Dispersions or Solutions? A Mechanism for Certain Thickening Agents*

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Synopsis

Hydrolyzed starch-polyacrylonitrile (H-SPAN) graft copolymers form highly viscoelastic mixtures with water, even at concentrations less than 1% by weight. In many ways these mixtures behave like ordinary polyelectrolyte solutions, but dilution experiments revealed that linear reduced viscosity-concentration plots could not be obtained even under ostensibly isoionic dilution conditions. This result, combined with a determination of gel content from centrifugation studies, led to the conclusion that high viscosity H-SPAN water mixtures consist of swollen, deformable gel particles closely packed in intimate contact. Under high dilution or at high ionic strength conditions, the gel particles no longer are tightly packed, solvent is present in excess, the viscosity drops precipitously, and the thickening action effectively disappears. For comparative purposes, a commercial thickening agent (Carbopol 941) was examined and found to act in the same way. All reduced viscosity-concentration curves obtained by dilution, either with salt solutions or water, can be shifted to a single normalized reduced viscosity plot. This shift is done by using as the concentration variable the quantity cQ, where c is the polyelectrolyte concentration and Q is the swelling which the gel particles undergo in an excess of solvent at the corresponding total ionic strength of the solution of concentration c.

INTRODUCTION

Thickening agents, both natural and synthetic, find wide use industrially. One class of thickening agent, a combination of both natural and synthetic polymers, is represented by hydrolyzed starch-polyacrylonitrile graft copolymers (H-SPAN), made by converting the polyacrylonitrile (PAN) graft in a starch-polyacrylonitrile (S-PAN) graft copolymer to the polyelectrolyte form, containing both carboxy and carboxamide groups, by hydrolysis with alkali. The material is prepared as a dry powder by precipitation and drying in the acid form. Stirring the dry powder into water and titrating to neutrality yields a highly thickened mixture. Even at a 1% by weight concentration level, the mixture is a stiff paste showing a yield point. At stresses above the yield point, the viscous mixture is highly non-Newtonian and very elastic. In addition, these systems exhibit properties

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that depend strongly on shear history prior to measurement. Sometimes, unique behavior is observed. For example, low-strain, low-frequency oscillatory pretreatment may cause a buildup of structure in the dispersion, observable as large overshoots in both torque and normal stress on subsequent examination of the sample in steady shear. This overshoot, as much as 400% above steady-state values, disappears after shearing but can be reproducibly built up again by oscillatory pretreatment (or, less effectively and rapidly, by sample aging) before reexamination in steady shear.

In H-SPAN water dispersions, there is visible evidence of the existence of highly swollen gel particles. G. F. Fanta of the Northern Laboratory has determined that a major portion of these mixtures can be readily centrifuged down in the presence of salt. It was not suspected until our study, that within the concentration regions where major thickening occurs there is little, if any, free solvent. The systems appear to consist of highly swollen, deformable gel particles closely packed in intimate contact. Although there may be some graft copolymer in solution in the gel, this soluble fraction appears to exert little influence on the rheological properties measured here.

It is worth remarking here than H-SPAN tends to form gels on a macroscopic scale spontaneously. Thus, films cast from H-SPAN-water dispersions do not redisperse in water except after vigorous mechanical treatment. These gel sheet films themselves are strongly hydrophilic, absorbing several hundred times their own weight in water while maintaining film integrity.

Parallel studies were carried out on Carbopol 941 because this product of B. F. Goodrich Chemical Co. shows rheological properties in water similar to H-SPAN. As in the H-SPAN system, we find that mixture properties of Carbopol and water depend predominantly on the gel fraction present. For both thickening agents, high viscosities and elasticities in water occur when the swollen gel particles are everywhere in intimate contact. If the mixtures are diluted to a level at which the swollen gel particles are no longer in contact, both mixture viscosity and elasticity decrease dramatically.

**EXPERIMENTAL**

**Materials**

S-PAN graft copolymers were prepared by the ceric ion initiation method with subsequent hydrolysis of the PAN moiety to a mixture of carboxylate and carboxamide, as reported earlier. The S-PAN product used was manufactured on a pilot-plant scale by General Mills under contract to USDA. One batch, H-SPAN(G), was converted at General Mills to the hydrolyzed form with approximately 50:50 ratio of carboxylate:amide functionality. This starch graft polymer was designated SGP-502 by General Mills. A second batch of material from the same S-PAN was
hydrolyzed by M. O. Weaver of the Northern Laboratory and designated here as H-SPAN(W). Since the hydrolyzed material may be either in acid or salt form, suitable descriptive modifiers can be appended to a particular sample number. Thus, an H-SPAN in acid form will be designated H-SPAN(H⁺).

