

Expansion Coefficients and Conformational Properties of Heterodisperse Poly(acrylamide-co-sodium acrylate)

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Synopsis

Calculations of expansion coefficients from light scattering and viscometric data on heterodisperse samples of poly(acrylamide-co-sodium acrylate) satisfactorily describe the solution properties of these polymers across the entire copolymer range, from polyacrylamide to poly(sodium acrylate). Light scattering results correlate well with the viscosity data provided that corrections are made for polymer heterodispersity and that a modified Krigbaum equation is used to estimate the unperturbed dimensions of the molecules. The expansion coefficients deduced from light scattering and Flory-Fox hydrodynamic theory were inaccurate and insensitive to fluctuations in charge density and molecular weight.

INTRODUCTION

Heterodisperse poly(acrylamide-co-sodium acrylate) samples were studied by light scattering, intrinsic viscosity, and gel permeation chromatography.¹ Hydrolyzed polyacrylamides are termed "linear polyelectrolytes." Incorporation of ionic charges into the polymer chain leads to large expansions of the macroion due to electrostatic repulsion. Through the addition of inorganic salts (counterions) to the system, one can minimize the charge interaction and effectively reduce the charge density of the polymer. If enough salt is added to the polyelectrolyte solution, theta (θ) conditions may be attained. "A theta solvent is one where the polymer chains tend to associate more with each other than they do with the solvent molecules and is normally characterized by polymer precipitation."² Under theta conditions, the second virial coefficient becomes zero, the Mark-Houwink exponent (α) is equal to 0.5, and the expansion coefficient α reduces to unity.

Viscosity data in 1M aqueous NaCl was used to calculate the Flory viscosity constant Φ from modifications of the original Kirkwood-Riseman theory.³ (The Flory viscosity constant is a relative measure of the permeation of solvent through the polymer coil.) It is uncertain whether light scattering hydrodynamic theory can be applied to the determination of polyelectrolyte dimensions. While most investigators assume a theoretical and asymptotic value for the Flory viscosity constant ($\Phi_0 = 2.2 \times 10^{21}$ if $[\eta]$, the intrinsic viscosity, is expressed in dL g^{-1} and the mean square radius of gyration $\langle \bar{s}^2 \rangle$ in cm^2), our data suggest that there is considerable variation of the viscosity

TABLE I
 Intrinsic Viscosity in 1M NaCl at 25° C, the Flory Viscosity Constant Φ in 1M NaCl, and the Light Scattering Expansion Coefficient α_{LS} in 1M NaCl.^a

Sample	$[\eta]$ 1M NaCl (dL g ⁻¹)	$\Phi \times 10^{-20}$ (dL g ⁻¹ mol cm ³)	α_{LS}
	Polysodium acrylate [Poly (NaAc)]		
1	0.956	4.58	1.002
2	1.264	3.96	1.001
3	1.198	4.38	1.002
4	2.187	4.81	1.001
5	2.912	6.43	1.002
	Poly(70 NaAc-30 AAm)		
6	1.633	1.78	1.002
7	1.657	3.74	1.001
8	2.422	1.93	1.001
9	2.649	6.85	1.002
10	3.345	5.96	1.001
11	—	—	—
	Poly(50 NaAc-50 AAm)		
12	1.596	0.32	1.001
13	3.210	5.59	1.002
14	4.228	4.72	1.002
15	4.360	4.70	1.001
16	5.230	5.13	1.002
	Poly(20 NaAc-80 AAm)		
17	0.681	4.25	1.001
18	—	—	—
19	2.282	5.77	1.001
20	4.207	5.27	1.002
21	8.087	6.08	1.023
	Poly(10 NaAc-90 AAm)		
22	1.216	6.58	1.003
23	3.025	4.88	1.002
24	3.096	2.71	1.001
25	4.691	6.51	1.002
26	9.708	6.56	1.002
	Poly Acrylamide (PAAm)		
27	0.645	2.03	1.001
28	1.369	9.87	1.014
29	—	—	—
30	—	—	—
31	8.166	10.64	1.006

^aThe slashes in the table represent missing experimental values due to sample aging. Units of Φ refer to $[\eta]$ in dL g⁻¹ and $\langle S^2 \rangle$ in cm².

constant from sample to sample in 1M aqueous NaCl. "The physical significance of the attainment of the asymptotic value is that under these conditions hydrodynamic interaction is so great that the chain can be visualized as carrying immobilized solvent within it as it rotates under the influence of the shear gradient."⁴ Flory firmly believed that most polymer systems experienced this asymptotic limit at molecular weights less than 30,000. The Flory viscosity constants and the light scattering expansion coefficients were calculated from the following classical Flory-Fox expressions, respectively. Table I

lists their values for the copolymer systems studied.

$$[\eta] = \frac{6^{3/2}\Phi_0 \langle \bar{s}^2 \rangle^{3/2}}{M} \quad (1)$$

$$\frac{A_2 \bar{M}_w}{[\eta]} = \frac{4\pi^{3/2}N_a}{(2.30) 6^{3/2}\Phi_0} \ln \left[1 + \frac{\sqrt{\pi}}{2} (\alpha^2 - 1) \right] \quad (2)$$

From Table I, it is quite clear that the polymer systems have not achieved Φ_0 , and in many cases are a full order of magnitude lower. In addition, all of the calculated values of the total light scattering expansion coefficient, α_{LS} , lie very close to 1.0, which is unreasonably small in 1.0N NaCl. The difficulty, again, lies in the low values of Φ calculated from eq. (1). Realistic ranges for α_{LS} are not obtained until the coefficient for Φ becomes 22. This confirms the findings by Kulkarni and Gundiah,⁵ where they reported Φ values for hydrolyzed polyacrylamides that were low. The data agrees with his conclusions that the dimensions deduced by light scattering for these polyelectrolytes are inaccurate as illustrated by the large differences between the total light scattering expansion coefficient (α_{LS}) and the total viscosity expansion coefficient (α_T). The total light scattering expansion coefficient cannot be unity for 1M aqueous NaCl systems as extracted from the data for it does not approximate θ conditions. More realistic viscosity expansion coefficients will be presented in the following discussion under Stockmayer-Fixman analysis.

