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ORIGINAL CONTRIBUTION

K. R. Rogan

The variations of the configurational and solvency properties of low molecular weight sodium polyacrylate with ionic strength

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Dr. K.R. Rogan (✉)
Research Department
ECC International
John Keay House
St. Austell, Cornwall PL25 4DJ
United Kingdom

Abstract The configurational and solvency properties of low molecular weight sodium polyacrylate have been determined for a wide range of ionic strength solutions, from intrinsic viscosity data in the polymer literature.

The variations of the polymer properties with ionic strength (I) are described very well by simple mathematical expressions. Thus, a linear relationship was found between the solvency parameter and $1/I^{(1/2)}$, while the variations of the expansion factor and the radius of gyration with $1/I^{(1/2)}$ were described by second order polynomials.

Low I solutions (i.e. < 0.01) have a high solvency for sodium polyacrylate. In such solutions the polymer is in a highly expanded configuration. Thus, the radius of gyration of a typical, low molecular weight (ca. 5000 g mol^{-1}) sodium polyacrylate approaches the limiting value of ca. 4.5 nm at $I < 0.01$.

Conversely, high ionic strength solutions (i.e. > 0.10) have a low solvency for sodium polyacrylate. In such solutions the polymer is in a virtually unexpanded configuration. Thus, the radius of gyration of a typical, low molecular weight sodium polyacrylate approaches the limiting value of ca. 2.0 nm at $I > 0.10$.

Key words Sodium-polyacrylate – low-molecular-weight – configuration – solvency – ionic-strength

Introduction

The performance of polyelectrolytes, such as sodium polyacrylate, in stabilising mineral dispersions will be related to their configurational and solvency properties [1]. These have been shown to be dependent upon the ionic strength of the dispersing medium [1–3]. For example, polyelectrolyte intrinsic viscosity, which is a simple measure of polymer configuration or size [4], is experimentally found [5, 6] to have a linear relationship with the inverse-square-root of ionic strength ($1/I^{(1/2)}$). Similarly, the Stockmayer–Fixman [7] long-range interaction parameter B, which is directly related to the polymer solvency parameter χ [3], is also found, experimentally [8, 9], to have a linear relationship with $1/I^{(1/2)}$. In addition, groups of workers [10, 11] have noted that an observed variation of polyelectrolyte adsorption with I could only be reconciled with that expected theoretically by assuming an ionic strength-dependency of χ. Apparently, salt modifies the thermodynamic affinity of the solvent for the polyelectrolyte in solution and, therefore, the solvent power with respect to adsorption [12].

Thus, the quantification of the variations with ionic strength, and particularly with $1/I^{(1/2)}$, of the configuration and solvency properties of low molecular weight sodium polyacrylate could give a better understanding of the performance of such a polyelectrolyte in stabilising mineral dispersions.

In this work, the values of the configurational and solvency properties of low molecular weight sodium polyacrylate have been determined, for a wide range of ionic strength solutions, from intrinsic viscosity data recorded in the polymer literature. The variations of these properties with ionic strength have been described by mathematical expressions.

Definitions of the configurational and solvency properties

The configurational property which is often used to characterise a polymer molecule is the radius of gyration (r_G, in units of nm), which is here defined as the root-mean-square distance of the segments of the polymer chain from its centre of gravity [13]. In order to distinguish between the perturbed and unpreturbed radii of gyration, the latter is subscripted as $(r_G)_0$ (also in units of nm).

r_G will differ from $(r_G)_0$ by another configurational property – the average molecular expansion factor (α, dimensionless) which is here defined as [13]

$$\alpha = \frac{r_G}{(r_G)_0}. \tag{1}$$

The solvency property of a polymer molecule is characterised by the solvency parameter (χ, dimensionless) [13]. This is here defined as the maximum interaction between a solvent molecule and a surrounding array of polymer molecules [14]. This quantity provides a measure of the solvent power of the given liquid (solution) for the polymer.

Under Θ conditions $\chi = 0.5$, while in a good solvent $\chi < 0.5$; χ diminishes to zero as the solvency of the liquid for the polymer increases.

Polymer literature data

The polymer literature data was the intrinsic viscosities ($[n]$) of molecular fractions of sodium polyacrylate in various ionic strength (I) solutions of a 1:1 electrolyte (NaBr), as measured by Takahashi and Nagasawa [8] and given in Table II of their paper. For this simple electrolyte, I was given by the electrolytes's molar concentration.