A purified H-SPAN was prepared in which the hydrolyzed product was freed of ionic impurities by the following procedure: A stock preparation of H-SPAN(H⁺) was stirred in 1M HCl for 1 hr. An equal volume of ethanol then was added to reduce solvent swelling of the suspended solids. After decanting the liquid, the resultant cake was washed thoroughly with 50% ethanol in water until the washings reached a pH of 3.4. A final washing with ethanol followed, and the powder was dried in a vacuum oven at room temperature. A 1.5% stock solution of this purified acid form of H-SPAN, neutralized to pH 7.7 with NaOH, contained 0.0194 M Na⁺. This sample was designated H-SPAN(P). Note that at pH 7.7, the acid groups are not completely titrated. Titration to a higher pH has the distinct disadvantage for this work of reducing the viscosity and increasing the ionic strength of the dispersion.

Another sample, H-SPAN(S), was a 10-ml portion of a standard preparation of H-SPAN which had been treated in a Branson (Stamford, Conn.) sonifier. It was held for 5 min at a setting of 7.

When Carbopol mixtures were made up for use, the appropriate dry weight in acid form was suspended in water and titrated to pH 7.7 with NaOH. A sample of Carbopol 941 was purified of ionic contaminants by dialyzing a suspension in 1M HCl against distilled water for four days. The suspension was then neutralized to pH 7.7 with NaOH and diluted to a concentration of 1.5% by weight. At this stage, the Na⁺ ion concentration was 0.182 M. This sample was designated as Carbopol(P).

Dextran T250 was from Pharmacia (Uppsala, Sweden).

About 0.01% Dowicide G (Dow Chemical Co., Midland, Mich.) was added to all H-SPAN and Carbopol mixtures to inhibit growth of microorganisms.

Viscoelastic Measurements

A cone-and-plate rheometer (Rheometrics Mechanical Spectrometer, marketed by IMASS, Inc., Accord, Mass., described by Macosko and Starita) was used with a cone 72 mm in diameter and a cone angle of 0.04 radians. Both viscosity (η) and primary normal stress difference (P₁₁ - P₂₂) were measured at room temperature (controlled to 73°F and 55% relative humidity), precautions being taken to prevent evaporation, as described earlier.

Centrifugation

Before centrifugation studies, refractive index increments (dn/dc) were determined using a Brice-Phoenix differential refractometer at 546 nm wavelength. The purified stock preparations were compared with water.
spective values for Carbopol(P) and H-SPAN(P) were 0.246 ml/g and 0.169 ml/g, the concentration basis being the acid form. Orofino and Flory report $dn/dc$ as 0.261 ml/g for neutralized poly(acrylic acid). An additive synthesis of literature values$^5$ for a hydrolyzed polyacrylonitrile 1:1 graft copolymer on starch is about 0.175, in reasonable agreement with our value for H-SPAN.

Sedimentation rates and gel volume were determined in a Spinco ultracentrifuge. Gel material was arbitrarily defined as the fraction sedimenting at 2000 rpm; soluble material was defined as that material having a sedimenting boundary observable at 40,000 rpm. Concentration was determined from areas under Schlieren boundaries by the Archibald method as modified by Trautman$^4$ and by Erlander and Foster.$^9$

The usual syringe filling method could not be used with H-SPAN and Carbopol materials. Consequently, a 3-ml single centerpiece cell (rather than the usual double sector cell) was selected. The cell was filled when partially assembled before the second cell window was inserted.

Gel volume was determined by measuring, on a photograph taken during centrifugation at 2000 rpm, the distance from the gel/solution boundary to the reference line. This distance was calibrated as volume from a series of runs with known weights of water in the cell. Even at low speeds, gel volume drifted down slowly with time; so we recorded only the highest gel volume observed and disregarded the slow decrease in volume with time at constant speed.

Settling experiments were also carried out for H-SPAN dispersions and the results compared with those obtained by centrifugation. Samples were diluted to a low viscosity level and allowed to settle overnight. The dilution level was determined by trial and error so that the settled gel occupied about half the total mixture volume.

