Polyelectrolyte Configuration of Low Molecular Weight Sodium Amylose Xanthate in Aqueous and Salt Solutions

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SUMMARY

The polyelectrolyte chain configuration of low molecular weight sodium amylose xanthate (NaAX) in aqueous and salt solutions has been studied by viscometry and light scattering. The viscometric results in aqueous solution have been found to be in accordance with the Fuoss's modified equation. The intrinsic viscosities of NaAX in salt solutions from 0.00125 to 0.25 M NaCl have been determined and the expansion factor α at each ionic strength has been determined. The dependence of α on ionic strength has been studied according to the theories of Hermans and Overbeek, Flory, etc. But though qualitative agreement between experimental and theoretical results has been found, quantitative agreement was far from expectations. The frictional coefficient per monomer unit ξ has been calculated from the relationship of Kirkwood and Riseman. The NaAX macromolecule has been found to have the polydispersed random coil chain configuration in 0.25 M NaCl. Some macromolecular configurational parameters such as effective bond length b, Kuhn-Kuhn equivalent chain length A_m, and steric factor σ has been determined.

INTRODUCTION

The viscometric behavior of high molecular weight sodium amylose xanthate (NaAX) in aqueous and salt solutions has been described earlier [1]. The evidence that the xanthate groups of NaAX are ionized in aqueous medium comes from viscosity measurements since the reduced viscosity η_{sp}/c increases with dilution. There seems to be little doubt that the dimensions of the NaAx polyelectrolyte chain do alter with charge and ionic strength as shown by independent measurement such as light scattering [2]. While Patel and Patel [3] during their investigation on dilute solution properties of sodium carboxy-methyl amylose (CMA) in salt solutions observed the intrinsic viscosity $[\eta]$ to decrease rapidly up to 0.12 M NaCl and then more slowly as the salt concentration was increased further, indicating that the viscosity decrease was due to contraction of the polymer molecules caused by the screening of their charge by the simple electrolyte. Recently Mathieson et al. [4] have pointed out that the viscosity behavior of a particular polyelectrolyte depends on a number of factors, one of which is the molecular weight. It is our purpose to investigate the polyelectrolyte behavior of a relatively low molecular weight NaAx in aqueous and salt solutions by viscometry and light scattering and to analyze the observed results in the light of some theories of polyion expansions. Finally an idea about the polyelectrolyte configuration of the NaAX macromolecule in 0.25 M NaCl solution has been obtained from the results of viscometry and light scattering.

EXPERIMENTAL

Preparation of Sodium Amylose Xanthate

An industrially prepared amylose sample was further purified as the amylose-butanol complex following the method of Schoch [5]. The purified sample (weight-average molecular weight in water = 2.33×10^5, iodine absorption value = 17.9%) was used for the preparation of the xanthate compound following the usual procedure [1]. The degree of substitution of NaAX has been found to be 0.46.

Viscometric Measurements

Solutions of NaAX either in double distilled water or in aqueous salt solutions were prepared by dissolving a known amount of the solute in the ice-cooled solvent in a volumetric flask stored in an ice bath. The concen-

tration of each solution was checked from determination of the weight of the dried solid obtained by drying a known volume of solution. Viscosity measurements were made with an Ostwald viscometer having a flow time of 173.9 sec with respect to water in a thermostatic bath maintained at a temperature of $30 \pm 0.1°C$. Kinetic energy corrections, being small, were neglected. Finally, intrinsic viscosities of NaAX in salt solutions were obtained by plotting reduced viscosity η_{sp}/c against polymer concentration c and extrapolating to zero concentration. The viscometric results in salt solutions are summarized in Table 1.

Table 1. Intrinsic Viscosity and Polyelectrolyte Expansion of NaAX in Salt solutions

No.	Molar conc. of NaCl [c_{salt}]	$[\eta]$ (dl/g)	$\alpha^2 = \dfrac{[\eta]^a}{[\eta]_{IS=\infty}}$	1/K (Å)	($\alpha^5 - \alpha^3$)
1.	0.2500	0.1450	1.074	6.095	0.082
2.	0.1000	0.1650	1.223	9.638	0.322
3.	0.0500	0.1900	1.408	13.63	0.683
4.	0.0250	0.2150	1.592	19.28	1.190
5.	0.0100	0.2800	2.074	30.49	3.208
6.	0.0050	0.3300	2.444	43.10	5.522
7.	0.0025	0.4400	3.200	68.10	13.58
8.	0.00125	0.5400	4.000	86.20	24.03

[a]Intrinsic viscosity at infinite ionic strength $[\eta]_{IS=\infty} = 0.1350$.