The theta molecular weight (M_Θ, in units of g mol^{-1}) of each fraction was calculated, by Takahashi and Nagasawa [8], from its intrinsic viscosity ($([n])_\Theta$, in units of cm^3 g^{-1}) in the Θ solution ($I = 1.5$ at 15 °C [15]) using the relation [13]

$$M_\Theta = \left[\frac{[n]_\Theta}{K_\Theta}\right]^2, \tag{2}$$

where $K_\Theta = 0.124$ cm^3 (mol g^{-3})$^{(1/2)}$ for sodium polyacrylates at $I = 1.5$ and 15 °C [16].

Table 1 Values of the Mark–Houwink parameters, K and a, for a wide range of ionic strength (I)

I	K cm^3 g$^{-(1+a)}$ mol^a	a
1.506	0.1193	0.5035
0.502	0.05348	0.6267
0.100	0.02329	0.7627
0.0502	0.02639	0.7746
0.0251	0.01599	0.8458
0.0100	0.01319	0.8961
0.00502	0.01739	0.9055
0.00251	0.02945	0.8806

Recalculation of molecular weights:

The molecular weight (M, in units of g mol^{-1}) of each fraction was recalculated for each I using the empirical viscosity relation [17]

$$M = \left[\frac{[n]}{K}\right]^{(1/a)} \tag{3}$$

and the appropriate values of K and a as determined from plots of log M_Θ versus log $[n]$. The values of K and a obtained at each I are given in Table 1, and the M of each fraction at each I is given in Table 2.

The variation of the expansion factor (α) of low molecular weight sodium polyacrylate with I

For each I, the α of each fraction was calculated using the relation [13]

$$\alpha = \left[\frac{[n]}{K_\Theta^1 M^{(1/2)}}\right]^{(1/3)}, \tag{4}$$

where K_Θ^1 (in units of cm^3 (mol g^{-3})$^{(1/2)}$) was obtained from a plot of the Stockmayer–Fixman equation [7], i.e.

$$[n]/M^{(1/2)} = K_\Theta{}^2 + 0.51\Phi_0 \mathrm{B} M^{(1/2)}, \tag{5}$$

where Φ_0 = the universal constant of Flory under Θ conditions, i.e. for unperturbed Gaussian coils ($\Phi_0 = 2.87 \times 10^{23}$ mol^{-1}), and B (in units of

Table 2 Recalculated molecular weights (g mol^{-1}) of the fractions at each ionic strength using the appropriate Mark–Houwink parameters (see Table 1)

Fraction	Ionic strength 1.506	0.502	0.100	0.0502	0.0251	0.0100	0.00502	0.00251
FL4	14571	15045	15074	14356	15178	14094	15450	16322
FL3	36935	36215	33283	33329	31831	38105	35431	32110
F2L7	44024	40664	44470	44388	46194	40645	41456	45440
F2L6	58495	59403	61640	64115	60038	61502	56959	55693
F2L4	123468	130557	122546	132536	128048	134448	129782	119 554
F2L1	346747	367463	367486	345836	366550	348205	386869	389980
FL1	499167	469 082	478229	474524	470968	471242	456379	478952

Table 3 Values of the parameters K_Θ^1 and B in the Stockmayer–Fixman equation

$[n]/M^{(1/2)} = K_\Theta^1 + 0.51\Phi_0 \, BM^{(1/2)}$

for a wide range of ionic strength (I)

I	K_Θ^1	B
	cm^3 (mol g^{-3})$^{(1/2)}$	10^{-26} cm^3 mol^2 g^{-2}
1.506	0.1234	0.0016691
0.502	0.1702	0.11399
0.100	0.2266	0.50333
0.0502	0.2781	0.69063
0.0251	0.2644	1.2148
0.0100	0.2627	2.0840
0.00502	0.3534	3.1377
0.00251	0.5722	3.6982

cm^3 mol^2 g^{-2}) is described by Munk [3] as

$$B = \frac{2v_2^2}{V_1 N}(1/2 - \chi) , \qquad (6)$$

where v_2 = the partial specific volume of sodium polyacrylate ($v_2 = 1.3^{-1}$ cm^3 g^{-1}), V_1 = the molar volume of the solvent (V_1 = 18.0152 cm^3 mol^{-1}), N is Avogadro's number, and χ is the dimensionless sodium polyacrylate/solvent interaction (or solvency) parameter. The values of the Stockmayer-Fixman parameters K_Θ^1 and B, obtained at each I, are given in Table 3.