The Stockmayer-Fixman expression:

$$\frac{[\eta]}{M^{1/2}} = K_0 + 0.51\Phi_0 BM^{1/2} \quad (3)$$

was used to determine the unperturbed molecular dimensions of the hydrolyzed polyacrylamides in 0.5M aqueous NaCl. Plots of the expression ($[\eta]/M^{1/2}$ vs. $M^{1/2}$) yield an intercept equal to the Mark-Houwink-Sakurada constant K_0 for Flory theta conditions. This value is substituted into the intrinsic viscosity-molecular weight equation for θ conditions:

$$[\eta]_\theta = K_0 M^{1/2} \quad (4)$$

Stockmayer-Fixman plots are presented in Figure 1. It was necessary to divide the plots into three separate graphs so as to clearly distinguish the individual data sets. The 20 mol % sodium acrylate least squares analysis was troublesome due to the considerable scatter of the data which was not as pronounced for the other copolymer systems. Since the significance of the Stockmayer-Fixman analysis is dependent upon sharp and similar molecular weight distributions, the plots were derived from viscosity average molecular weights which have been corrected for polymolecularity.¹ Table II lists K_0 values for the intrinsic viscosity-molecular weight expression under θ conditions for the poly(acrylamide-co-sodium acrylate) systems investigated. It is evident from the magnitude of K_0 in each of these expressions that the highest intrinsic viscosity at theta conditions $[\eta]_\theta$ is found in 50 mol % hydrolyzed samples and the lowest in the poly(sodium acrylate)s. This finding suggests that there are serious problems in the calculation of viscosity expansion coefficients with reference to the parent polyacrylamide rather than poly(sodium acrylate). Figure 2 plots the variations of the theta intrinsic

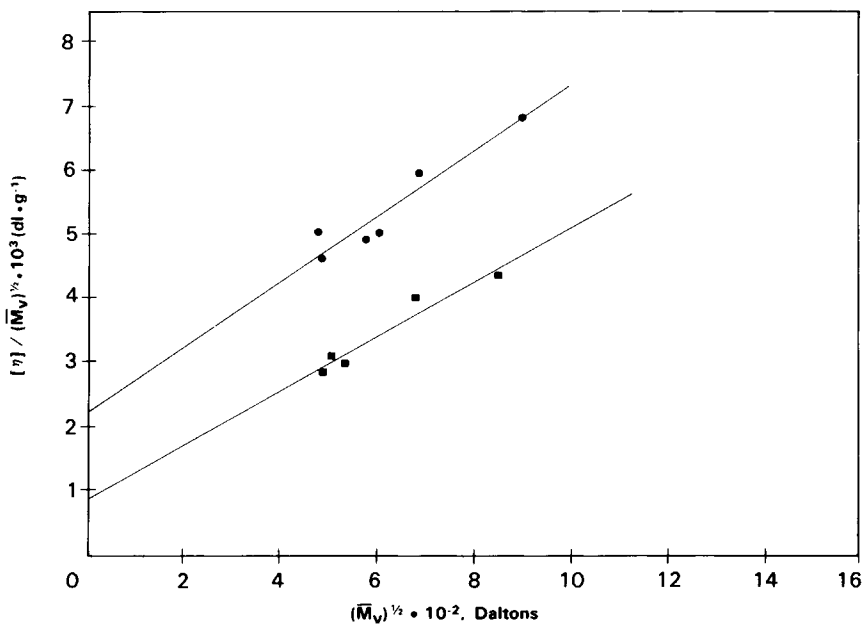


Fig. 1(a). Stockmayer-Fixman plots for hydrolyzed polyacrylamide samples in 0.5M NaCl: (■) Poly(sodium acrylate); (●) 70 mol % NaAc.

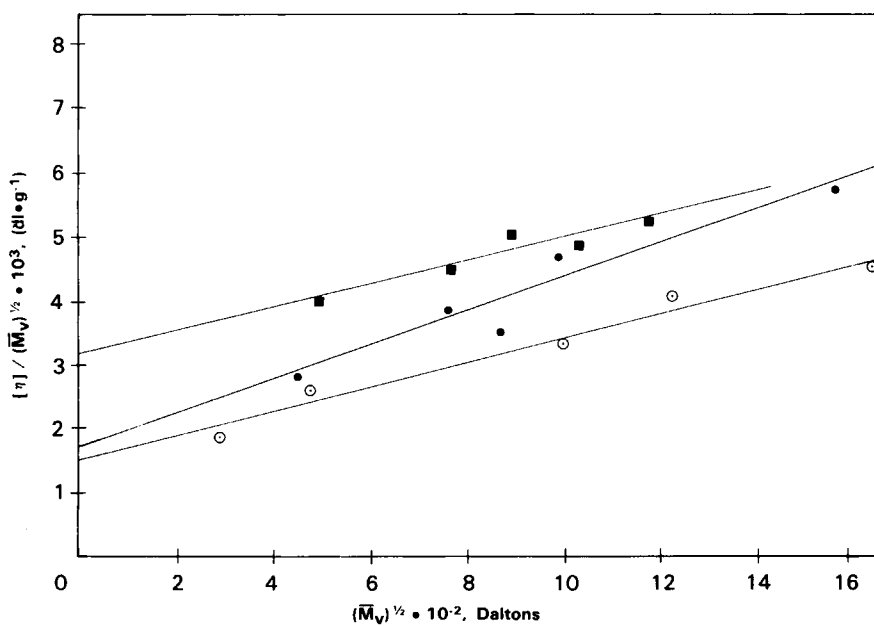


Fig. 1(b). Stockmayer-Fixman plots for hydrolyzed polyacrylamide samples in 0.5M aqueous NaCl: (■) 50 mol % NaAc; (●) 10 mol % NaAc; (○) polyacrylamide.

