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NON-NEWTONIAN FLOW OF DILUTE POLYMETHACRYLIC ACID SOLUTIONS AT DIFFERENT DEGREES OF NEUTRALIZATION AND IONIC STRENGTHS

RAGNAR STROMBERG

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FOREWORD

This report was prepared by the Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden, under USAF Contract AF 61(052)-392. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena." Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules." The research reported in this report has been sponsored by Air Force Materials Laboratory, Research, United States Air Force, Dr. W. E. Gibbs, project engineer.

This report covers work conducted from 1 January 1964 to 1 January 1965.

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The manuscript of this report was released by the author 1 September 1965 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

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ABSTRACT

A careful experimental study of the gradient dependence of viscosity for dilute solutions of polymethacrylic acid (M = 112,000) has been performed. Measuremens have been made at six degrees of neutralization between 10 and 90 percent and ionic strengths between 0.5×10^{-3} M and 5.0×10^{-3} M. The velocity gradient range covered is 2 - 71,000 sec $^{-1}$. Isoionic dilution has been employed to permit linear extrapolation to zero concentration. As expected the gradient dependence is most pronounced when the polymer is highly charged and the ionic strength is low. The experimental results are mainly viewed in the light of theories concerning the rigidity of the macromolecular coil.

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SECTION I

INTRODUCTION

The gradient dependence of viscosity has been studied extensively for solutions of uncharged polymers. However, little work has been done on polyelectrolytes. Some papers have appeared on sodium carboxymethylcellulose (References 1, 2, 3) and Eisenberg (Reference 4), among others, performed a low gradient study on DNA. Partially neutralized (60%) polymethacrylic acid (PMA) of high molecular weight ($M = 2 \cdot 10^6$) has been investigated by Alexander and Hitch (Reference 5) in the range 25 - 5000 $\sec^{-1}$. The aim of the present work is to determine the gradient dependence of a typical polyelectrolyte in an extended region of shear rates (0 - 50,000 $\sec^{-1}$) especially in connection with a simultaneous variation of polymer charge and the ionic strength of the solvent. It is well established, that the ionic strength has an extreme influence on the configuration of polyelectrolytes, the molecule tending to a more extended form at low ionic strengths. Owing to electrostatic repulsion between charges of the same sign situated on the backbone of the coil the configuration is also strongly dependent of the number of charges that is, the degree of neutralization. A viscometric study of these two effects in combination might give a valuable contribution to the theoretical aspects of polyelectrolytes and non-newtonian behavior. The experiments are also a direct continuation of previous measurements performed at this Institute in the same field.

SECTION II

EXPERIMENTAL

The PMA sample investigated has been obtained from AB Bofors, Nobelkrut. The procedure for purification and, to a certain extent, fractionation of this sample was in principle the same one as was used by Katchalsky (Reference 6). PMA (3, 5% by weight) was dissolved in methyl alcohol and precipitated twice with diethylether. The precipitate was collected and dissolved in triple distilled water and centrifuged at 5600 r.p.m. for two hours in a preparative centrifuge type MSE "Major", after which the solution was freeze-dried.

In making solutions the following procedure has been adopted. To 0.1 - 0.3 g PMA 150 ml triple distilled water was added and a calculated amount of 0.1 M NaOh brought the neutralization to the desired extent, which was varied from 10 to 90 percent. The resulting stock solution was shaken over-night at +3°C and stored in a refrigerator. The measuring solutions were obtained by means of isoionic dilution with a NaCl-solution of appropriate concentration. Each degree of neutralization was investigated at three different ionic strengths between $0.5 \cdot 10^{-3}$ M and 5.0. 10^{-3} M.

In the present work three viscometers were used to cover the different regions of investigation. The high gradient range (q_{max} = 8000 - 71,000 sec^{-1} for water) was covered by a specially constructed Ostwald viscometer using extra driving pressure from a mercury manostat (Reference 7). In the medium range (q_{max} = 400 - 1700 sec^{-1}) an Ubbelohde viscometer with four bulbs was used and in the low range (q_{max} = 2 - 300 sec^{-1}) a viscometer consisting of two cylindrical tubes connected by a capillary (Reference 8). However, in most cases the viscosity could be extrapolated to zero gradient from measurements made in the medium range. This last viscometer was only used for the highest concentrations of 90 percent NaPMA.

All measurements to be discussed here were performed at 25.0°C. The viscosity of the solutions was measured relative to that of water which was considered as solvent irrespective of the existence of low molecular salt. The contribution to the viscosity from NaCl was found to be negligible. Flow times were generally taken in duplicate to 0.1 of a second. In most cases the same solution could be measured in the high and medium shear ranges. For measurements with the Ostwald viscometer the η_r - values were held within the limits 1.1 - 2.0 and with the Ubbelohde viscometer between 1.2 and 2.1. To meet this condition some solutions of high concentration and low ionic strength could not be measured in the medium range.

Appropriate kinetic energy corrections were applied to the viscosity and velocity gradient values and these were furthermore corrected to the corresponding values at the wall of the capillary by the method introduced by Weissenberg (Reference 9), that is, by division and multiplication respectively by $\frac{3+F(P)}{4}$, where $F(P) = \frac{d\ln t}{d\ln P}$ and was obtained by a plot of outflow time against driving pressure (Reference 10).

The molecular weight of the PMA sample was determined by means of Staudinger equations in two different solvents. In methanol the following equation is valid at 26°C (Reference 11): $[\eta] = 2.42 \cdot 10^{-3} M^{0.51}$ and in 0.002 M HCl at 30°C (Reference 6): $[\eta] = 6.16 \cdot 10^{-3}. (D.P.)^{0.50}$. The meaurements gave M = 111,000 and 113,000 resp., which corresponds to a D.P. of about 1300.

SECTION III

RESULTS

It is well known that the viscosity behavior of polyelectrolyte solutions is quite different from ordinary polymer solutions in that the reduced viscosity increases as the solution is diluted. There are three methods to determine the intrinsic viscosity in spite of this anomaly. One has been derived by Fuoss (Reference 12) and implies a plot of $\frac{1}{\eta_{sp}/c}$ against $\sqrt{c}$ according to the empirical equations $\frac{\eta_{sp}}{c} = \frac{A}{1+B\sqrt{c}}$. Another method is dissolving the polyelectrolyte in a salt solution, that suppresses the charge effects, and the third one, which has been used in this work, is the isoionic dilution technique introduced by Pals and Hermans (Reference 13). It is assumed that no configurational change will occur if the polyelectrolyte were diluted with a salt solution the concentration of which is chosen so that the effective ionic strength of the system is kept constant. Since there is some question as to what the effective ionic strength is, this technique would call for methods of trial and error. However, Terayama and Wall (Reference 14) have determined the counterion binding in potassium polyacrylate solutions which can be supposed to show a similar behaviour as sodium polymethacrylate. The assumption proved to be correct and the values of r in Table II agree fairly well with data found in Reference 14.