The variation of ($\alpha^5 - \alpha^3$) with $M^{(1/2)}$ for the four lowest molecular weight fractions is shown in Fig. 1, for each value of I. The data in this figure were described very well by second order polynomials.

Values of ($\alpha^5 - \alpha^3$) at the arbitrary M values of 2500, 5000, 10 000 and 15 000 g mol^{-1} were obtained by extrapolation of each $M^{(1/2)}$ versus ($\alpha^5 - \alpha^3$) curve. These values were translated into α values which are plotted as a function of $1/I^{(1/2)}$ in Fig. 2. The data in this figure were described very well by third order polynomials; the coefficients of the polynomials are given in Table 4.

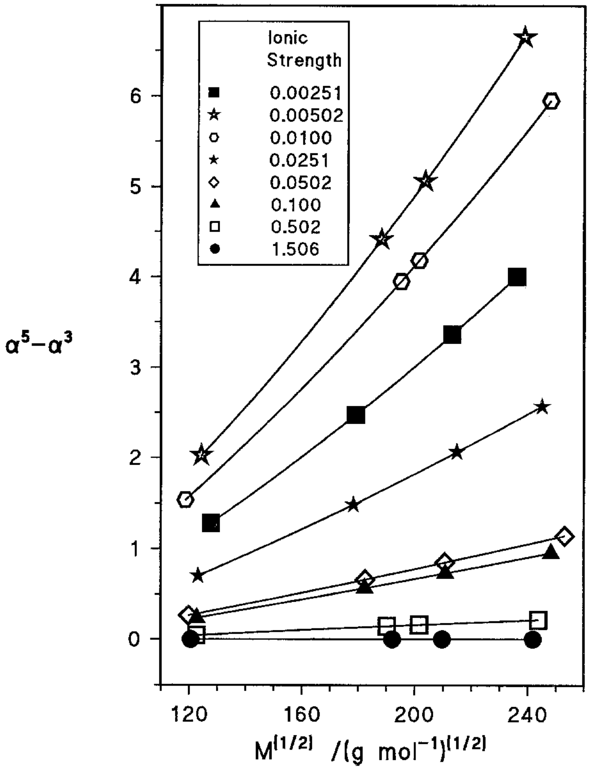


Fig. 1 Expansion factor relation ($\alpha^5 - \alpha^3$) as a function of molecular weight (M, square root)

Table 4 Values of the coefficients b_0, b_1 and b_2 in the third order polynomial

$\alpha b_0 + (b_1/I^{(1/2)}) + (b_2/I) + (b_3/I^{(3/2)})$

for a range of molecular weight (M)

M g mol^{-1}	b_0	b_1	b_2	b_3
2 500	1.037	− 0.06348	0.006885	− 2.086E-4
5 000	0.9965	− 0.01495	0.003942	− 1.511E-4
10 000	0.9814	+ 0.01428	0.002160	− 1.177E-4
15 000	0.9739	+ 0.03016	0.001184	− 9.929E-5

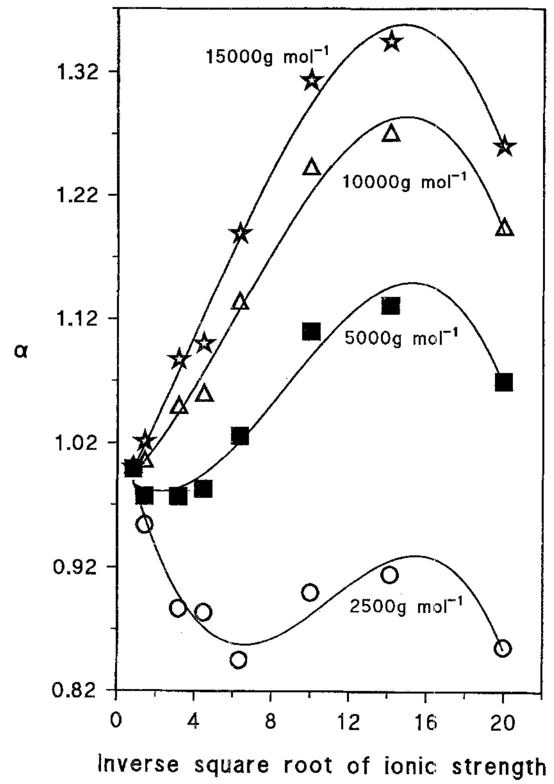


Fig. 2 Expansion factor (α) as a function of ionic strength (inverse square root)