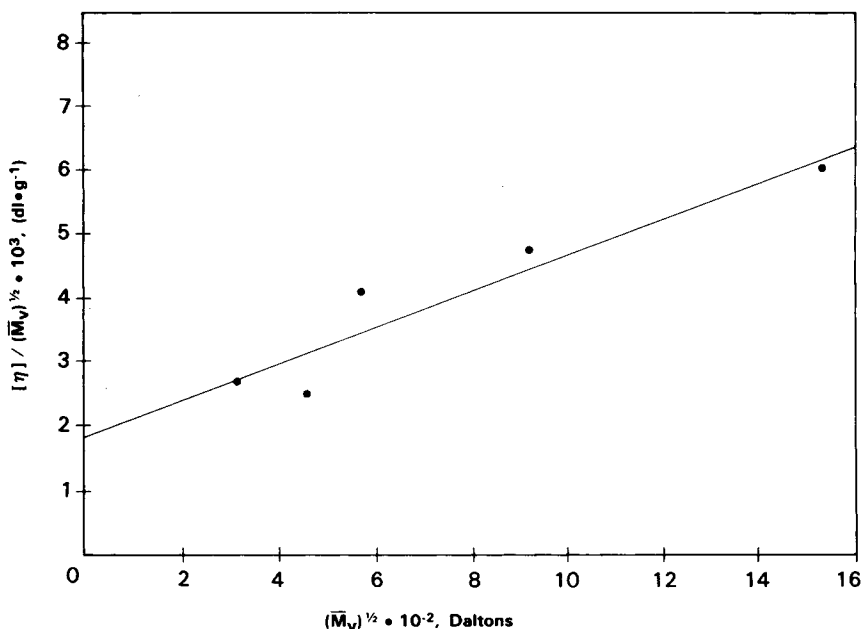


Fig. 1(c). Stockmayer-Fixman plots for poly(20 mol % sodium acrylate-80 mol % acrylamide) (in 0.5M aqueous NaCl).

viscosity and the intrinsic viscosities in 0.5M and 1M NaCl against the mol % hydrolysis. The three curves illustrate another interesting phenomena at 50 mol % where the intrinsic viscosities in the 0.5M and 1M aqueous NaCl solutions approach closest to the $[\eta]_\theta$ at this point. In fact, it is surprising that the $[\eta]_{1.0M}$ is close to the θ value. The solvent power (or goodness of the solvent) in 0.5M and 1M NaCl solutions is apparently minimized at 50 mol %.

Other investigators have reported unperturbed polyacrylamide K_0 values of 7.89×10^{-4} (water, Scholtan),⁶ 2.78×10^{-3} (water, Collinson et al.),⁷ 1.06×10^{-3} (0.12M NaCl, Kulkarni and Gundiah)⁸, and 1.11×10^{-3} (for monodis-

TABLE II
Expression for the Viscosity-Molecular Weight Relationship under Theta
Conditions with Corrections for Heterodispersity of Samples.^a

(1a) Polyacrylamide	$[\eta]_\theta = 1.55 \times 10^{-3} M_v^{0.50}$
(2a) Poly(10 mol % sodium acrylate-90 mol % acrylamide)	$[\eta]_\theta = 1.72 \times 10^{-3} M_v^{0.50}$
(3a) Poly(20 mol % sodium acrylate-80 mol % acrylamide)	$[\eta]_\theta = 1.95 \times 10^{-3} M_v^{0.50}$
(4a) Poly(50 mol % sodium acrylate-50 mol % acrylamide)	$[\eta]_\theta = 3.18 \times 10^{-3} M_v^{0.50}$
(5a) Poly(70 mol % sodium acrylate-30 mol % acrylamide)	$[\eta]_\theta = 2.25 \times 10^{-3} M_v^{0.50}$
(6a) Poly(sodium acrylate)	$[\eta]_\theta = 0.933 \times 10^{-3} M_v^{0.50}$

^a From linear regression analysis of Stockmayer-Fixman plots.

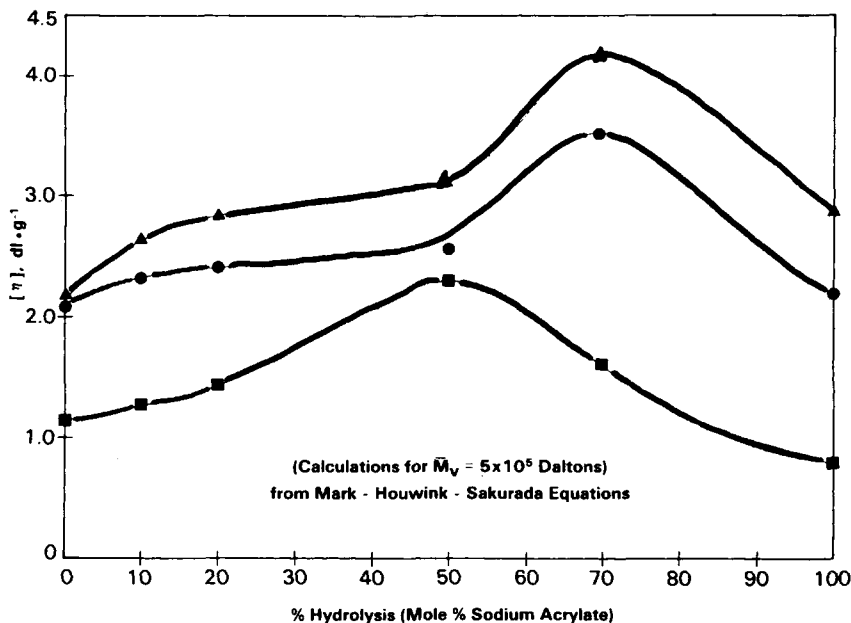


Fig. 2. Plot of intrinsic viscosity at θ temperature $[\eta]_{\theta}$ (■), in 0.5M NaCl $[\eta]_{0.5}$ (▲), and 1M NaCl $[\eta]_{1.0}$ (●) vs. mol % sodium acrylate.

persed Schulz-Zimm distribution, Kulkarni and Gundiah).⁸ Kulkarni and Gundiah⁹ also reported K_0 values of 1.19×10^{-3} and 1.50×10^{-3} for 10 and 20 mol % hydrolyzed samples, respectively. Noda, Tsuge, and Nagasawa¹⁰ listed K_0 values of 1.02×10^{-3} , 1.20×10^{-3} , and 1.85×10^{-3} for 10, 20, and 100 mol % sodium acrylate, respectively.