The following degrees of neutralization have been examined: 10, 20, 40, 60, 75 and 90 percent. It is best to avoid fully neutralized acid since any excess sodium hydroxide might easily provide a non-negligible concentration of low molecular salt. Table II shows the concentrations of the stock solutions. The quantity r is defined as $\frac{c_1}{c_0}$, where c_1 is the concentration of the NaCl solution used for dilution and c_0 the original total concentration of the sodium ions from the polyelectrolyte. It has been found that the value of r necessary to make the plot $\frac{\eta_{sp}}{c}$ vs. c a straight line is insensitive to the value of c_0. This compatible with the observation that the degree of counterion binding is relatively insensitive to concentration.

In Figure 1 is shown the gradient dependence of the relative viscosity in the high region for PMA neutralized to 10 percent and dilute with $3.05 \cdot 10^{-3}$ M NaCl. Measurements were made at four different polymer concentrations. It is observed that the dependence is rather small which is a consequence partly of the low charge of the polymer and partly of the relatively high ionic strength. Both factors have an influence on the molecular configuration that will turn into a more spherical one. Especially noteworthy is that the marked increase in the viscosity for gradients below 10,000 sec^{-1} is missing. Similar curves are shown in Figure 2 for 40 percent NaPMA diluted with $1.01 \cdot 10^{-3}$ M NaCl that is, a third of the foregoing ionic strength). The gradient dependence here is very pronounced, as a consequence of the high charge of the polymer which causes an expansion of the molecule. From curves of this type η_r-values have been taken at fixed gradients, namely 50,000, 25,000, 10,000, 5000, 1000 and 0 sec^{-1}. The next step is to make the usual plot of $\frac{\eta_{sp}}{c}$ vs. c with the gradient as a parameter. Figures 3 and 4 are examples of such curves, the first one representing a low ionic strength and the other one a high ionic strength. In the case of high ionic strength the curve for 1000 sec^{-1} differs very little from that obtained at zero gradient and is accordingly not shown on Diagram 4. As can be seen, the points fall on straight lines. Thus, the intrinsic viscosity $[\eta]$ is easily obtained at the different velocity gradients from these plots. As the ionic strength increases the slope of the lines decreases. It can be further seen that low velocity gradients give higher slopes. Results from different degrees of neutralization and ionic strengths are collected in Table III.

In Figure 5 three illustrative cases are compared. The uppermost curve is an example of the behavior at high degree of neutralization and low ionic strength (60 %, $0.65 \cdot 10^{-3}$ M), the intermediate one represents a highly charged polymer studied at high ionic strength (90%, $4.54 \cdot 10^{-3}$) and the bottom curve is valid for PMA solutions neutralized to a small extent (10%, $1.44 \cdot 10^{-3}$). 60 percent NaPMA at low ionic strength has the most marked dependence while in the case of 90 percent NaPMA the high ionic strength reduces the effect of the considerable charge of the molecule. One may remark, though, that above $q = 25{,}000\ \mathrm{sec}^{-1}$ the curves almost coincide. The 60 percent NaPMA has accordingly been distorted by the gradient field so that the configurations are qualitatively similar. Ten percent NaPMA shows a linear dependence with a very small slope indicating that the charges are not numerous enough to extend the molecule.

Figure 6 shows the intrinsic viscosity $[\eta]$ as a function of the ionic strength for 75 percent NaPMA with the velocity gradient as a parameter. The general trend is the same for the other degrees of neutralization investigated except for 10 percent NaPMA. At 50,000 sec^{-1} $[\eta]$ shows a very small increase whereas at zero gradient the effect is quite pronounced (being more than doubled in the case of 75 percent NaPMA). The molecule can be considered to have the same configuration at all ionic strengths at 50,000 sec^{-1} but at the other gradients the configuration is changed by changes in ionic strength. The picture for 10 percent NaPMA differs considerably from Figure 6. The slope is about the same but the curves representing the different velocity gradients lie close to each other and there is no marked increase of $[\eta]$ at low ionic strengths.

In Figure 7 the intrinsic viscosity is considered as a function of the degree of neutralization while the ionic strength is kept constant ($3 \cdot 10^{-3}$ M). The similarity between the curves for separate gradients should be noted as it seems to indicate a saturation value at about 60 percent NaPMA. A further increase of the polymer charge has evidently no influence on the configuration. This observation is in accord with measurements performed by Kuhn and his collaborators (Reference 15). They found that PMA in water solution is fully extended already at 42 percent neutralization. That the corresponding value at the higher ionic strength $3 \cdot 10^{-3}$ M should be 60 percent is plausible. The saturation value corresponding to $1 \cdot 10^{-3}$ M is about 50 percent NaPMA.

SECTION IV

DISCUSSION

The problem of polyelectrolyte expansion has been the subject of several theoretical treatments. A very comprehensive review of the various theories is found in the book by Rice and Nagasawa (Reference 16). No theory has appeared yet relating the gradient dependence of viscosity and polyelectrolyte expansion. Thus, we are only able to calculate dimensions and extensions of the PMA coil from data extrapolated to zero gradient.

One starting point is the equation of Flory and Fox (Reference 17), which relates the intrinsic viscosity $[\eta]$ and the root-mean-square end-to-end distance $(\overline{h^2})^{\frac{1}{2}}$.

$$[\eta] = \phi \frac{(\overline{h^2})^{3/2}}{M} \qquad (1)$$

ϕ is the well known universal constant of Flory having the value $2.1 \cdot 10^{21}$ for uncharged polymers. It is doubtful whether this equation can be applied at all to polyelectrolytes because of the underlying assumption that the mass distribution is Gaussian. Orofino and Flory (Reference 18) have, however, published data on polyacrylic acid and arrived at $\phi = 0.86 \cdot 10^{21}$, which is a mean value obtained from measurements at different degrees of neutralization and ionic strengths. Using this value of ϕ, coil dimensions have been calculated in three representative cases namely, high ionic strength and low degree of neutralization, medium values of both quantities and low ionic strength and high percent of NaPMA (Table IV).

In order to get an idea of the coil extensions, it is also necessary to know the unperturbed dimensions of the coil. In a recent article by Takahashi and Nagasawa (Reference 19) discussing the behavior of polyelectrolytes in salt solution, primarily the excluded volume effect, it is shown that the equations relating intrinsic viscosity, molecular weight and coil dimensions for nonionic polymers (References 17, 20, and 21) can also be applied to polyelectrolytes at different salt concentrations. The unperturbed dimensions, $(\overline{h_0^2})^{\frac{1}{2}}$, may be roughly estimated from data in Reference 19.