**RESULTS AND DISCUSSION**

**Viscosity and Normal Stresses**

Figure 1 shows $\eta$ and $P_{11} - P_{22}$ versus shear rate for a 1.5% mixture of H-SPAN(P) in water. The data were taken after shearing the suspension for 10 min at 100 sec$^{-1}$. This preshear treatment hardly affected viscosity values but reduced normal forces by about 10%. No transient overshoot in either $\eta$ or $P_{11} - P_{22}$ was observed, and on this sample stress overshoot did not develop on oscillatory treatment. A comparison of the results of Figure 1 with those of an H-SPAN not purified by removal of ionic contaminants indicates that at $\dot{\gamma} = 1$ sec$^{-1}$, steady-state viscosity was about 30% greater for the purified material than for the stock H-SPAN, whereas values of $P_{11} - P_{22}$ of H-SPAN(P) were three times that of routine unpurified H-SPAN preparations.

For the Carbopol(P) sample (Fig. 2), transient overshoots in both $\eta$ and $P_{11} - P_{22}$ were observed at the start of shear. The steady-state viscosity
and normal stress values for the dialyzed preparation were within 10% of the usual values for routine preparations. Overshoot values could be increased by oscillatory treatment, as reported earlier.¹

Both Figures 1 and 2 are similar to the results expected with normal, shear thinning polymer solutions. The normal force values are perhaps a little higher than might be expected for polymer solutions of equivalent viscosity level. In Figure 2, a slight concavity upward is seen, both in viscosity and normal stress. But on the whole, results are much as would be expected for polymer solutions, except that even at shear rates of less than 1 sec⁻¹ there is no evidence of any approach to a Newtonian viscosity region. Some evidence of an incipient approach to the Newtonian region would certainly be expected if these H-SPAN and Carbopol materials were in solution in water.
Dilution Effects

The effects of dilution on aqueous dispersions of H-SPAN(P) are indicated in Figure 3, where the ratio of the reduced viscosity ($\eta_p/c$) of the diluted suspension to that of the original 1.5% suspension, at the same shear rate, is plotted against concentration. This is not the usual way of plotting intrinsic viscosity data, but is designed to bring all curves to unity at a concentration of 1.5%, independent of shear rate. This modified plot serves to magnify the differences in degree of non-Newtonianism between a 1.5% mixture and a diluted mixture, at the same shear rate. Four series of curves are shown, each labeled with a parameter $r$, which is a ratio of the sodium concentration in the diluent to that in the stock polymer suspension.

The upper set of four curves (solid lines) indicates the effect of dilution of the 1.5% stock solution with deionized water, at several shear rates as indicated on the figure caption. Note particularly that the higher the shear rate, the larger the reduced viscosity ratio, although the value of viscosity alone decreases with increasing shear rate.

![Figure 3](image-url)

Fig. 3. Effect of dilution in water ($r = 0$) and in NaCl solutions ($r = 0.17, 0.30$, and $0.67$) on reduced viscosities $\eta_p/c$ of H-SPAN(P). Reduced viscosities are normalized to unity at concentration of 1.5% by weight. Normalizing factors are $\eta_0$ and $\eta_0^*$. For dilution with water ($r = 0$), effect of shear rate is indicated by the four curves designated: (O) 250 sec$^{-1}$; (X) 100 sec$^{-1}$; (●) 10 sec$^{-1}$; (+) 1 sec$^{-1}$. Results at 100 sec$^{-1}$ are shown for the other dilution processes with values of $r$ as indicated in the figure. The vertical lines indicate the concentration of polymer in gel swollen with excess solvent for each value of $r$, the vertical lines (solid, broken, etc.) being drawn in the same way as the corresponding curve, as described in text under "Effect of Ionic Strength on Gel Volume."
The initial rapid increase in the reduced viscosity ratio with decreasing concentration at $r = 0$ is the expected behavior for a polyelectrolyte in solution, as is the maximum and subsequent decrease in reduced viscosity below a critical concentration. For H-SPAN, this peak, however, occurs at a relatively high concentration (about 0.07%) as compared to that observed for sodium poly(methyl methacrylate) (0.01%) or thymus sodium deoxyribonucleate (also around 0.01). At the lowest shear rate of Figure 3, the reduced viscosity ratios are lowest, and the maximum is shifted to around 0.23%.

Reduced viscosities for three series of dilutions with sodium salt solutions are also indicated in Figure 3. Data are given only for the shear rate of 100 sec$^{-1}$, but data at other shear rates for salt diluents were within 15% of those shown. The $r = 0.17$ example shows a maximum, while in the other two series there is no maximum; but note that all three curves are concave down.