Perhaps the best representation of the molecular dimension parameters is from the intrinsic viscosity expansion coefficients. Kulkarni and Gundiah¹¹ presented a realistic description of each coefficient and determined their relative applicability to the study of polyelectrolytes. The three viscosity expansion coefficients evaluated with our data are the electrostatic, the total, and the long range. Gundiah described each parameter as

$$\alpha_{el}^3 = \text{electrostatic expansion} = [\eta]/[\eta]_{PPAAm} \quad (5)$$

$$\alpha_T^3 = \text{total expansion} = [\eta]/[\eta]_{\theta, PPAAm} \quad (6)$$

$$\alpha_L^3 = \text{long range expansion} = [\eta]/[\eta]_{\theta} \quad (7)$$

where $[\eta]_{PPAAm}$ = intrinsic viscosity of parent polyacrylamide, $[\eta]_{\theta, PPAAm}$ = intrinsic viscosity of parent polyacrylamide at its θ temperature, and $[\eta]_{\theta}$ = intrinsic viscosity of sample at its theta temperature.

Table III lists the expansion coefficient comparisons for the three expressions. Figures 3 and 4 illustrate the variation of the electrostatic, total, long range, and steric expansion coefficients vs. the charge density for a 5×10^5 daltons viscosity average molecular weight sample. The steric expansion coefficient α_S will be defined in subsequent discussion. The long range parameter increases slightly from polyacrylamide to 20 mol % sodium acrylate and then drops substantially to a minimum at 50 mol % and again increases

TABLE III
 Expansion Coefficient Comparison from Gundiah's Viscosity Expressions (for 0.5M NaCl)

Sample	α_T	α_L	α_{el}
Poly(sodium acrylate)			
1	1.23	1.46	1.04
2	1.27	1.50	1.07
3	1.23	1.46	1.04
4	1.38	1.64	1.11
5	1.41	1.67	1.09
Poly(70 mol % sodium acrylate-30 mol % acrylamide)			
6	1.44	1.27	1.22
7	1.60	1.41	1.36
8	1.46	1.23	1.15
9	1.63	1.44	1.33
10	1.80	1.58	1.44
11	1.27	1.12	0.98
Poly(50 mol % sodium acrylate-50 mol % acrylamide)			
12	1.36	1.07	1.15
13	1.43	1.12	1.12
14	1.48	1.17	1.14
15	1.46	1.15	1.10
16	1.49	1.17	1.09
Poly(20 mol % sodium acrylate-80 mol % acrylamide)			
17	1.21	1.12	1.10
18	1.16	1.08	0.99
19	1.40	1.29	1.16
20	1.47	1.36	1.12
21	1.56	1.45	1.10
Poly(10 mol % sodium acrylate-90 mol % acrylamide)			
22	1.22	1.18	1.05
23	1.36	1.31	1.07
24	1.31	1.27	1.01
25	1.46	1.41	1.10
26	1.55	1.49	1.08
Polyacrylamide			
27	1.07	1.07	0.99
28	1.20	1.20	1.02
29	1.29	1.29	0.98
30	1.39	1.39	1.01
31	1.44	1.44	1.00

sharply to 100 mol %. The total and electrostatic expansion curves follow a quite different pattern from the long range expansion, where they achieve a maximum inflection point at 70 mol % hydrolysis. The increase in the expansion coefficient is also more substantial at the low charge densities for the total and electrostatic curves. Values for Figures 3 and 4 were calculated from Mark-Houwink-Sakurada expressions in Ref. 1 and the Stockmayer-Fixman relations of this paper.

Within a particular copolymer system, the α_T was larger than α_L except for the poly(sodium acrylate) samples. This arises from the fact that the intrinsic viscosity of the parent polyacrylamide at θ temperature is lower than all the other hydrolyzed $[\eta]$ viscosities except for the 100 mol % product. The very fact that the poly(sodium acrylate) samples have the smallest $[\eta]_\theta$ suggests they might serve as the reference or parent compound. In a good solvent (i.e.,