Following the Stockmayer and Fixman (Reference 21) treatment, extrapolation of an $[\eta]/\sqrt{M}$ vs. $\sqrt{M}$ plot will give a value of K according to the equation

$$\frac{[\eta]}{\sqrt{M}} = K + 0.51\, \phi_0\, B \sqrt{M} \qquad (2)$$

where ϕ_0 is the universal constant at θ point ($\sim 2.87 \cdot 10^{21}$) and B the excluded volume factor. K is related to the unperturbed dimensions by the equation

$$K = \phi_0 \left(\frac{\overline{h_0^2}}{M} \right)^{3/2} \qquad (3)$$

Takahashi and Nagasawa obtained values of K at different ionic strengths for the sodium salt of polyacrylic acid. It turns out that K changes only slightly with ionic strength, $1.6 \cdot 10^{-3}$ being a reasonable figure at low ionic strengths. Assuming the same value for the present data on NaPMA may be somewhat hazardous but will give an approximate value of the unperturbed dimension. Thus, $(\overline{h_0^2})^{\frac{1}{2}}$ can be evaluated to 275 Å. The last column in Table IV gives an idea of the molecular extension in the different cases. Bearing in mind the approximations involved, these figures show that the coil extensions are considerable.

From a combination of Equation 2 with an experimentally determined expression for the excluded volume factor B of polyelectrolytes Takahashi and Nagasawa obtained the following equation at constant molecular weight

$$[\eta] = (\text{const.})_1 + (\text{const.})_2 \frac{1}{\sqrt{c_0}} \qquad (4)$$

An equation of this form was first presented by Pals and Hermans (Reference 13) and has been confirmed for many polyelectrolytes by Cox (Reference 22). The same equation is also applicable to the present data on PMA. When plotting the intrinsic viscosity at zero gradient against the inverse square root of salt concentration, straight lines are obtained for the different degrees of neutralization. These lines can be extrapolated to the same point on the $[\eta]$ -axis indicating that the degree of neutralization has no influence on $[\eta]$ at infinite ionic strength. The slopes, however, being proportional to the charge, increase as the percent NaPMA is increased.

The gradient dependence of the intrinsic viscosity can be written in the general form

$$[\eta]_q = [\eta]_0 (1 - Bq^n + \cdots) \qquad (5)$$

where $[\eta]_q$ and $[\eta]_0$ are the intrinsic viscosities at shear rate q and 0 respectively and B is a constant for any given polymer of given molecular weight in a given solvent. Regarding the constant n a value of 2 should be expected from theoretical considerations. However, other values of n have been used by several workers, for instance n = 1. Very few papers concerning polyelectrolytes have appeared. Strauss and Fuoss (Reference 23) have proposed the following equation on the basis of measurements on water solutions of poly-4-vinyl-N-n-butylpyridinium bromide

$$[\eta]_q = [\eta]_0 (1 - \alpha [\eta]_0 q) \qquad (6)$$

where α is an empirical constant. An attempt to fit the present data into this equation was unsuccessful, as it gave steadily increasing values of α with decreasing q. This implies that the above simple equation is only valid in the limited range 2000 - 5000 sec^{-1} investiated by Strauss and Fuoss. In the range 0 - 50,000 sec^{-1} an equation involving higher terms in q is probably necessary to satisfy the data.

Figures 8 and 9 are in every respect analogous showing the interdependence of relative intrinsic viscosity $\frac{[\eta]_q}{[\eta]_0}$ and shear rate for 40 percent and 90 percent neutralization at different ionic strengths. In Figure 8 is also seen a curve for 10 percent NaPMA. All graphs representing neutralization degrees greater than 40 percent are very similar although the lowest ionic strength curve of 90 percent NaPMA shows a steeper descent than the others. From these figures it is observed that the ratio $\frac{[\eta]_q}{[\eta]_0}$ will display a stronger gradient dependence at low ionic strength and high degree of neutralization.

It is known that, among other factors, the rigidity of a macromolecular coil causes a gradient dependence of the intrinsic viscosity. Kuhn and Kuhn (Reference 24) have developed a theory that takes into account the inner viscosity of the macromolecular coil but neglects hydrodynamic interaction. The theory is valid for a rigid Gaussian coil. Hydrodynamic interaction is concerned with the orientation of a rigid coil, causing a decrease in $[\eta]$ with increasing shear rate. Peterlin and Copic (Reference 25) and Cerf (Reference 26) have also presented theories in this field. The first authors ascribe the gradient dependence to "anisotropic hydrodynamic interaction" and "nonuniform expansion of the macromolecular coil" while Cerf uses the same model (internal viscosity) as Kuhn and Kuhn.

In order to get a conception of the rigidity of the polyelectrolyte coil we have compared our experimental data with the theory of Kuhn and Kuhn. The parameter occurring in the various theories is the generalized expression $\beta_0 = \frac{M[\eta]_0 \; \eta_0 \; q}{RT}$ (M = molecular weight, η_0 = solvent viscosity, R = universal gas constant and T = absolute temperature), which is plotted versus the relative intrinsic viscosity $\frac{[\eta]_q}{[\eta]_0}$. In Figure 10 the experimental curves of 60 percent NaPMA for the different ionic strengths investigated are shown together with the theoretical curve K, which is valid for a completely rigid coil without hydrodynamic interaction. From Figure 10 it is clear that the rigidity of the coil increases considerably as the ionic strength is lowered. It is known that an increase in the charge would produce the same effect. The curves shown are consequently an additional indication that changes in the effective charge of the polyelectrolyte occur as the salt concentration is altered. The corresponding curves for the other degrees of neutralization are similar to those in Figure 10 but are somewhat displaced to higher or lower positions on account of the charge effect (% NaPMA). However, all experimental curves lie below the theoretical one (K), calculated for a rigid coil without charges. A corresponding curve valid for polyelectrolytes has not yet been calculated. The very large discrepancies from the theory must depend essentially on th charges on the PMA coil, as these tremendously increase the interaction between the polymer molcules in solution. Hydrodynamic interaction may also cause a considerable deviation as the molecules are highly extended and are easily oriented in the gradient field. Similar large discrepancies have been found for the polyelectrolyte sodium carboxymethylcellulose by Lohmander and Stromberg (Reference 3). Unfortunately the theories have not been developed further than to give a fairly good approximation at low rates of shear. A widening of the validity interval will certainly give account for the great deviations now shown at high velocity gradients (that is, high β_0-values).