Light-Scattering Measurements

The solution of NaAX in aqueous 0.25 M NaCl was prepared in the same way as that for viscometric measurement. The method of clarification of both the solvent and the solution has been described elsewhere [1]. A Brice-Phoenix universal 1999-10 series light-scattering photometer was used for measurements while the refractive index increment of the xanthate solution was determined at a wavelength of 546 mμ with a Brice-Phoenix Differential Refractometer. The intensities of scattered light at a wavelength of 546 mμ and over the range from 40 to 135° were measured in a 15-ml capacity circular cell of the Witnauer-Scherr type [6] at several concentration levels, and the results were

treated according to the method of Zimm [7] where values of $KC/R\theta$ were plotted as functions of $\sin^2 (\theta/2) + 100C$ and extrapolated to $\theta = 0$ and $C = 0$, K being a constant for a particular solute-solvent system at a particular wavelength and $R\theta$ denoting the Rayleigh ratio at an angle θ. The molecular weight $\bar{M}_W$ was obtained from the intercept of Zimm plot (Fig. 1)
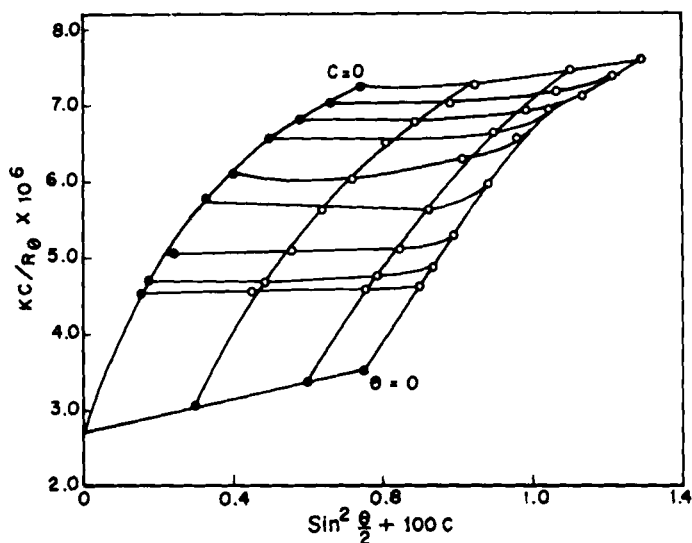
Fig. 1. Zimm plot of sodium amylose xanthate in 0.25 M NaCl solution.

using $\bar{M}_W = 1/(Kc/R\theta)_{\substack{c=0 \\ \theta=0}}$. The second virial coefficient, A_2, was determined from the slope of the zero angle line while the dimension $(\bar{S}_z^2)^{1/2}$, the root-mean-square radius of gyration from the center of mass of the particle, was calculated from the ratio of the slope of the zero angle line to the intercept

$$(\bar{S}_z^2)^{1/2} = \left(\frac{3}{16\pi^2} \frac{\text{initial slope}}{\text{intercept}}\right)^{1/2} \frac{\lambda}{n} \tag{1}$$

where λ/n is the wavelength of light in solution of refractive index n. The macromolecular shape of NaAX in salt solution was estimated from the variation of intensity of scattered light with scattering angle θ.

RESULTS AND DISCUSSION

Viscometric Measurements in Aqueous Solution

It is evident from the plot of reduced viscosity η_{sp}/c vs. concentration c of NaAX in water (Fig. 2) that the increasing trend in the value of η_{sp}/c with dilution, even from an initial high polymer concentration of approximately 1.3 g/dl, is in marked contrast with that of high molecular weight NaAX [1]
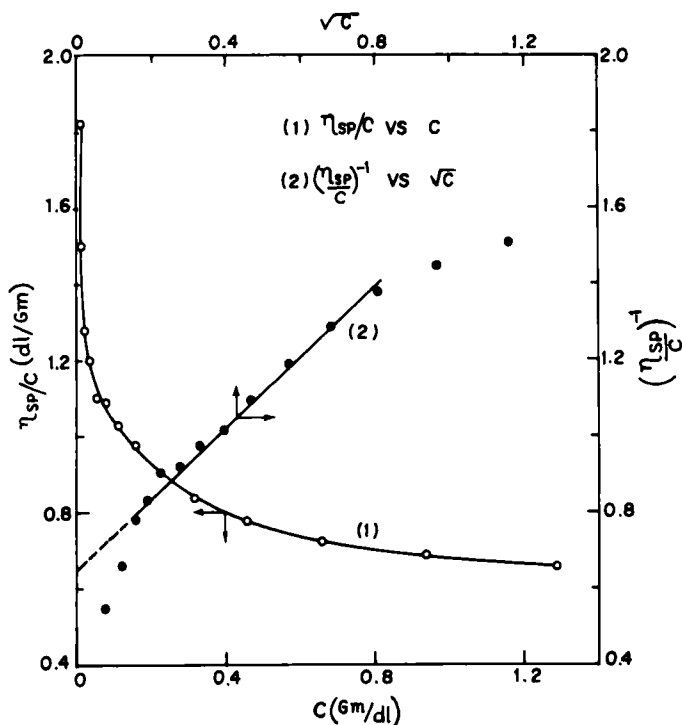
Fig. 2. Viscosity behavior of sodium amylose xanthate in water.

where the η_{sp}/c value first decreases to a polymer concentration of 0.3 g/dl (approx) and then rises with further dilution, reaching its maximum at about 0.05 g/dl when the molecules have attained their greatest size. Hence further dilution has caused a rapid fall in viscosity. The value of η_{sp}/c at finite concentration is a product of 1) the classical electroviscous effect, 2) the size of the polyion, and 3) the interactions between polyions and their atmospheres.