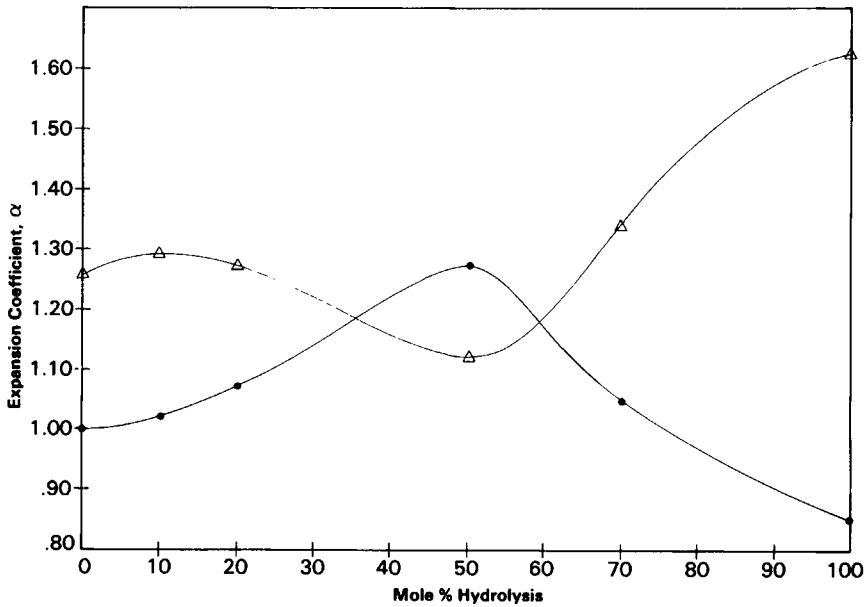


Fig. 3. Plot of total and electrostatic expansion coefficients vs. mol % sodium acrylate (for $M_v = 5 \times 10^5$, $[\eta] = 0.5M$ NaCl): (Δ) α_L (long range), defined by Gundiah; (\bullet) α_S (steric).

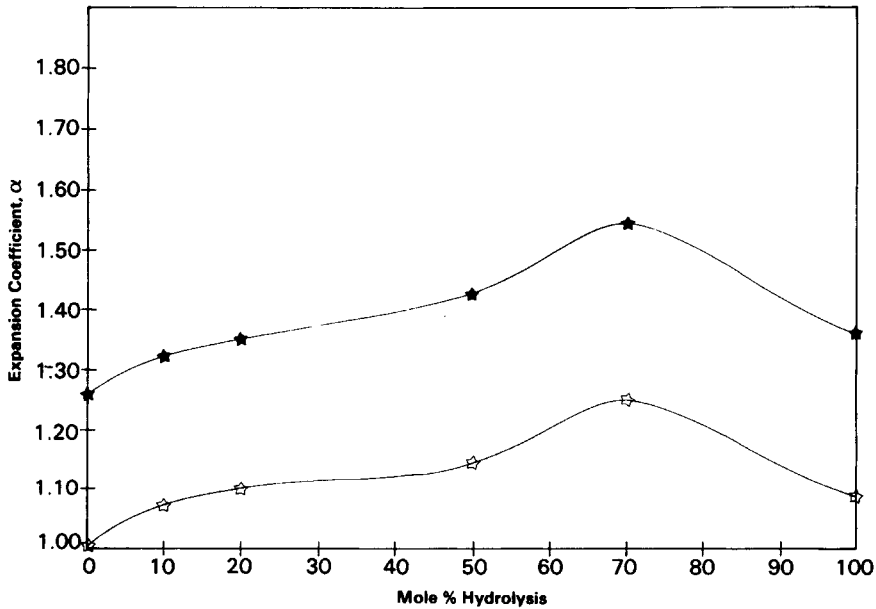


Fig. 4. Plot of total and electrostatic expansion coefficients vs. mol % sodium acrylate (for $M_v = 5 \times 10^5$, $[\eta] = 0.5M$ NaCl): α_T (total) (\star) and α_{el} (electrostatic) (\star), defined by Gundiah.

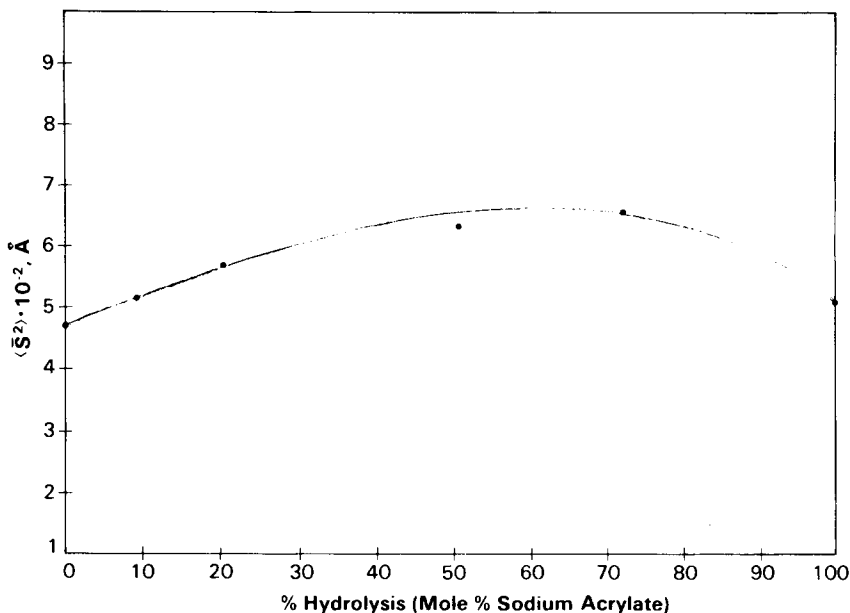


Fig. 5. Variation of root-mean-square radius of gyration vs. change in charge density (% hydrolysis). Calculations for $\bar{M}_v = 5 \times 10^5$ daltons (dimensions in $1M$ NaCl).

low ionic strength) the expansion of a polyelectrolyte is dependent upon its effective charge density; however, under θ conditions where the effective charge density of the polyelectrolyte is reduced to zero, the excluded volume parameter describes the expansion properties. The compressibility of the poly(sodium acrylate) over that of polyacrylamide is governed strongly by excluded volume effects in addition to charge neutralization as evidenced by the dimensional parameters at θ temperature. Refer to Figure 2 and examine the $[\eta]_\theta$ curve for excluded volume effects. The excluded volume concept will be elaborated upon later in the discussion of the steric factor.

The root-mean-square radius of gyration deduced from light scattering, the intrinsic viscosity in $0.5M$ and $1M$ aqueous NaCl, and the total and electrostatic expansion coefficients from viscosity measurements all show similar behavior with respect to copolymer composition. Comparison of Figures 2, 4, and 5, illustrates the consistency. A maximum inflection point occurs at 70 mol % sodium acrylate in all five data sets. We would have expected the polyelectrolytes to exhibit increasingly expanded molecular dimensions as the % hydrolysis (i.e., % ionizable groups) increased due to electrostatic repulsion. The data supports this hypothesis up to and including the 70 mol % composition, and then there is a marked decrease in the dimensions as one approaches the 100% hydrolyzed sample.