This result was surprising. The objective of this dilution study was to carry out experiments at different values of $r$ in the expectation that a correctly chosen $r$ value, for which polymer configuration is constant during dilution, would give a linear plot of reduced viscosity versus concentration. Such an isoionic dilution would be expected for H-SPAN with $r = 0.3$, but the actual result found for $r = 0.3$ is also concave down (as for 0.17 and 0.67), in contrast to the results reported by Terayama and Wall for postassium cellulose sulfate. This difference between the behavior of H-
SPAN mixtures and previously reported work on polyelectrolyte solutions implies a different mechanism in our systems than in systems in which the polymer is truly in solution. Furthermore, in the H-SPAN experiments, the reduced viscosity ratio is almost constant from \( c \leq 0.7 \) to \( c = 1.5 \), but below 0.7 it falls off rapidly with decreasing concentration.

The effect of dilution at various \( r \) values on the reduced viscosity of Carbopol(P) can be seen from Figure 4. As for H-SPAN, no value of \( r \) giving linear plots could be found.

This inability to obtain linear reduced viscosity–concentration plots under isoionic dilution conditions led us to examine the extent to which the gel fraction in H-SPAN and Carbopol mixtures in water was responsible for these unexpected rheological results.

**Gel and Soluble Fractions**

As noted earlier, it was visibly evident and confirmed by preliminary centrifugation experiments\(^{15}\) that H-SPAN could contain a significant percentage of gel particles. Subsequent ultracentrifugation experiments indicated that gel in aqueous dispersions of H-SPAN would sediment rapidly at 2000 rpm (290 g) when excess solvent is present. In only a few minutes, a discontinuity between gel and solution phases is observable as a steep discontinuity in the Schlieren pattern or as a turbid layer. This boundary was observed to drift slowly with time as the gel compresses under the centrifugal forces in the ultracentrifuge.

A similar effect occurs with Carbopol 941. For this material, the gel sediments with a boundary at a rate of 3500 Svedbergs in 0.05\( M \) NaCl (27°C) and 20,000 Svedbergs in 0.45\( M \) NaCl. The effects of time on boundary position are indicated in Figure 5 for a 0.075% Carbopol(P) mixture in 0.2\( M \) NaCl solution at 83 and 163 min, respectively. As the boundary sediments, a gel layer builds up simultaneously from the bottom of the cell. When these meet, the interface between gel and solution sharpens, and this sharp boundary (Fig. 5B) then drifts slowly lower with time. The sedimentation rates indicate that the gel particles are rather small microscopically but large on a molecular scale, fitting the usual definition of a microgel.

The soluble fractions of both H-SPAN and Carbopol 941 were observed as a sedimenting boundary on increasing the centrifuge speed to 40,000 rpm. Concentration of material represented by the area under the Schlieren curve was calculated using the measured refractive index increments (Table I).

Both our original laboratory preparation H-SPAN(W) and the General Mills H-SPAN(G) had only about 16–20% soluble fraction. The H-SPAN(P) had only a few per cent of soluble material because purification by aqueous solvent extraction tends to remove smaller, water-soluble molecules. Both purified and unpurified Carbopol had about 20% soluble fraction because even small polymeric molecules, while soluble, would not be lost during dialysis.
TABLE I
Fraction of Soluble Polymer as Defined by Area Under Sedimenting Peak During Centrifugation

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Polymer concentration, $C_p$</th>
<th>NaCl concentration, $M$</th>
<th>Soluble fraction recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-SPAN(P), ionic contaminants removed</td>
<td>0.25</td>
<td>0.2</td>
<td>0.021</td>
</tr>
<tr>
<td>Carbopol(P), ionic contaminants removed</td>
<td>0.077</td>
<td>0.3</td>
<td>0.21</td>
</tr>
<tr>
<td>Dextran T-250</td>
<td>0.33</td>
<td>0</td>
<td>0.93</td>
</tr>
<tr>
<td>H-SPAN(W), laboratory preparation</td>
<td>0.13</td>
<td>0.3</td>
<td>0.16</td>
</tr>
<tr>
<td>H-SPAN(G), commercial product</td>
<td>0.25</td>
<td>0.3</td>
<td>0.18</td>
</tr>
<tr>
<td>H-SPAN(S), sonified</td>
<td>0.25</td>
<td>0.3</td>
<td>0.92</td>
</tr>
</tbody>
</table>


Fig. 5. Sedimentation diagram of 0.077% Carbopol(P) in 0.2M NaCl, at 2000 rpm: (a) after 83 min; (b) after 166 min. Bar angle was 45°.