Furthermore, the data have been treated on the basis of Huggins' equation

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \qquad (7)$$

From plots of $\frac{\eta_{sp}}{c}$ vs. c (cf. Figures 3 and 4) k' can be calculated. Huggins' constant can be interpreted as a measure of the mutual interactions between polymer molecules at finite concentrations and values ranging from 0.4 to 0.6 have been registered for uncharged flexible coils. In solutions of ionized colloids strong electrostatic interactions exist between the charged particles and between their mutually interpenetrating atmospheres. Accordingly much higher values would be expected and have in fact been recorded (Reference 27), the magnitudes strongly increasing in solutions of low salt concentration. Regarding the various NaPMA systems investigated, the slopes, that is $k'[\eta]^2$, steadily increase with decreasing velocity gradient and ionic strength. The magnitude of k', however, does not show such a regular tendency because of the uncertainty in the $[\eta]$ determinations. The highest value of k' is about 15 and the lowest about 0.3. It has been found by Pals and Hermans (Reference 13) that a plot of k' vs. (ionic strength)$^{-1}$ gives a straight line though the theoretical significance of this fact has not yet been explained. Figure 11 shows that the same kind of linear relationship is also valid for measurements at different velocity gradients.

Comparing the polyelectrolyte data with those previously found with the same apparatus for non-ionic polymers (Reference 28), we notice that k' never vanishes at high velocity gradients as was the case for high molecular weight cellulose nitrate in ethyl acetate. This may be due to the retarding effect of the ionic cloud on the spinning of the PMA molecule in the strong gradient field. Another explanation is the relatively low molelular weight of the sample (M = 112,000). Alexander and Hitch (Reference 5) studied the non-newtonian behavior of a very high molecular weight PMA (M = $2 \cdot 10^6$, 60% neutralized) and found that $\frac{\eta_{sp}}{c}$ was independent of concentration even at q = 1000 sec^{-1}. Even the polyacid itself exhibited non-newtonianism.

SECTION V

CONCLUSION

The shear dependence of the intrinsic viscosity has been shown to undergo strong variations with polymeric charge and ionic strength of the solvent. This behavior can be well understood qualitatively. The further analysis of the material is, however, very complicated as the theories of polyelectrolytes and non-newtonianism are not yet fully developed.

SECTION IV

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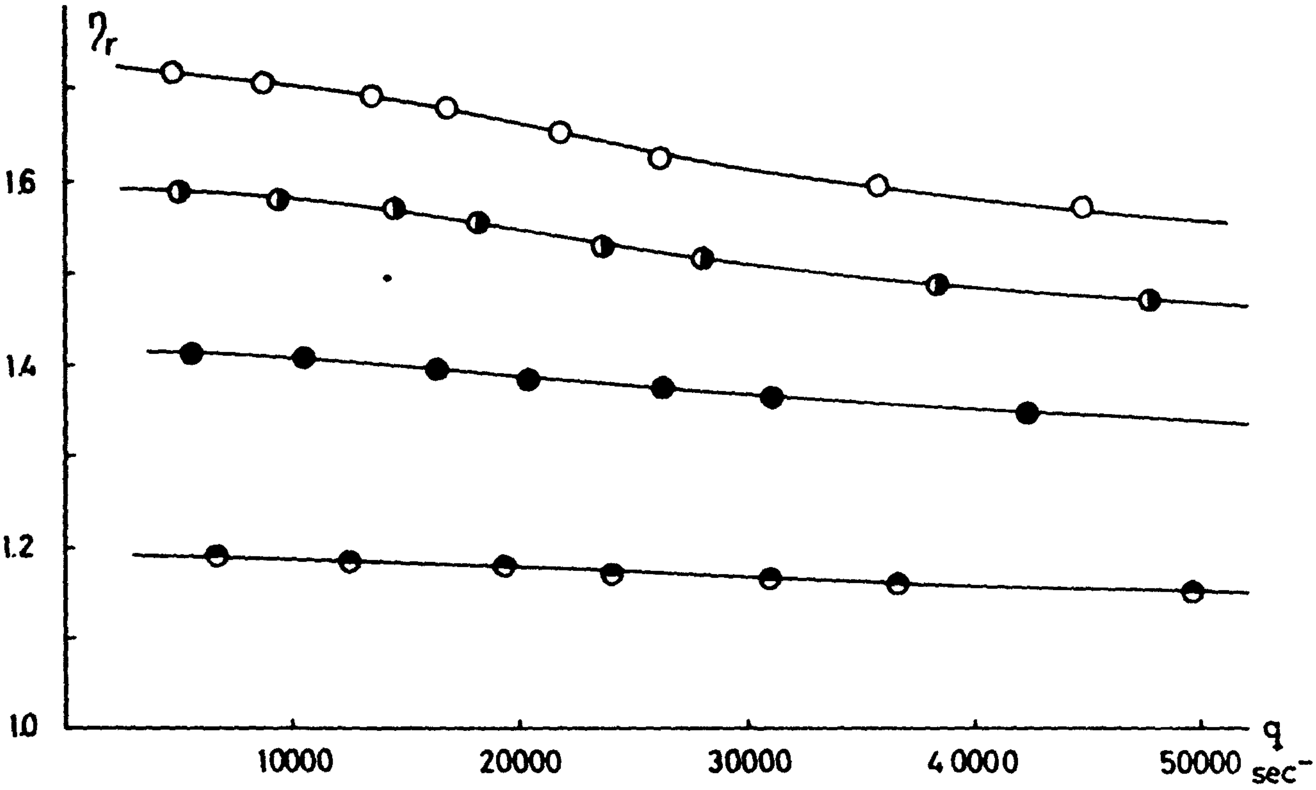

Figure 1. The gradient dependence of the relative viscosity for 10 percent NaPMA at different concentrations. Isoionic dilution with 3.053 · 10^{-3} M NaCl. 25.49 (0), 22.55 (◑), 18.30 (●), 10.38 · 10^{-4} moles of monomer per 100 g (◒).

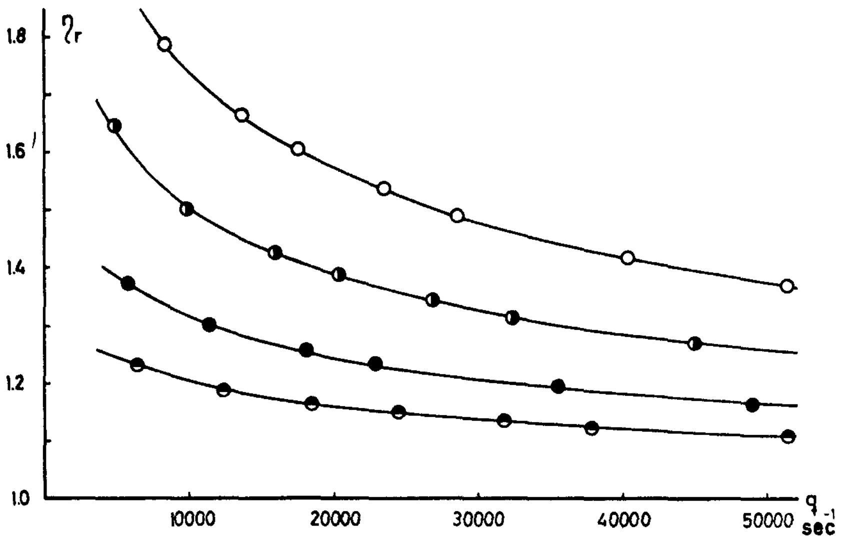

Figure 2. The gradient dependence of the relative viscosity for 40 percent NaPMA at different concentrations. Isoionic dilution with 1.012 · 10^{-3} M NaCl. 3.535 (○), 2.707 (◑), 1.995 (●), 1.448 · 10^{-4} moles of monomer per 100 g (◒).