The only dimensional parameter that continues to increase after 50 mol % that reaches a maximum at 100% sodium acrylate is Gundiah's long range expansion coefficient which represents the expansion relative to the sample's dimensions at θ temperature. This expansion corresponds to Flory's total expansion due to electrostatic interactions alone. From the shape of the curves in Figures 2 and 4 it is clear that calculations of the intrinsic viscosity of these

TABLE IV
Long Range, Steric, and Total Expansion Coefficients for the Poly(acrylamide-co-Sodium Acrylate) in 0.5*N* NaCl for 5×10^6 Molecular Weight

(Mol %) Acrylate	α_S	α_L	α_T
0	1.0	1.26	1.26
10	1.03	1.29	1.32
20	1.08	1.28	1.37
50	1.27	1.12	1.42
70	1.13	1.37	1.56
100	0.84	1.62	1.36

copolymers in good solvents, i.e., 0.5*N* NaCl, must provide for the large decrease in viscosity when the acrylate-acrylamide ratio exceeds 70 mol %.

It can be argued that the final viscosity of any of these copolymers will be a function of the long range effects and steric contributions. This is expressed in

$$[\eta] = \alpha_L^3 \cdot \alpha_S^3 \cdot [\eta]_{\theta, \text{PPAAm}} \quad (8)$$

where $[\eta]$ represents the intrinsic viscosity of any copolymer at any salt concentration, and α_L is the overall expansion due to long range effects as defined by Gundiah in eq. (7). α_S is the contribution from steric factors and is expressed as

$$\alpha_S^3 = [\eta]_{\theta} / [\eta]_{\theta, \text{PPAAm}} \quad (9)$$

An examination of Figure 3 shows that α_L is not an increasing function of charge density as would be expected but has a pronounced minimum at 50 mol % beyond which it increases rapidly. The minimum at 50 mol % means that α_L cannot be determined exclusively by electrostatic effects, but must also have significant steric contributions.

It's reasonable to assume that α_S consists predominantly of steric effects. When the charge density exceeds 70 mol % acrylate these predominate and the final viscosity drops. The values for the expansion coefficients are listed in Table IV.

It is apparent that over the restricted charge density variation of 0–30 mol % sodium acrylate, α_S , assumes an almost linear character due to small and smoothly increasing contributions from the steric factor. At higher charge variations α_S becomes the determining factor in the final viscosity.

Since correlations between light scattering and viscosity data were so poor when expansion coefficients are calculated from eq. (2), it was convenient to adopt a modification of the empirical approach suggested by Krigbaum.¹²

Equation (10) was used to make the necessary calculations:

$$[\eta] = [\eta]_{\theta, \text{SF}} + \Psi A_2 \bar{M}_w \quad (10)$$

where $[\eta]$ is the experimentally determined intrinsic viscosity of a polymer in a particular solvent, $[\eta]_{\theta, \text{SF}}$ is the intrinsic viscosity of the polymer under θ conditions, calculated from Stockmayer-Fixman plots (SF), Ψ is a constant for the polymer and is determined by its composition, A_2 is the second virial

coefficient obtained from light scattering, and \overline{M}_w is the measured molecular weight.

This approach is considered valid since it combines independent experimental values from both light scattering and viscosity. Data from Ref. 1 and Table II of this paper was used to calculate Ψ 's for all the compounds examined. From these calculations a single value of Ψ was selected for each acrylamide-acrylate ratio, based on the one which provided the best fit to eq. (10). The selected values of Ψ were then used to calculate new $[\eta]_\theta$, and these were compared to those calculated from the SF plots. Long range expansion

TABLE V
Comparison of Long Range Expansion Coefficients from Eq. (10) and the Long Range Expansion Coefficient from Stockmayer Fixman Analysis for 1.0M NaCl^a

Sample	Ψ	α_L [[η] $_\theta$ from eq. (10)]	α_L ([η] $_\theta$ from S-F)	Variance %
Poly(sodium acrylate)				
1	0.19	1.54	1.28	+20
2		1.69	1.37	+23
3		1.73	1.33	+30
4		1.44	1.50	-4
5		1.56	1.54	+1
Poly(70 NaAc-30AAm)				
6	0.13	—	1.14	—
7		1.31	1.13	+16
8		1.26	1.23	+2
9		1.24	1.24	0
10		1.36	1.29	+5
11		1.00	—	—
Poly(50 NaAc-50AAm)				
12	0.05	1.08	0.96	+12
13		1.10	1.08	+2
14		1.10	1.13	-3
15		1.11	1.10	+1
16		1.16	1.11	+4
Poly(20 NaAc-80AAm)				
17	0.18	1.26	1.01	+24
18		—	—	—
19		1.20	1.26	-5
20		1.26	1.32	-5
21		1.45	1.34	+8
Poly(10 NaAc-90 AAm)				
22	0.20	1.49	1.12	+33
23		1.33	1.29	+3
24		1.24	1.39	+8
25		1.24	1.39	-11
26		1.25	1.53	-18
Polyacrylamide				
27	0.17	1.16	1.11	+4
28		1.18	1.20	-2
29		—	—	—
30		—	—	—
31		1.42	1.43	-1

^a α_L values listed in Table IV are dimensions in 0.5M NaCl.

coefficients α_L for 1M aqueous NaCl were then calculated with these $[\eta]_\theta$ values from eq. (10) and compared to the expansion coefficients in 1M NaCl calculated with $[\eta]_\theta$ values from Stockmayer-Fixman expressions. Table V lists the best-fit Ψ , the comparative long range expansion coefficients, and the % variance.

