for PAM

C_s, M	ζ[b]	$D_p^0 \times 10^8$,[c] cm²/s	R_p^0,[d] Å	a,[e] Å	Z[e]	$A_2 \times 10^{-7}$,[f] L/M	$D_p^0 \times 10^8$,[g] cm²/s	Z_{app}[h]
0.1	0.02	6.21	393	385	360	1.65	6.21	2590
0.5	0.02	6.28	389	385	360	0.85	6.28	4150
0.1	0.31	5.48	445	400	895	4.89	5.48	4510
0.5	0.31	5.79	422	400	895	3.34	5.80	8220
0.1	0.63	4.66	523	375	1510	9.63	4.67	6390
0.5	0.63	5.53	441	375	1510	4.18	5.53	9270
0.1	1.85	3.83	637	377	2015	18.89	3.83	8920
0.5	1.85	4.95	493	377	2015	7.14	4.94	12100

[a] Parameters used in these calculations were $\eta = 0.008\,937$, $\epsilon = 78.54$, and a small-ion diffusion coefficient of $D_s = 1.526 \times 10^{-5}$ cm²/s (cf. eq 1, 2, 4, and 5). This corresponds to conditions at 25 °C and a small-ion radius of 1.6×10^{-8} cm. [b] Reported value for the charge density based on potentiometric titration data (cf. footnote *a* of Table I). [c] Reported value for the intercept of D_p vs. $C(\%)$.[1] [d] Computed from the Stokes-Einstein relationship, $R_p^0 = kT/6\pi\eta D_p^0$. [e] Computed from eq 1, 2, and 4; simultaneous solutions for the two ionic strengths at fixed ζ. [f] Estimated from eq 7, where Z was computed from D_p^0. [g] Theoretical value computed from eq 4. [h] Apparent charge computed from the slope with $A_2 = 0$ (cf. eq 7).

reported intercept (Table II of ref 1). Comparison of eq 5 and 6 leads to the identity

$$S = D_p^0[(Z^2/2C_s) + 2A_2](C_p/C(\%)) \qquad (7)$$

where $C_p/C(\%)$ is the concentration conversion factor, which on the basis of the reported viscosity-average molecular weight ($M_\eta = 1.5 \times 10^6$) is estimated to be $10/(1.5 \times 10^6 \times 100) = 6.67 \times 10^{-8} = C_p/C(\%)$. The slope S was determined in the present analysis from D_p^0 and the value of D_p at $C(\%) = 0.1$ of Figures 1 and 2 of ref 1. These parameters are summarized in Table I of this paper.

There are three parameters associated with the polyion in eq 5–7: the polyion radius a, the polyion charge Z, and the direct polyion–polyion interaction term A_2. There are two extremum conditions that can be imposed upon these equations which can adequately reproduce the experimental observations. In the first extreme the total decrease in the intercept D_p^0 can be attributed to an expansion of the polyion as the charge density is increased, which represents a maximum increase in a of 25% in going from $\zeta = 0.02$ to $\zeta = 1.85$. Concomitantly the direct interaction term A_2 would be expected to increase due to the increase in repulsive interactions between the polyions as well as an increase in the Donnan term. At the other extreme the polyion radius is assumed to be *independent* of the *ionic strength* over the range employed but is *allowed to "float"* in regard to the *charge density* of the polyion. For the purpose of computation we therefore require the values of Z and a to be the same for both the 0.1 and 0.5 M NaCl solvents for those polyions with the same value of ζ. The two expressions for D_p^0 can then be used to compute unique values for Z and a and then the slope S can be used to obtain a value for A_2. The results of these analyses for the various charge densities are summarized in Table II, where the computed value of D_p^0 was required to be within 0.3% of the reported value of D_p^0.

There are four points that should be emphasized on the basis of the data in Table II. First, the decrease in D_p^0 can be fully interpreted in terms of electrolyte dissipation effects *without having to invoke an expansion of the polyion.* This *does not mean*, however, that the polyion does *not* expand but rather that hydrodynamic methods may not be a reliable method for determining the *extent of expansion.* A more reliable method, for example, might be the determination of the radius of gyration from static light scattering studies. A second observation is that the apparent change in Z is considerably less than the change in ζ. A similar observation that the titration and dynamic charges are not equivalent was recently reported for mononucleosomes by our group[5,6] and by Hantz et al.[7] This apparent discrepancy between the two types of charges is due to the fact that the titration charge is a measure of the *surface* charge whereas the dynamic charge based on quasi-elastic light scattering (cf. eq 1, 2, and 4) or electrophoretic light scattering[5-7] also includes effects of the associated ion cloud as well as the surface charge. The third observation is that the apparent charge computed from the slope S ($A_2 = 0$ in eq 7) is much larger than the value of Z computed from D_p^0 on the basis of eq 4. It might be inferred that direct polyion–polyion interactions are very important in these systems. The fourth observation is that the data of Kowbansky and Zema are adequately interpretable in terms of current polyelectrolyte theories without having to postulate the occurrence of a "critical concentration". We therefore suggest the term "pivotal concentration" for apparent points of intersection of *linear* D_p vs. C_p plots in the absence of other data that might suggest the fomation of a "critical concentration". For example, Strand et al.[8] also reported intersecting data for the sodium alginate system, which they interpreted in terms of the first extremum case described above. Likewise, polylysine also exhibited a point of intersection.[4] Clearly, the understanding of polyelectrolyte systems requires more data on diversified systems over a wide range of polyion and small-ion concentrations.

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