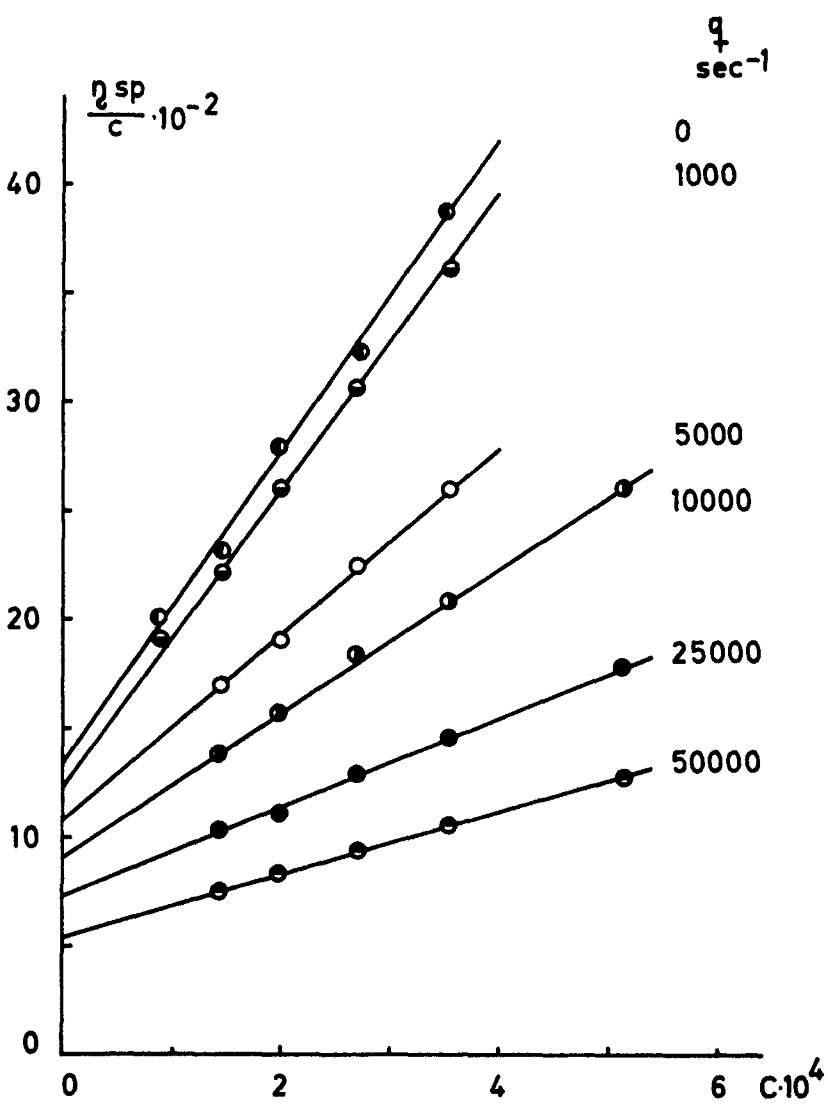

Figure 3. Reduced viscosity (η_{sp}/c) plotted versus concentration (c) for different values of the velocity gradient (q). Concentrations are expressed in moles of monomer (methacrylic acid) per 100 g. Degree of neutralization 40 percent, NaCl-concentration 1.012 · 10^{-3} M.

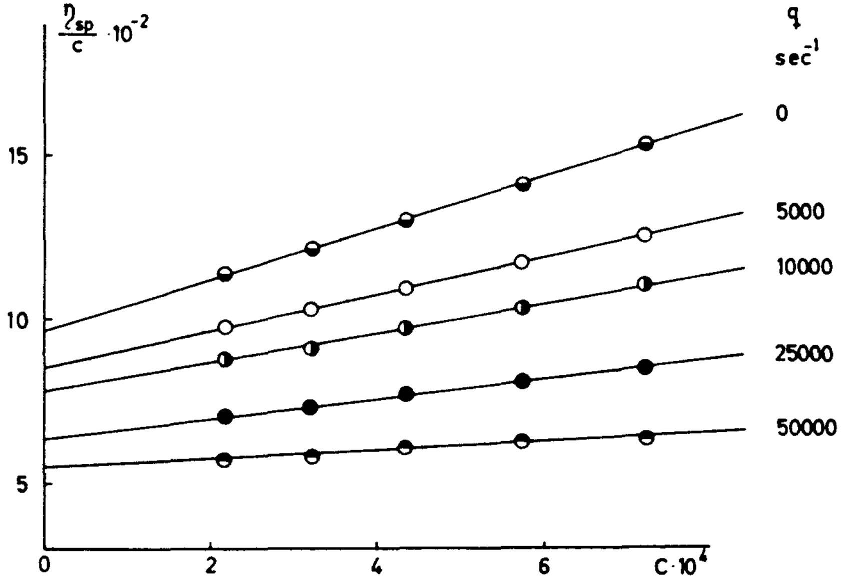

Figure 4. Reduced viscosity vs. concentration for different velocity gradients. 90 percent NaPMA, concentration of NaC1 $4.542 \cdot 10^{-3}$ M.