While the values of α calculated from eq. (10) are reasonable and compare roughly to those obtained from the SF plots, there are large differences in some cases. Since this type of empirical approach has been successfully applied by Krigbaum,¹² the differences are felt to lie not so much in the failure of light scattering to be able to provide accurate values of the second virial coefficient, but rather in the difficulty in obtaining accurate estimates of the slope of the $C = 0$ line when the Zimm plots display some curvature, as they did in some instances in this work.

STERIC FACTOR AND EXCLUDED VOLUME EFFECTS

The steric factor σ includes the effects of restricted rotation and excluded volume. This dimensional parameter is defined as

$$\sigma = \langle \bar{r}_o^2 \rangle^{1/2} / \langle \bar{r}_{fr}^2 \rangle^{1/2} \quad (11)$$

where $\langle \bar{r}_o^2 \rangle^{1/2}$ is the unperturbed (θ) rms end to end distance and $\langle \bar{r}_{fr}^2 \rangle^{1/2}$ is the rms end to end distance for a polymer chain with bond angle restrictions, but no restrictions on rotation. The unperturbed rms end to end distance used in the determination of σ was calculated from the equation

$$K_0 = \Phi_0 \left(\frac{\langle \bar{r}_o^2 \rangle^{1/2}}{M^{1/2}} \right)^3 \quad (12)$$

A value of 2.10×10^{21} dL g^{-1} mol cm^3 was used for the universal Flory constant.¹³ The expression for the rms end to end distance with bond angle restrictions is

$$\langle \bar{r}_{fr}^2 \rangle^{1/2} = N \cdot L^2 \frac{(1 - \cos \theta)}{(1 + \cos \theta)} \quad (13)$$

where $\theta = 109.5^\circ$, $L = 1.54$ Å, and $N = \#$ carbon-carbon bonds in each sample. Other unperturbed molecular dimensions that are of interest is the volume per unit weight ratio $\langle \bar{r}_o^2 / M \rangle^{1/2}$ and volume per unit chain atom ratio $\langle \bar{r}_o^2 / n \rangle^{1/2}$. Table VI lists values for these parameters. In the volume per unit chain atom ratio, $n = M_w / M_0$, where M_0 is the molecular weight of the subunit. Figure 6 shows the variation of the average steric factor, the average volume/weight ratio, and the average volume/unit chain atom ratio as a function of mol % hydrolysis. These curves are similar to the $[\eta]_\theta$ curve of Figure 2 because they are all proportional to the magnitude of K_0 . These curves most clearly describe any excluded volume effects that arise solely from variations in the compositional nature of the copolymers and not from electrostatic interaction. It can be seen that poly(sodium acrylate) molecules occupy less volume per unit weight than polyacrylamide molecules of the

TABLE VI
 Unperturbed Molecular Dimensions for the Poly(acrylamide-co-Sodium Acrylate) System

Sample	$\langle \bar{r}_0^2 \rangle^{1/2}$ (Å)	$\langle \bar{r}_r^2 \rangle^{1/2}$ (Å)	Average σ	Average $\langle \bar{r}_0^2/M \rangle^{1/2} \times 10^{11}$	Average $\langle \bar{r}_0^2/n \rangle^{1/2}$ (Å)
Poly(sodium acrylate)					
1	370	165			
2	400	177			
3	410	183	2.26	758	7.36
4	530	232			
5	660	289			
Poly(70 NaAc-30 AAm)					
6	500	165			
7	530	173			
8	600	196	3.06	1031	9.63
9	630	206			
10	700	230			
11	940	302			
Poly(50 NaAc-50AAm)					
12	640	188			
13	910	267			
14	1070	312	3.41	1142	10.40
15	1190	349			
16	1390	406			
Poly(20 NaAc-80 AAm)					
17	330	114			
18	460	160			
19	570	196	2.89	973	8.46
20	910	315			
21	1690	582			
Poly(10 NaAc-90 AAm)					
22	470	168			
23	760	272			
24	830	297	2.79	938	8.03
25	940	338			
26	1480	530			
Polyacrylamide					
27	270	101			
28	460	173			
29	910	340	2.67	895	7.54
30	1120	418			
31	1630	605			

same molecular weight. In addition, poly(sodium acrylate) has a lower volume per chain atom ratio than the polyacrylamide.

The last method investigated for the determination of the expansion coefficients is of recent development (1983). It has been illustrated by Lenka, Nayak, and Dash⁴ that there exists a "crossover point concentration" for intrinsic viscosities of a polymer sample in different solvents. This common concentration point has been shown to be independent of the solvent and is a property unique to the polymer alone. Two other studies^{15,16} have observed that the crossover point concentration is equal to the intrinsic viscosity at the precipitation point in a theta solvent. Lenka et al. have derived an expression relating this crossover point concentration C_0 (g/dL) to the unperturbed