The last two effects are not independent of one another since the extent of interaction clearly depends on the size of the polyions at the same concentration. While the major part of the interaction is probably of an electrostatic nature as shown by the influence of added salt, some contribution is to be expected from hydrodynamic entanglements. The reason why the change in type of viscosity behavior of a polyelectrolyte in salt-free solution occurs with change in molecular weight has not yet been elucidated but it has been discussed qualitatively [8] on the basis of electrostatic interactions between polyions and between polyions and their counterions, in conjunction with the folding chain theory of Fuoss and others.

The viscometric results of NaAX in aqueous solution have been treated according to the equations of Fuoss [9], Schaefgan and Trivissono [10], and Wiley et al. [11]. Fuoss's modified equation of the type

$$\eta_{sp}/c = \frac{A}{1 + B\sqrt{c}} + D \qquad (2)$$

(A and B are constants, D equals η_{sp}/c when c becomes infinite) has been found to be applicable over all of the concentration region investigated (Fig. 3). The constants A and B have the values 2.86 and 14.55, respectively. But Fuoss's simple equation of the type $\eta_{sp}/c = A/(1 + B\sqrt{c})$ is only valid in the intermediate concentration region. (Fig. 1), while a plot of $(\eta_{sp}/c - D)^{-1}$ vs. c, according to the equation of Schaefgan and Trivissono [10], has been found unsuccessful in the higher concentration region, although the same relation has been found applicable for describing the behavior of potassium-p-vinyl benzene sulfonate in water and polyamides in formic acid. The plot of log η_{sp}/c vs. log c for NaAX in water is shown in Fig. 4. It suggests that the results are in good agreement with the predictions of the equation $\eta_{sp}/c = ac^b$ (a and b are constants) put forward by Wiley et al. [11].

Dependence of Intrinsic Viscosity [η] on Ionic Strength in Salt Solutions

The change in the value of [η], the intrinsic viscosity of NaAX in salt solutions, has been investigated in the range 0.00125 to 0.25 M NaCl. The viscometric data obtained are presented in Table 1.

An examination of the relevant published data on simple polyelectrolytes shows that once a threshold concentration has been reached, further addition of salt to solutions of polyelectrolytes leads to a decrease in viscosity that can be characterized by the relation [12]

$$[\eta] = [\eta_0] \left(c_{salt}/c^0{}_{salt}\right)^{-m} \tag{3}$$

where $[\eta]$ and $[\eta_0]$ are the limiting viscosity numbers in solutions of electrolyte of concentration c_{salt} and $c^0{}_{salt}$, respectively (the latter concentration being that of any reference solution) and m is a constant, independent of molecular weight and equal to 0.4 for permeable and to 0.6 for impermeable coils, respectively.
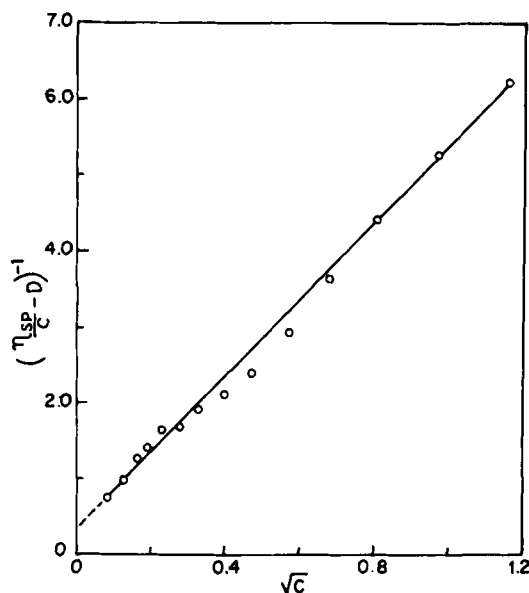
Fig. 3. $(\eta_{sp}/c - D)^{-1}$ vs. $\sqrt{c}$ of sodium amylose xanthate in water.

When such a plot of log $[\eta]$ vs. log c_{salt} was made for NaAX in salt solutions (Fig. 5.), a good linear relationship was obtained and the slope of the straight line was found to be in the range 0.3-0.4, which is characteristic of typical stiffened chain arising due to the increased permeability of solvent molecules to polymer coils of low degree of polymerization.

Fig. 4. Log η_{sp}/c vs. log c of sodium amylose xanthate in aqueous solution.