The variation of the solvency parameter (χ) of sodium polyacrylate with I

For each I, χ was evaluated from the slope of the appropriate Stockmayer–Fixman plot (see above) via a knowledge of the parameter B. χ is plotted as a linear function of $1/I^{(1/2)}$ in Fig. 3. This function may be expressed as

$$\chi = -(0.02167/I^{(1/2)}) + 0.5232 \tag{7}$$

correlation coefficient $= 0.997$.

The variation of the radius of gyration (r_G) of low molecular weight sodium polyacrylate with I

The r_G of each molecular weight fraction was calculated, at each I, using the relation [18]

$$r_G = (10^7/6^{(1/2)}).\left[\frac{[\eta]M}{\Phi}\right]^{(1/3)}, \tag{8}$$

where Φ = the Flory constant [13] (in units of mol^{-1}) under non-Θ conditions. Unfortunately, Φ for polyelectrolytes, such as sodium polyacrylate, changes drastically

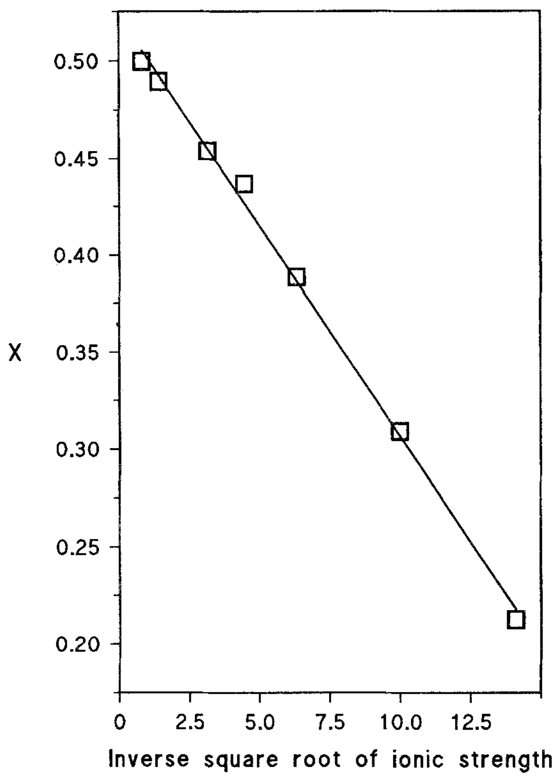
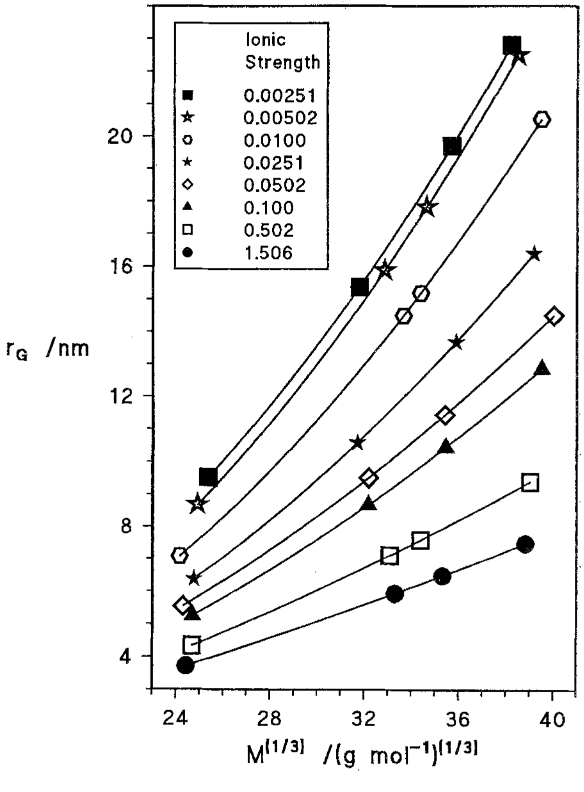


Fig. 3 Solvency parameter (χ) as a function of ionic strength (inverse square root)

