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On the Ionic-Strength Dependence of the Intrinsic Viscosity of DNA

In a recent paper Harrington¹ obtained the electrostatic persistence length of DNA as a function of ionic strength from intrinsic-viscosity and flow-birefringence data. His values contrast markedly with those predicted by the theories of Odijk² and Skolnick and Fixman³ if one takes account of an effective charge correction.⁴ In this communication we show that the excluded-volume effect overshadows the theoretical increase in the persistence length in the range of salt concentrations employed by Harrington.¹ We derive the increase in the intrinsic viscosity using the novel Weill-des Cloizeaux theory.⁵ Without making use of adjustable parameters, we find good agreement with the experiments of Harrington¹ and of Rosenberg and Studier⁶ at ionic strengths lower than 0.1M NaCl, where one may neglect nonelectrostatic excluded-volume effects.

We view DNA as a wormlike chain of contour length l and bare persistence length L_p , bearing charges which interact via a Debye-Hückel potential. The charges stiffen the chain locally, and the electrostatic persistence length is given by⁴

$$L_e = 1/4Q\kappa^2 \quad (1)$$

where κ^{-1} is the Debye screening length and Q is the Bjerrum length. Equation (1) is only correct if the total persistence length $L_t = L_p + L_e$ is much larger than the Debye length^{4,7} and $A\kappa \ll 1$, where A is the contour distance between charges. The two length scales κ^{-1} and Q can be expressed as

$$\kappa^2 = 8\pi Qn \quad (2)$$

$$Q = q_e^2/Dk_B T \quad (3)$$

where n is the concentration of added 1:1 electrolyte, D is the dielectric permittivity of the solvent, k_B is Boltzmann's constant, T is the temperature, and q_e is the elementary charge. In Eq. (1) a charge correction has been used in accordance with Manning's theory,^{4,8} i.e., the polyelectrolyte has a charge density of Q^{-1} elementary charges per unit length. If the chain has flexibility, Onsager's argument⁸ leading to the condensation conjecture remains unchanged.⁹

If $\kappa L_t \gg 1$ and $l \gg L_t$, Odijk and Houwaart⁴ have shown that the mean-square radius of gyration is given by

$$\langle S^2 \rangle = 1/3 l L_t \alpha_S^2 (Z_{el}) \quad (4)$$

where α_S is the excluded-volume expansion factor and Z_{el} is the electrostatic excluded-volume parameter:

$$Z_{el} = \left(\frac{3^{3/2}}{32\pi^{3/2}} \right) \beta_{el} l^{1/2} L_t^{-7/2} \quad (5)$$

The electrostatic excluded volume β_{el} between effective Kuhn segments can be reasonably approximated by⁴

$$\beta_{el} = 2\pi L_t^2 d \quad (6)$$

Here d is the effective diameter of a Kuhn segment, and it has recently been calculated by Fixman and Skolnick¹⁰:

$$d \simeq \kappa^{-1} (-\ln Q\kappa + \ln 4\pi + \gamma - 1/2) \quad (7)$$

In Ref. 4 a cruder estimate of d was given.

TABLE I
Theoretical and Experimental values of the Intrinsic Viscosity of DNA as a Function of NaCl Concentration

n (M)	κ^{-1} (Å)	L_e (Å)	L_t (Å)	α_S^2 ^a	$[\eta]_{\text{theor}}$ (dl/g)	$[\eta]_{\text{exp}}$ ^b (dl/g)
0.5	4.30	0.65	600.7	1.049	107	110
0.2	6.80	1.62	601.6	1.090	113	119
0.1	9.61	3.24	603.2	1.137	120	125
0.05	13.6	6.48	606.5	1.200	130	132
0.02	21.5	16.2	616.2	1.315	152	150
0.01	30.4	32.4	632.4	1.423	176	172
0.0053	41.8	61.2	661.2	1.534	209	200
0.0023	63.4	140.8	740.8	1.671	282	258
0.0013	84.3	249	849	1.736	364	312

^a Contour length, 1.335×10^5 Å.

^b Data reported by Rosenberg and Studier (Ref. 6). $[\eta]_0 \simeq 102$ dl/g.

Finally, we may write an expression for the intrinsic viscosity,

$$[\eta] = [\eta]_0 (L_t/L_p)^{3/2} \alpha_\eta^3 \quad (8)$$

where $[\eta]_0$ is the value of the intrinsic viscosity extrapolated to infinite salt concentration, $(L_t/L_p)^{3/2}$ signifies the hypothetical theta-state expansion,⁴ and α_η is a complicated function of α_S . Weill and des Cloizeaux⁵ derive a relation for α_η which seems to be in better agreement with experiments on uncharged polymers than other theories.¹¹ We must choose α_S from polymer excluded-volume theory, and a reasonable choice is the Yamakawa-Tanaka equation¹¹

$$\alpha_S^2 = 0.541 + 0.459 (1 + 6.04Z_{el})^{0.46} \quad (9)$$

We note that the application of the excluded-volume theory is justified if the contour length is very much larger than the total persistence length.¹²

In the comparison with experiment, we take $L_p = 600$ Å,¹³ $D = 78.5$ (H₂O), $T = 298$ K, $Q = 7.14$ Å, $\kappa^{-1} = 3.04 n^{-1/2}$ (Å) if n is given in mol/l. Extrapolation of Rosenberg and Studier's measurements⁶ leads to $[\eta]_0 \simeq 102$ dl/g. (At high concentrations the intrinsic viscosity is almost linear in the Debye screening length. The value of $[\eta]$ at the highest concentration appears to be anomalous.) For Harrington's sample, we find $[\eta]_0 \simeq 215$ dl/g. Tables I and II reveal the rather good agreement between the theory, Eqs. (1)–(9), and the experiments at ionic strengths lower than 0.1 mol/l. In Harrington's measurements, the excluded-volume

TABLE II
Second Comparison of Theoretical and Experimental Values of the Intrinsic Viscosity of DNA as a Function of NaCl Concentration

n (M)	κ^{-1} (Å)	L_e (Å)	L_t (Å)	α_S^2 ^a	$[\eta]_{\text{theor}}$ (dl/g)	$[\eta]_{\text{exp}}$ ^b (dl/g)
1.0	3.04	0.32	600.3	1.065	229	245
0.2	6.80	1.62	601.6	1.145	254	294
0.1	9.61	3.24	603.2	1.221	276	320
0.02	21.5	16.2	616.2	1.572	410	415
0.005	43.0	64.8	664.8	1.934	623	565

^a Contour length, 6.92×10^5 Å.

^b Data given by Harrington (Ref. 1). $[\eta]_0 \simeq 215$ dl/g.

effect dominates. Furthermore, in the other case, at low ionic strength, the two respective expansion factors are of the same order, and yet the theory predicts the experimental values quite well. An important feature is that no adjustable parameters have been used.

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