Polyelectrolyte Expansion and Its Dependence on Ionic Strength

As the ionic strength of the solvent is lowered, there is dissociation of the substituent xanthate groups with a corresponding expansion of the chain 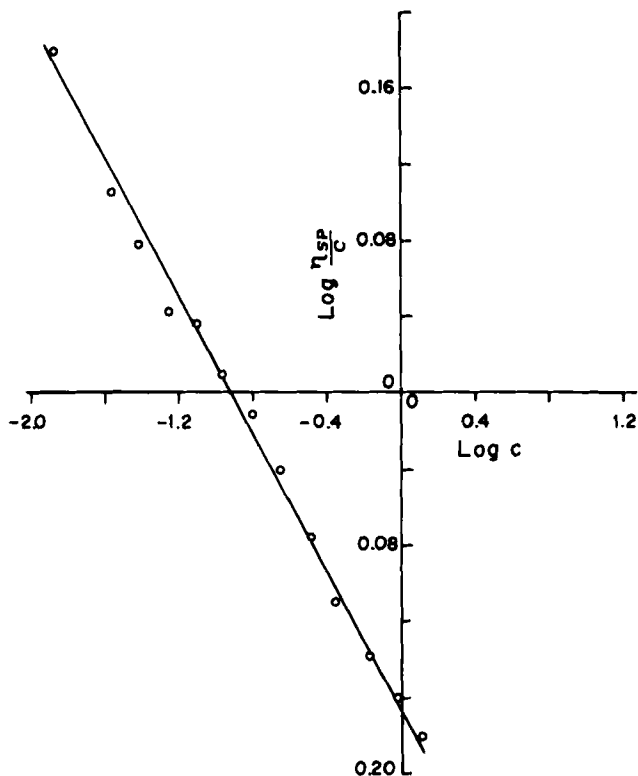as a result of long-range electrostatic interactions between the increased number of charges. The expansion factor α has been calculated from the relation $\alpha^2 = [\eta]_{IS}/[\eta]_{IS=\infty}$, where $[\eta]_{IS=\infty}$ is the intrinsic viscosity at infinite ionic strength. The use of the above relation, which is more appropriate for free draining coils, is justified by the fact that the system under investigation has this characteristic as has been shown above and also confirmed from the values of some macromolecular parameters determined from the results of viscometry and light scattering.
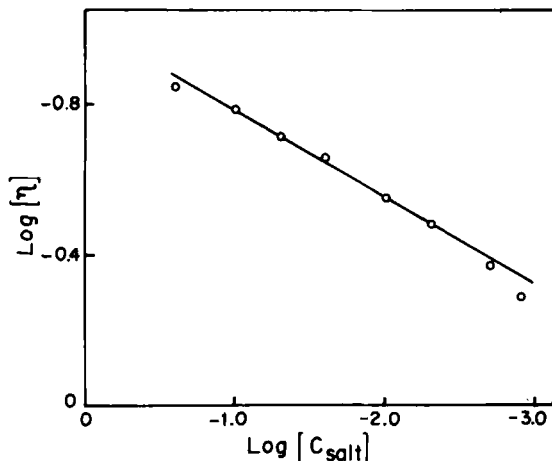
Fig. 5. Log $[\eta]$ vs. log $[c_{salt}]$ of sodium amylose xanthate in NaCl solutions.

Several attempts have been made in the past few years to calculate the thermodynamic properties of polyelectrolyte solutions from some molecular model of the polyion in solution. In the theory of Hermans and Overbeek [13] the polyion was considered as a spherical distribution of charges, and the distribution of small ions in the system was assumed to be that described by the Poisson-Boltzmann equation. The following expression relating size and ionic strength was derived:

$$1 + \alpha^2 = 1.55 + 0.53 \frac{a}{K} \tag{4}$$

where $\alpha^2 = \overline{r}^2 / \overline{r_0^2}$; $\overline{r}^2$ being the mean-square end-to-end length for the charged polymer chain and r_0^2 is the corresponding value in the uncharged state. The value of "a" is given by $a^2 = (36/5)(\overline{r_0^2})^{3/2}(3Z^2 e^2 / 2\epsilon kT)$, where k = Boltzmann's constant, T = absolute temperature, Z representing the number of charges per polyion, e the elemental charge, ϵ the dielectric constant of the medium, and K the reciprocal Debye radius. Such a plot of α^2 vs. $1/K$ for sodium amylose xanthate in salt solutions of varying ionic strength is shown in Fig. 6. Having seen that the functional relationship of Hermans and Overbeek is supported, it is of interest to see whether our data are in quantitative agreement with Eq. (4). Hence the theoretical value of "a" was calculated using the weight-average charge per molecule, Z, and weight-average value of r_0^2, and we find
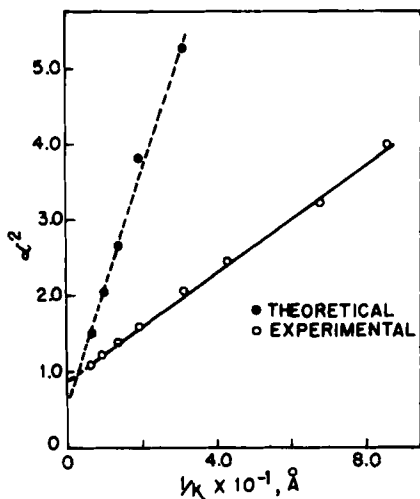
Fig. 6. α^2 vs. 1/K of sodium amylose xanthate in NaCl solutions.