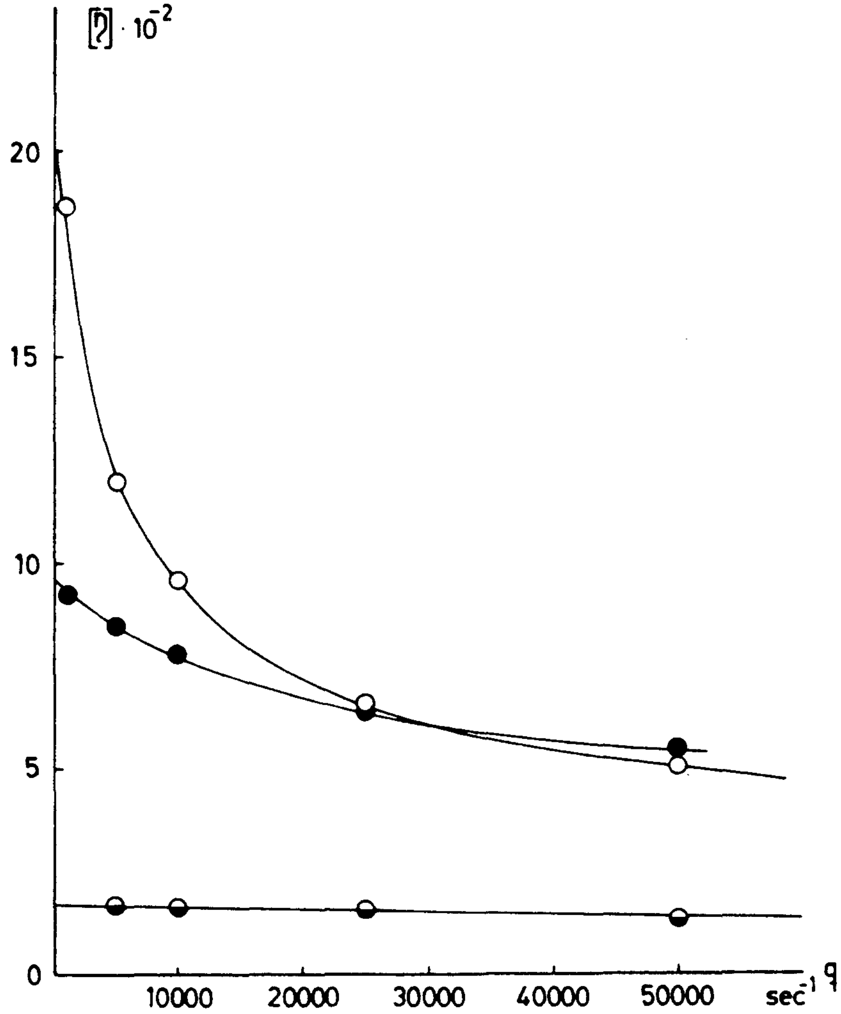

Figure 5. Gradient dependence of the intrinsic viscosity for different degrees of neutralization and salt concentrations. 60 percent NaPMA diluted with $0.649 \cdot 10^{-3}$ M NaC1 (0), 90 percent resp. $4.542 \cdot 10^{-3}$ M NaC1 (●), 10 percent resp. $1.441 \cdot 10^{-3}$ M (◒).

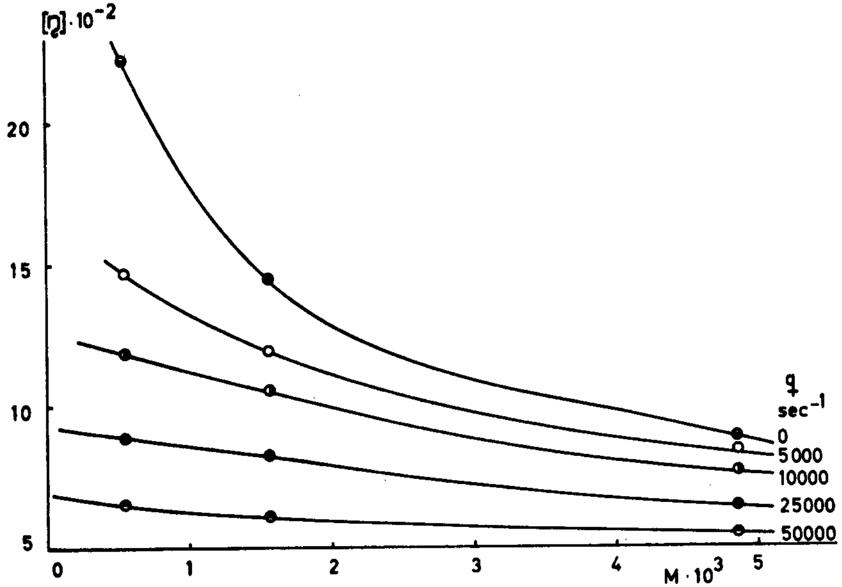

Figure 6. Intrinsic viscosity as a function of ionic strength for 75 percent NaPMA with the velocity gradient as a parameter.

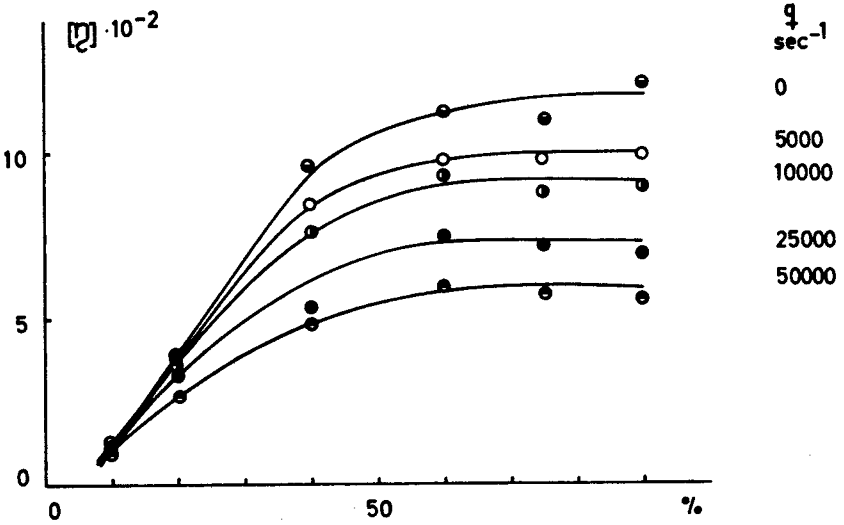

Figure 7. Intrinsic viscosity as a function of the degree of neutralization (%) for constant ionic strength ($3 \cdot 10^{-3}$ M).