Fig. 4 Radius of gyration (r_G) as a function of molecular weight (M, cube root)



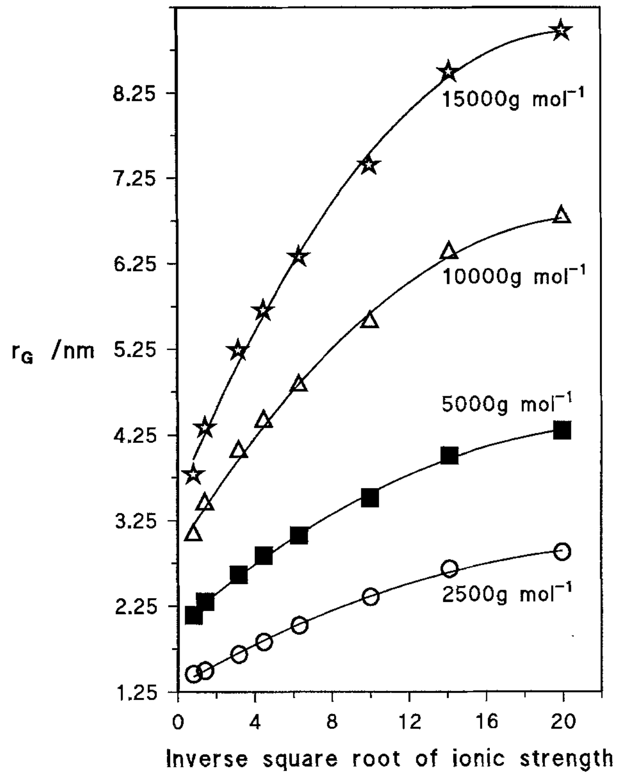


Fig. 5 Radius of gyration (r_G) as a function of ionic strength (inverse square root)

with the expansion of the polyion coil [19–21] (i.e. Φ depends upon α via I). The variation of Φ with α for polyelectrolyte was taken to be that recorded by Takahashi et al. [20]. This variation was described very well by the following third order polynomial

$$\Phi/10^{23} = 9.0874 - 8.7685\alpha + 2.7765\alpha^2 - 0.231643\alpha^3 \ . \quad (9)$$

Thus, for each I a value of Φ was calculated for each fraction from a knowledge of its associated α value, using Eq. (9).

The variation of the calculated values of r_G with $M^{(1/3)}$, for the four lowest molecular weight fractions, is shown in Fig. 4, for each value of I. The data in this figure were described very well by second order polynomials.

Finally, values of r_G at the arbitrary M values of 2500, 5000, 10 000 and 15 000 g mol^{-1} were obtained by extrapolation of each $M^{(1/3)}$ versus r_G curve. These values are plotted as a function of $1/I^{(1/2)}$ in Fig. 5. The data in this figure were described very well by second order polynomials; the coefficients of the polynomials are given in Table 5.

Table 5 Values of the coefficients b_0, b_1 and b_2 in the second order polynomial

$r_G = b_0 + (b_1/I^{(1/2)}) + (b_2/I)$

for a range of molecular weight (M)

M g mol^{-1}	b$_0$	b$_1$	b$_2$
2 500	1.325	0.1287	− 0.002516
5 000	2.018	0.1943	− 0.003987
10 000	2.907	0.3583	− 0.008226
15 000	3.539	0.5273	− 0.01279

Conclusions

Low ionic strength (I) solutions (i.e. $I < 0.01$) have a high solvency for sodium polyacrylate. In such solutions, the polymer is in a highly expanded configuration due to strong inter-segmental, electrostatic repulsions. Thus, the radius of gyration of a typical, low molecular weight (ca. 5000 g mol^{-1}) polyacrylate approaches the limiting value of ca. 4.5 nm at $I < 0.01$.

Conversely, high ionic strength solutions (i.e. $I > 0.1$) have a low solvency for sodium polyacrylate. In such solutions, the polymer is in a virtually unexpanded configuration due to the effective shielding of the charge centres present on the polymer segments. Thus, the radius of gyration of a typical, low molecular weight polyacrylate approaches the limiting value of ca. 2.0 nm at $I > 0.10$.

This quantification of the variations of the configurational and solvency properties of sodium polyacrylate with ionic strength will give a better understanding of the performance of this polyelectrolyte in stabilising mineral dispersions.

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