a = 0.2914, giving rise to the dashed line in Fig. 6. The slope of the experimental plot had a value 0.036, from which the magnitude of "a" turned out to be 0.0679. The slope of the dashed line obtained theoretically is about 5-fold greater than the one drawn through the experimental points. Thus the Hermans-Overbeek theory predicts about a one and half times greater rate of expansion with increasing Debye-radius, 1/K, than is found experimentally for NaAX. If we use a number-average value for both Z and $\bar{r_0^2}$ and calculate "a," we conclude that the difference between the value of "a" computed by using measured values of $\bar{r_0^2}$ and Z and determined experimentally is substantially reduced. Results of many other polyelectrolytes, such as NaCMC [14] and lipolyphosphates [15], have been found to be in agreement with the theory qualitatively, but quantitative agreement between theoretical and experimental results was far from expectations.

However, Kimball, Cutler, and Samelson [16] suggested that the effect of the electrostatic potential is not adequately approximated by the Debye-Huckel approximation and, in turn, assumed that the distribution of small ions could be calculated using the Donnan condition. But the maximum expansion permitted by this theory is only a factor of $\sqrt{2}$, which is far less than the experimental values. The situation is analogous to what has been shown by Schneider and Doty from experiments with NaCMC [14].

Turning next to the Flory theory [17], we find the spherical model is again employed and the method used is an extension of his calculation of the expansion of nonelectrolyte polymers by long-range interactions. The use of the Donnan equilibrium theory to calculate the osmotic condition of the mobile ions to the free energy of expansion of the polymer molecules leads to the formulation of a relation between expansion factor α and ionic strength S which is given by the expression:

$$(\alpha^5 - \alpha^3) = A + 2c_1 i^2 M^{1/2} S^{-1} + \tag{5}$$

The first term on the right is the contribution to the expansion of the uncharged macromolecule and is a measure of excluded volume of molecules in solution. It is generally small compared with the second term, which is the ionic term. c_1 is given by

$$c_1 = (3^3 \times 10^3 / 2^{9/2} \pi^{3/2})(M/\overline{r_0^2})^{3/2} N^{-1} M_0^{-2}$$

where M is the molecular weight of the polyelectrolyte, i is the effective degree of ionization, N is Avogadro's number, and M_0 is the molecular weight of the structural unit. The values of $(\alpha^5 - \alpha^3)$ calculated at different ionic strengths are presented in Table 1.

The experimental values of $(\alpha^5 - \alpha^3)$ have been plotted against $1/[c_{salt}]$ in Fig. 7 and yield a perfectly straight line passing through the origin. This is expected from theoretical considerations because at infinite ionic strength the expansion of the molecules in their hypothetical uncharged state vanishes and thus the factor A of Eq. (5), which is a measure of excluded volume of molecules in solution, should vanish. Thus the experimental results are found to be in good agreement with the theory qualitatively. The slope of the straight line has a value of 3.0×10^{-2}, while the theoretical value of the slope calculated using Eq. (5) was found to be 1.4. Thus the experimental value has been found to decrease about fifty times from that of the theoretical value. Such discrepancies have also been observed for lipolyphosphates [15], polyacrylic acid [18], etc.

The deviation of experimental results from theoretical ones, as in the theory of Hermans and Overbeek or in Flory's treatment, has been expressed in terms of a parameter p, defined by

$$p = \left[(X_1)_{exp}/(X_1)_{theo} \right]^{1/2} = i_{exp}/i_{theo} \qquad (6)$$

where (X_1) is given by the equation

$$X_1 = 10^3(3^{3/2}/2^2\pi^{3/2})(1/NV_1)(MV_u/M_0)^2(\overline{S}^2)^{-3/2}\left(1/2 - \chi_1 + \right.$$

$$\left. \frac{V_1 i^2}{4V_u^2 S} \right) \qquad (7)$$

and is related to the second-virial coefficient A_2 by the expression [19]

$$A_2 = (16\pi/3^{3/2})\left((\overline{S}^2)^{3/2}/M^2\right)\ln\left[1 + \left(\frac{\pi^{1/2}}{4}\right)X_1\right] \qquad (8)$$