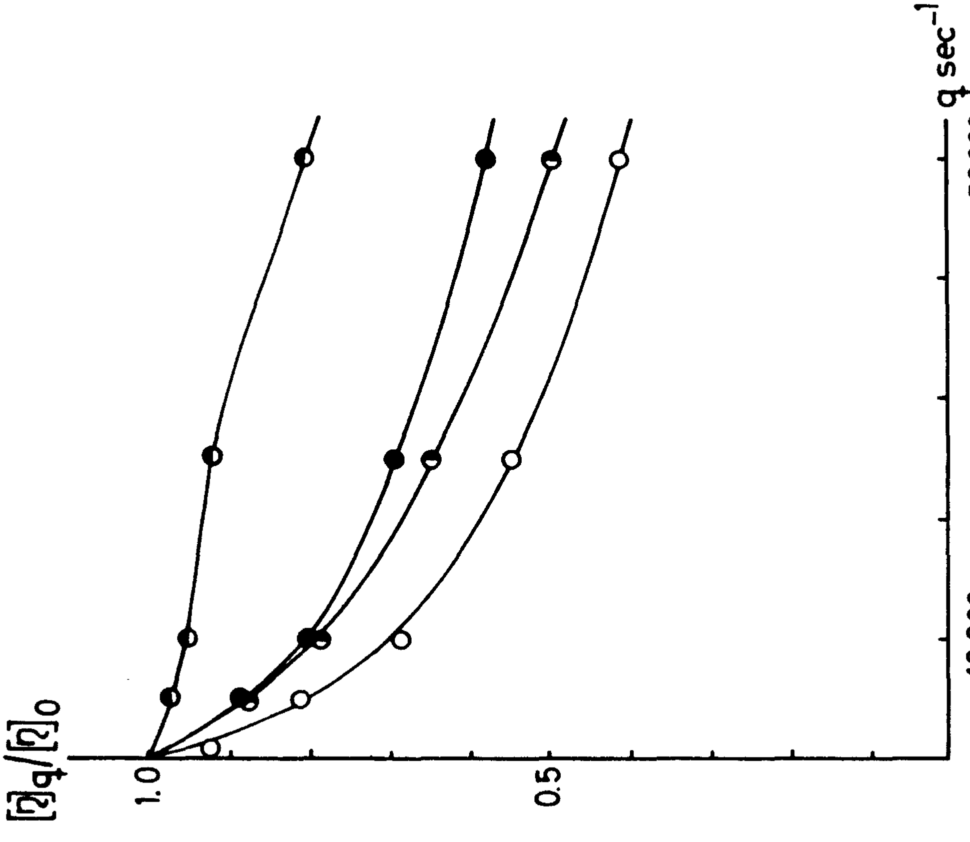

Figure 8. Relative intrinsic viscosity $\frac{[\eta]_q}{[\eta]_o}$ vs. q for 40 percent NaPMA at different ionic strengths. 0 = 1.012 · 10^{-3} M, ◐ = 2.593 · 10^{-3} M, ● = 4.871 · 10^{-3} M, NaCl. ◐ = 10 percent NaPMA in 1.441 · 10^{-3} M NaCl.

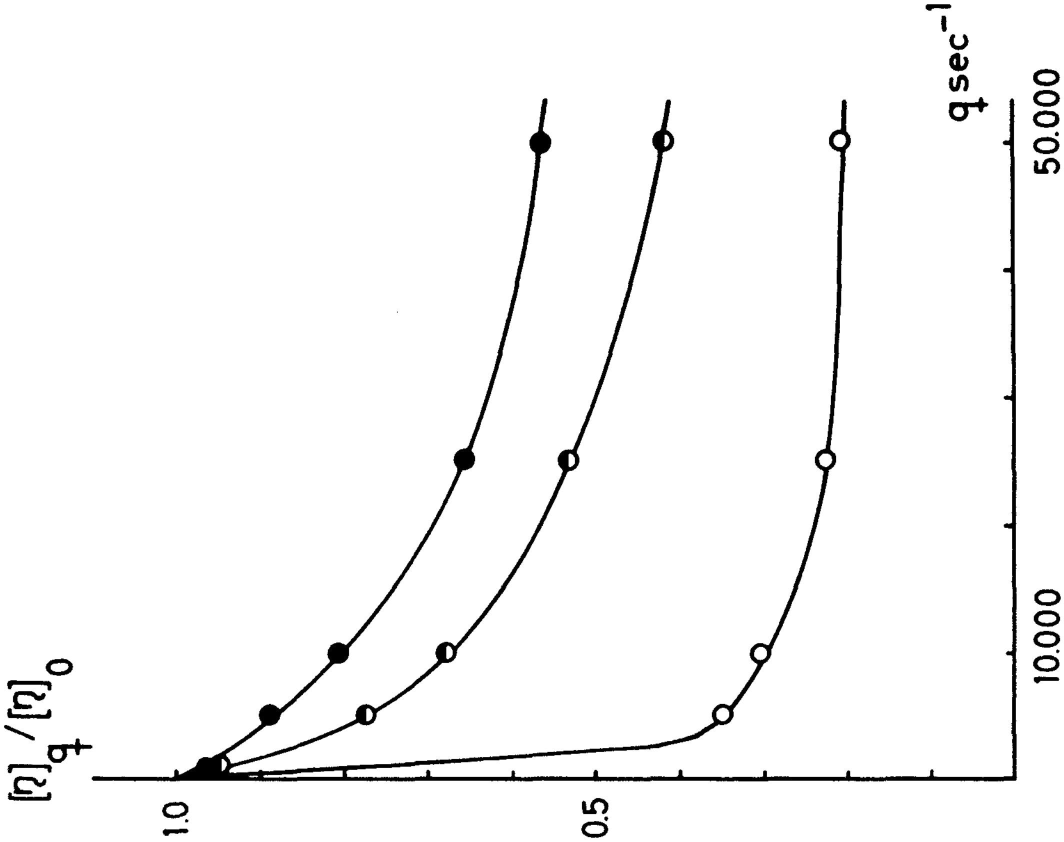

Figure 9. $\frac{[\eta]_q}{[\eta]_o}$ vs. q for 90 percent NaPMA at different ionic strengths. 0 = 0.574 · 10^{-3} M, ◐ = 2.056 · 10^{-3} M, ● = 4.542 · 10^{-3} M NaCl.

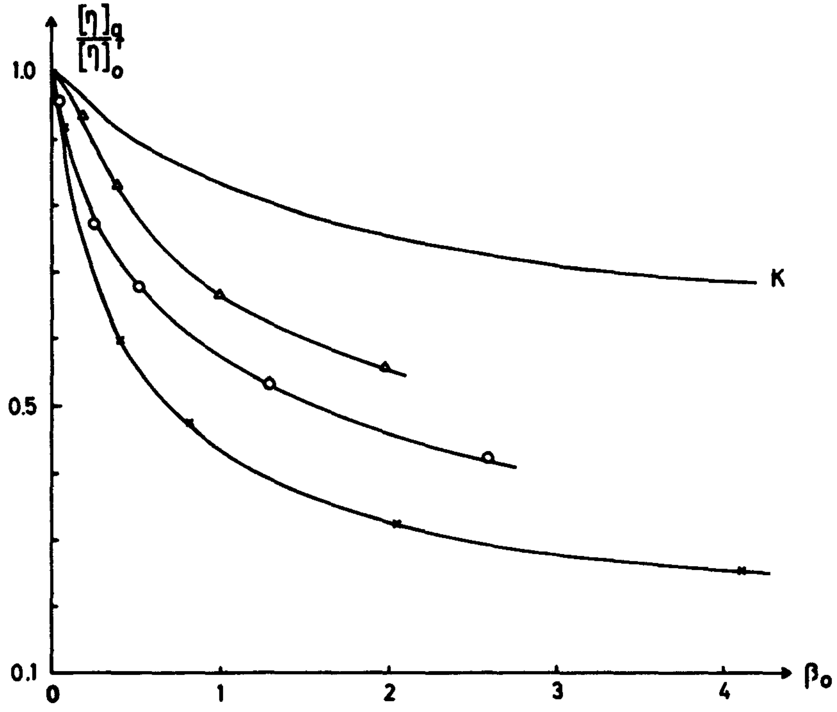

Figure 10. $\frac{[\eta]_q}{[\eta]_o}$ vs. the generalized parameter β_o for 60 percent NaPMA at different ionic strengths. x = 0.649 · 10^{-3} M, 0 = 2.264 · 10^{-3} M, Δ = 4.490 · 10^{-3} M NaCl. K is the theoretical curve of Kuhn and Kuhn.