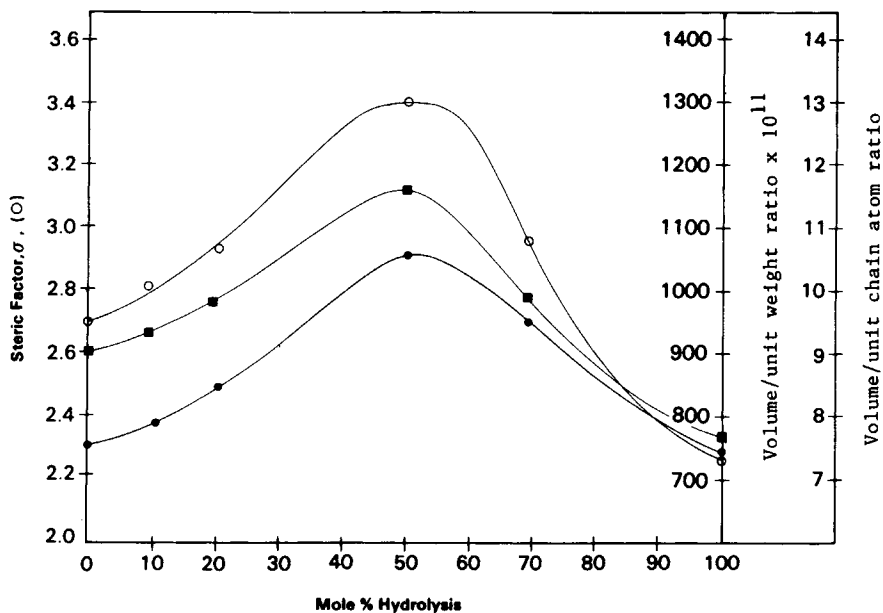


Fig. 6. Variation of steric factor (○), volume/weight ratio $\langle \bar{r}_0^2/m \rangle^{1/2}$ (■), and volume/chain atom ratio $\langle \bar{r}_0^2/n \rangle^{1/2}$ (●) vs. mol % sodium acrylate.

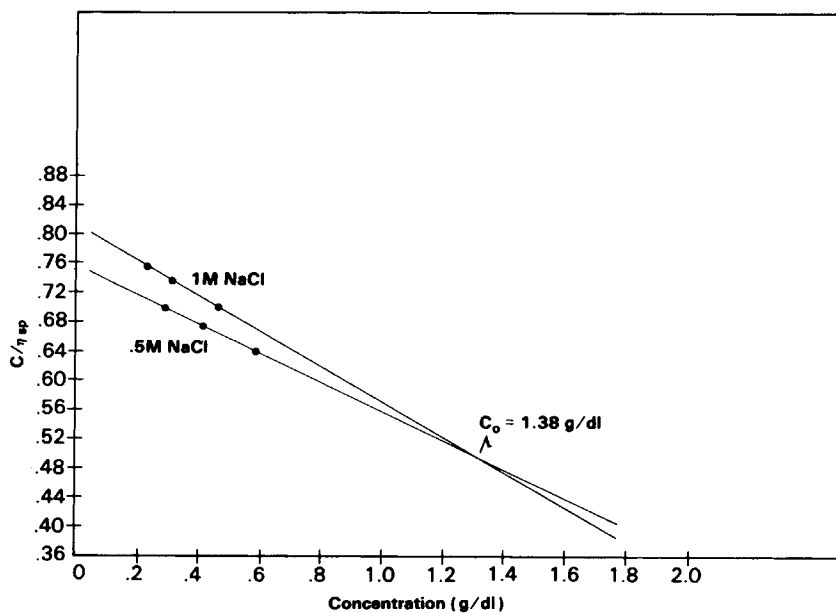


Fig. 7. Determination of crossover point concentration.

TABLE VII
 Expansion Coefficient (1M NaCl) from "Crossover Point" Determination

Sample	C_0 (g dL ⁻¹)	$\langle \bar{r}_0^2 \rangle^{1/2}$, Å	α_{C_0}
Poly(sodium acrylate)			
1	3.60	414	1.92
2	25.74	226	4.24
3	10.29	313	2.97
4	—	—	—
5	2.56	676	2.21
Poly(70 NaAc-30 AAm)			
6	2.59	463	2.81
7	3.64	426	2.47
8	4.77	424	3.82
9	2.48	545	2.08
10	1.52	692	2.00
11	—	—	—
Poly(50 NaAc-50 AAm)			
12	3.83	444	2.31
13	2.28	667	2.30
14	1.46	858	2.30
15	3.35	702	3.07
16	2.55	849	2.90
Poly(20 NaAc-80 AAm)			
17	2.57	363	1.57
18	—	—	—
19	1.76	590	1.87
20	3.31	657	2.91
21	2.04	1164	2.94
Poly(10 NaAc-90 AAm)			
22	1.38	578	1.33
23	—	—	—
24	—	—	—
25	0.73	1142	1.70
26	0.19	2397	1.39
Polyacrylamide			
27	3.66	298	2.22
28	—	—	—
29	0.65	1192	1.43
30	0.27	1828	1.02
31	0.14	2902	1.01

dimension of polymer molecules $\langle \bar{r}_0^2 \rangle^{1/2}$:

$$\langle \bar{r}_0^2 \rangle^{1/2} = 2.204 \times 10^{-8} (\bar{M}_w / C_0)^{1/3} \quad (14)$$

It does seem apparent that there should be a concentration where the expansion coefficient approaches unity due to polymer coil contraction with increasing polymer concentration. A typical extrapolation used in the determination of the C_0 is shown in Figure 7 where the reciprocal of the reduced viscosity (c/η_{sp}) is plotted vs. polymer concentration in 0.5M and 1M NaCl. As seen from Table VII, the expansion factor calculated with the crossover point concentration expression is in most cases at least a factor of 2 higher and much more diverse. The method did not appear applicable nor valid for

the characterization of unperturbed molecular dimensions for this polyelectrolyte system.

CONCLUSIONS

Stockmayer-Fixman plots yield satisfactory values for the Mark-Houwink-Sakurada constant K_0 , under theta conditions, for heterodisperse polyelectrolytes. Correlations improve if polydispersity corrections are applied.

Expansion coefficients calculated directly from light scattering data do not agree with those calculated from viscosity data, since hydrodynamic theory developed for non-electrolytes does not apply to polyelectrolytes. Values of the estimates of $\langle \bar{s}_0^2 \rangle^{1/2}$ are especially in error. A modified empirical approach, similar to that of Krigbaum, combining data from light scattering and viscosity, yields calculated expansion coefficients in reasonable agreement with those obtained from viscosity data alone.

These compounds are very convenient to work with. The desired variations in monomer ratio and molecular weight are easy to obtain in well-characterized form. In addition to which they are economically important due to their wide industrial use. Unfortunately, the steric contributions to the behavior of the system over the entire copolymer range cannot be safely ignored, and this makes the compounds a poor choice for study if one is interested in only electrostatic effects.

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