where χ_1 is a polymer-solvent interaction parameter, and V_1 and V_u are the molar volumes of the solvent and chain segment, respectively. The quantities $(X_1)_{theo}$ and $(X_1)_{expt}$ are calculable by using Eqs. (7) and (8), respectively.
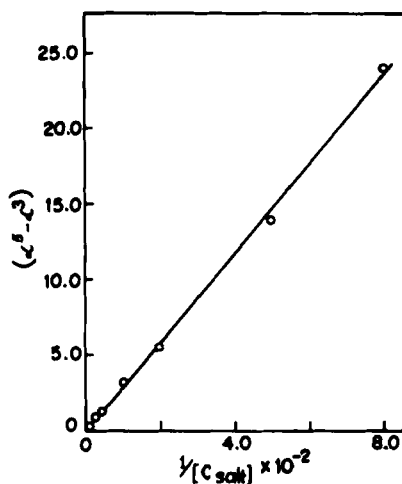

Fig. 7. $(\alpha^5 - \alpha^3)$ vs. $1/[c_{salt}]$ of sodium amylose xanthate in NaCl solutions.

Thus it is implied that the charged sites on the polyion restrict the mobility of counterions which then gives rise to a lower effective degree of ionization of the polyelectrolyte groups than expected from, for instance, titration

measurements. Brown and Henley [20] found the discrepancy between the observed and calculated expansion of sodium carboxymethyl cellulose solely a consequence of counterion binding, and an assumption of p = 0.34 gives good agreement between theory and experiment. The calculated value of p for our system has been found to be about 0.15. Thus the discrepancy between the observed and calculated expansion can be explained as a consequence of an effective binding of approximately 85% of the counterions. Orofino and Flory [19] ascribed the value p = 0.1 for polyacrylic acid. In view of the low charge density of NaCMC in comparison with synthetic polyelectrolytes, it is likely that the quantity p should be somewhat less for NaCMC than mentioned above.

In contrast to the model assumed by the above authors, Katchalsky and Lifson [21] and Harris and Rice [22] base their calculations on the model of a randomly coiled chain, which is a more realistic representation of the polyion. However, while the uniform sphere model of Hermans and Overbeek and Flory requires that the square of the chain expansion ratio is linear in the reciprocal electrolyte concentration, for very long chains and at fairly high electrolyte content Katchalsky and Lifson predict a linear first-power dependence of the chain expansion ratio on the reciprocal electrolyte concentration which greatly overestimates the molecular expansion from electrostatic forces. However, from such a plot of α vs. $1/K$ it is concluded that though a linear relationship is obtained at higher ionic strength, deviation is observed at lower ionic strength.

The calculations of Harris and Rice only take into account interactions between charges on nearest neighboring statistical elements. The comparative success of the theory of these authors with the NaCMC results of Schneider and Doty [14] arose partly from the apparently extended nature of the uncharged polymer as indicated by the latter authors (A_m = 335 Å). With the flexible polymethacrylic acid (A_m = 10 Å) the calculations were considerably less successful. We find, however, that the uncharged NaAX molecule is substantially less extended (A_m = 180 Å); the theory then appreciably underestimates the expansion owing to the neglect of higher order electrostatic interactions and so there will be some disagreement between the calculated expansions and those of experiment.

We now turn to the relations of $[\eta]$ to the sizes determined from the light-scattering. Having seen that the polymer behaves as a free draining coil in 0.25 M NaCl, the Kirkwood-Riseman equation [23] can be employed to calculate the frictional coefficient per monomer unit, ξ, which is given by the expression

$$\xi = 3600 \, \eta_0 M_0 \, [\eta] \, / \overline{r^2_w} N \tag{9}$$

where η_0 is the viscosity of the solvent, and the other terms being defined earlier. The ξ value was calculated to be 0.33×10^{-9} g/sec, while this value for amylose of approximately the same molecular weight in 0.33 M KCl [24] is 25.2×10^{-9} g/sec. Thus the value ξ of NaAX in 0.25 M NaCl has been found to be less than the approximate value of 4×10^{-9} g/sec based on the diffusion coefficient of sucrose, while Sitaramaiah and Goring [25] computed the ξ values of NaCMC to range from 0.34×10^{-9} to 2.4×10^{-9} g/sec in salt solutions of decreasing ionic strength. The deviation in the value of either NaAX or NaCMC from that of ξ of sucrose may be explained as being due to the polydispersity of the samples as well as to the inadequacy of the model on which they are based. The higher value of ξ of amylose in 0.33 M KCl may be due to molecular solvation.

The Macromolecular Chain Configuration of Sodium Amylose Xanthate in 0.25 M NaCl.