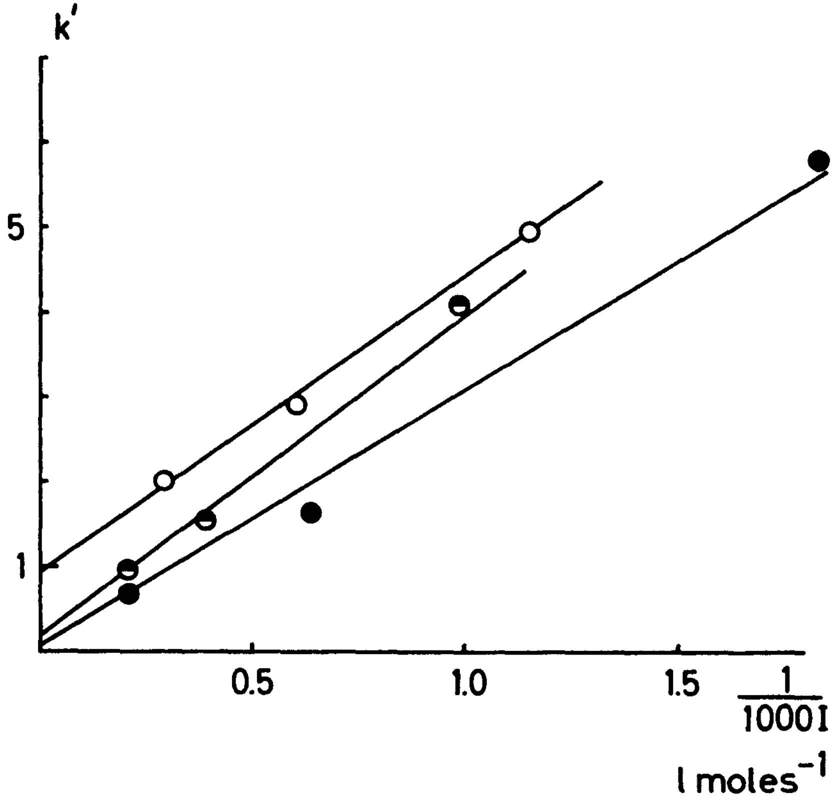

Figure 11. Huggins′ constant k′ as a function of inverse ionic strength. 0 = 20 %, q = 1000 sec^{-1}; ◐ = 40%, 0 sec^{-1}; ● = 75%, 5000 sec^{-1}.

TABLE I

APPARATUS CONSTANTS FOR THE UBBELOHDE VISCOMETER

Efflux volume (ml)	Mean hydrostatic head (cm)	Flow time for water at 25°C (sec)	Capillary length (cm)	Capillary radius (cm)
2.50	28.3	56.1	29.9	0.0325
2.01	23.5	53.8		
1.21	14.7	51.3		
0.60	6.67	56.3		

TABLE II

CONCENTRATIONS OF STOCK SOLUTIONS

Degree of neutralization (%)	Concentration of stock solution. Moles of monomer (methacrylic acid) per 100 g(c)	Concentration of salt solution used for dilution. Moles of NaCl per 1 (c_1)	r
10	$17.57 \cdot 10^{-4}$	$1.441 \cdot 10^{-3}$	0.82
	37.23	3.053	
20	6.376	0.867	0.68
	12.24	1.665	
	25.07	3.410	
40	5.164	1.012	0.49
	13.23	2.593	
	24.85	4.871	
60	3.489	0.649	0.31
	12.17	2.264	
	24.14	4.490	
75	2.692	0.545	0.27
	7.710	1.561	
	24.01	4.862	
90	2.657	0.574	0.24
	9.520	2.056	
	21.03	4.542	

TABLE III
INTRINSIC VISCOSITIES AT VARIOUS VELOCITY GRADIENTS

Degree of neutralization (%)	Ionic strength (moles/1)	q (sec^{-1})	$[\eta]$ 100g per mole of monomer	$\frac{[\eta]_q}{[\eta]_o}$
10	1.441 10^{-3}	0	1.70 10^2	1.000
		5000	1.65	0.971
		10000	1.62	0.953
		25000	1.57	0.923
		50000	1.37	0.806
40	1.012	0	13.25	1.000
		1000	12.20	0.921
		5000	10.72	0.809
		10000	9.06	0.684
		25000	7.23	0.546
		50000	5.44	0.411
60	0.649	0	20.1	1.000
		1000	18.7	0.928
		5000	12.0	0.597
		10000	9.52	0.474
		25000	6.50	0.323
		50000	5.05	0.251
90	4.542	0	9.65	1.000
		1000	9.27	0.960
		5000	8.50	0.881
		10000	7.78	0.806
		25000	6.34	0.657
		50000	5.47	0.567

TABLE IV
DIMENSIONS OF THE PMA COIL

Degree of neutralization (%)	Ionic strength (moles/1)	$(\overline{h^2})^{\frac{1}{2}}$ (Å)	$\frac{(\overline{h^2})^{\frac{1}{2}}}{(\overline{h_o^2})^{\frac{1}{2}}}$
10	$3.05 \cdot 10^{-3}$	560	2.0
40	2.59	1100	4.0
90	0.55	1400	5.1

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13. ABSTRACT

A careful experimental study of the gradient dependence of viscosity for dilute solutions of polymethacrylic acid (M 112,000) has been performed. Measurements have been made at six degrees of neutralization between 10 and 90 percent and ionic strengths between $0.5.10^{-3}$ M and $5 . 10^{-3}$ M. The velocity gradient range covered is 2 - 71,000 sec^{-1}. Isoionic dilution has been employed to permit linear extrapolation to zero concentration. As expected the gradient dependence is most pronounced when the polymer is highly charged and the ionic strength is low. The experimental results are mainly viewed in the light of theories concerning the rigidity of the macromolecular coil.

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Polymethacrylic Acid						
Viscosity						
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