In order to study the polymer solvent interaction, the ionization of substituent xanthate groups should be kept at minimum by increasing the ionic strength of the solvent through the addition of a simple electrolyte which will screen the polymeric charges and decrease the electrostatic forces between them so that the polyelectrolyte molecules will behave as uncharged polymers. The viscometric and light-scattering experiments of NaAX were therefore carried out in 0.25 M NaCl. The corresponding light-scattering results were treated according to the method of Zimm [7] and the plot is shown in Fig. 1. The molecular weight $\overline{M}_W$ and root-mean-square radius of gyration $(\overline{S^2_z})^{1/2}$ were found to be 3.7×10^5 and 1166 Å, respectively. The second virial coefficient was calculated to be 5.36×10^{-5} ml mole/g^2. The heterogeneity correction was applied to the molecular weight following the method of Doty et al. [26]. The ratio $\overline{M}_w/\overline{M}_n$ thus found from the curvature of the extrapolation of the line C = 0 of the Zimm plot was 3.7. The high value of the ratio suggests the heterogeneous nature of the sample. The upward curvature of the Zimm plot may have resulted through several causes, among which is the extended nature of the chain configuration. However, the chain extension was not found to be of sufficient magnitude to lead to the choice of a rod model in solution. This is shown in Fig. 8 where the experimental values of the inverse particle scattering factor $p(\theta)^{-1}$ were plotted against $\sin^2 (\theta/2)$, and the curve was compared with those of rod and polydispersed coil models obtained theoretically. It was found that the
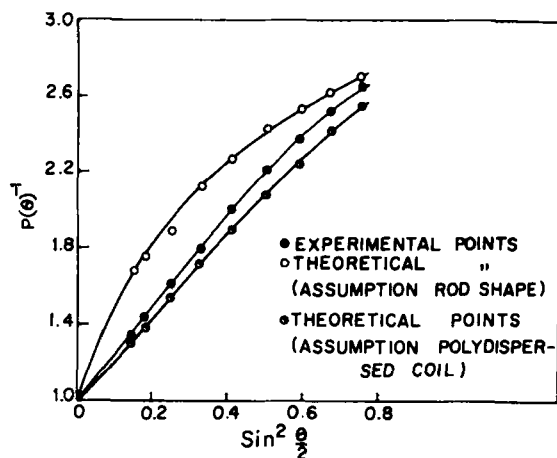
Fig. 8. $p(\theta)^{-1}$ vs. $\sin^2 (\theta/2)$ of sodium amylose xanthate in 0.25 M NaCl solution.

molecules essentially retained the coiled configuration in solution. However, the slight deviation of the experimental plot from that of theoretical one of polydispersed random coil model may be accounted for as being due to the heterogeneous nature of the sample. Under this assumption, the end-to-end distance $(\bar{R}^2)_Z^{1/2}$ has been calculated from the root-mean-square value of radius of gyration obtained from the Zimm plot. When this dimension was compared with the contour length $(R_{max})_Z$, the ratio $(R_{max})_Z/(\bar{R}^2)_Z^{1/2}$, i.e., the coiling factor, was found to be 5.5. Since the Gaussian distribution of segments is no longer a good approximation for chains with valence angle near $100°$ and for coiling factors <10, we should better treat the amylose chain as behaving non-Gaussian.

The Flory's hydrodynamic constant ϕ was calculated as 0.1×10^{21} using the end-to-end distance value of 1637 Å obtained from dissymmetry measurements which compare favorably with values obtained from other polymeric systems which deviate from Gaussian statistics. In agreement with our results, Cowie [27] observed that the Flory-Fox theory is unsuitable for describing the hydrodynamic behavior of amylose in solvent media such as dimethyl sulfoxide or aqueous KOH as the asymptotic value of ϕ (2.2×10^{21}) was approached only in the high molecular weight region above 1.4×10^6 and thus the lowering in the value of ϕ in the low molecular weight region was attributed to the deviation of the polymer coils from Gaussian statistics.

The expansion factor α in 0.25 M NaCl was calculated to be 1.01 by using the Flory-Orofino equation [28] and this seemed to be of a somewhat lower magnitude. Such lower magnitudes of expansion factors were also reported for cellulose derivatives such as hydroxyethyl cellulose (HEC) and NaCMC in aqueous solvents [29, 30], which were much smaller than those obtained from the Kurata-Stockmayer method. The excluded volume factor, $A_2 \overline{M}_w / [\eta]$, was found to have a value of 161.4, and this is the highest limit attainable by this quantity and signifies the good solvent effect of 0.25 M NaCl solution for relatively low molecular weight sodium amylose xanthate.

Important parameters for designating a polymer coil as flexible or stiff in solution are b, the effective bond length; and A_m, the Kuhn-Kuhn equivalent chain length. The first of these parameters is given by $b = [(\overline{R}_0^2)/\overline{Z}]_Z^{1/2}$, where $\overline{Z}_z$ is the Z-average degree of polymerization. The Kuhn-Kuhn equivalent chain length A_m is given by $A_m = [6(\overline{S}_0^2)/R_{max}]_Z$. The values of b and A_m for this system has been found to be 30.4 and 180.0 Å, respectively, while for high molecular weight NaAX in salt solution these two quantities have been found to be 6.74 and 8.8 Å, respectively, as reported in our earlier paper [1].

Another important parameter for characterizing a given polymer chain in solution is the steric factor σ which is given by the ratio $(\overline{R}_0^2)^{1/2}/(\overline{R}_f^2)^{1/2}$ where $(\overline{R}_0^2)^{1/2}$ is the unperturbed root-mean-square end-to-end distance and $(\overline{R}_f^2)^{1/2}$ is the unperturbed value calculated for the hypothetical case of free rotation about each bond in the amylose chain. $(\overline{R}_f^2)^{1/2}$ was calculated from the relation $(\overline{R}_f^2)^{1/2} = 6.144 \times Z^{0.5}$ [1].

The value of σ was found to be 4.95 for low molecular weight NaAX while for a high molecular weight sample it was found to be 1.1 as reported earlier [1]. The low value signifies the highly flexible nature of amylose chain in the high molecular weight region but this value increases to 4.95 for the low molecular weight sample which is typical of stiffened chain molecules. Similar to our findings, Cowie [27], in his study on amylose in DMSO and aqueous KOH, found an increase in restriction to free rotation with decrease in molecular weight, as is shown by the increase in the ratio $(\overline{R}_0^2)^{1/2}/(\overline{R}_f^2)^{1/2}$ with decrease in the molecular weight, i.e., the ratio changed from 2.89 to 4.56 for a decrease in molecular weight from 3.06×10^6 to 2.2×10^5. Contrary to the above findings, Banks and Greenwood [24] in their study on amylose in 0.33 M KCl (θ-solvent) observed no increase in restriction to free rotation with decreasing molecular weight as shown by the constancy in the ratio $(\overline{R}_0^2)^{1/2}/(\overline{R}_f^2)^{1/2}$.

The extended nature of the molecule, which is particularly evident in the low molecular weight region, might have been caused chiefly by short-range interaction forces in addition to swelling of the molecule by polymer-solvent interaction. Thus the chain is obviously sterically hindered and one can account for this effect either by allowing a limited rotation through an angle ±B about the C—O bond or by considering the existence of potential energy barrier W_0 defined as $W = (W_0/2)(1 - \cos \phi)$ where

$$\overline{\cos \phi} = \frac{\int_0^{2\pi} \cos \phi \exp (-W/kT)d\phi}{\int_0^{2\pi} \exp(-W/kT)d\phi} = \frac{\sin B}{B} \tag{10}$$

For linear polymers, we can obtain a measure of the steric hindrance to rotation in the chain using the expression between $\overline{R_0^2}$, Z and $\overline{\cos \phi}$ which is given by

$$\overline{R_0^2} = Zl^2\left(\frac{1 - \cos \theta}{1 + \cos \theta}\right)\left(\frac{1 + \overline{\cos \phi}}{1 - \overline{\cos \phi}}\right) = \overline{R_f^2}\frac{1 + \overline{\cos \phi}}{1 - \overline{\cos \phi}} \tag{11}$$

where l is the length of the anhydroglucose unit, 5.15 Å, and θ is the oxygen valence angle ($\approx 100°$) for amylose and its derivatives. The value of $\overline{\cos \phi}$ was found to be 0.92. However, it can be noted that $\overline{\cos \phi} = 0$ corresponds to free rotation about the C—O bonds linking the pyranose rings in the chain and $\overline{\cos \phi} = 1$ to the absence of rotational freedom and maximum extension of the molecule. The sodium amylose xanthate molecule is thus obviously flexible in the high molecular weight region but there appears to be an increase in restriction to free rotation in the low molecular weight region as evidenced by the values of σ, $\overline{\cos \phi}$, etc., giving rise to pronounced molecular extension to these macromolecules.

CONCLUSIONS

Sodium amylose xanthate molecule has been found from a viscometric study to behave as a typical polyelectrolyte in aqueous solution. The dependence of intrinsic viscosity $[\eta]$ on ionic strength has been studied and the polymer molecule has been found to have a stiff chain character. The dependence of α^2 on $1/K$ according to Hermans and Overbeek and $(\alpha^5 - \alpha^3)$ on S^{-1} according to Flory have been investigated, and the

deviation of experimental results from the theoretical ones has been explained in terms of the binding of counterions.

From a study of the dependence of the particle scattering factor $p(\theta)^{-1}$ on scattering angle θ it is observed that the NaAX molecule in 0.25 M NaCl retains a polydispersed random coil chain configuration. The magnitude of Flory's hydrodynamic constant ϕ for this system has been found to be lower than the accepted value and so the distribution of chain segments in the polymer molecule can no longer be approximated by Gaussian statistics. The values of effective bond length b, Kuhn-Kuhn equivalent chain length A_m, steric factor σ, etc., have been determined, and it is concluded that the polymer molecule has a typical stiff chain character in salt solutions.

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