A commercial dextran (which should be completely soluble) was about 93% recoverable (Table I) as soluble material by the centrifugation procedures we employed. An amount indicating that this method for gel/soluble ratio analysis is reasonably valid. Ultrasonification appears to solubilize a large part of the gel: subsequent measurement leads to 92% recovery of the sonified H-SPAN as soluble (Table I). Sonification can lower the viscosity of an H-SPAN dispersion by a factor of $10^3$, the magnitude of the viscosity decrease depending on sample size and total time of sonification. The
viscosity level of 20 cp represents a stable lower limit for our samples, and samples which have reached this level show a time-independent viscosity. A 1% H-SPAN can be reduced from 30,000 cp (γ = 10) to 20 cp. At this level, the viscosity is not only low but Newtonian and the H-SPAN is in solution in the sense that it appears in the boundary sedimenting at 40,000 rpm.

Although the centrifugation method is not highly precise, the result appears unambiguous. Both H-SPAN and Carbopol mixtures consist primarily (80% or more) of gel particles. The H-SPAN gel can be mechanically broken down (by sonification) to a level at which it appears to be largely soluble with a low, shear rate-independent viscosity.

**Effect of Ionic Strength on Gel Volume**

As would be expected for polyelectrolyte gels, the swelling volume of both Carbopol and H-SPAN gel is strongly affected by salt concentration. A preliminary report on the effect of salt on H-SPAN gel sheet swelling was given by Weaver et al. In Figure 6, the weight concentration of polymer in the gel, $Q^{-1}$, is shown as a function of ionic strength. The extent of swelling, $Q$, is the weight of gel per dry weight of polymer. Ionic strength, $\mu$, referred to in Figure 6 is total ionic strength, that is, the added salt concentration plus the ionic concentration contributed by the partial ionization of the polyelectrolyte. The degree of ionization is 30% for H-SPAN and 18% for Carbopol, corresponding to $0.3 \times 0.0794M$ and $0.18 \times 0.182M$ for the 1.5% by weight of initial stock solutions. The $Q^{-1}$-versus-$\mu^{1/2}$ plots are linear for both Carbopol and H-SPAN, and this effect, within the limits of our data, implies infinite swelling at zero ionic strength. This limit is not attainable experimentally, since the polyelectrolyte itself contributes significantly to ionic strength. The relation $Q^{-2} = K\mu$ fits our data better than the expression proposed by Hermans, which is

$$q^{1/2} = A + \frac{B\sigma^2}{\mu}, \quad (1)$$

where $q$ is the degree of swelling defined as volume of gel divided by the volume of the dry material. (Note Hermans' $q$ is equal to $Q\rho$, where $\rho$ is the density of dry polyelectrolyte.) In eq. (1), $\sigma$ is the concentration of the fixed charges in the dry electrolyte. $A$ and $B$ are constants, and $\mu$, is the ionic strength of the outside solution.

The relation of these swelling results to rheological behavior is shown in Figure 3, where the concentrations indicated by the vertical lines show the equilibrium swelling concentrations of H-SPAN microgel at ionic strengths corresponding to the four diluents. Thus, for any dilution series at constant $r$, there is excess solvent present at polymer concentrations less than that designated by the corresponding vertical line. Above that concentration, all the solvent present is in the swollen gel. As long as added solvent is not in excess, the system consists of only swollen gel particles, in intimate contact, and under these conditions the viscosity is high. When the gels
Fig. 6. Reciprocals of swelling volumes $Q^{-1}$ (g dry polymer; g swollen gel) for H-SPAN(P) and Carbopol(P) as functions of $\mu^{1/2}$. For H-SPAN(P) the symbols indicate (▲) data from ultracentrifuge, (△) from settling experiments. For Carbopol(P), all data were from the ultracentrifuge: (●) appropriate polymer concentration for gel volume to be 1/3 to 2/3 of total volume; (○) comparison tests at half this polymer concentration.

are swollen to their maximum extent, which varies with ionic strength. Further addition of diluent serves to separate the swollen particles and provides an interparticle–solvent interface. Under these conditions, viscosity becomes extremely low. These critical concentrations indicated by vertical lines on Figure 3 are determined experimentally. They represent the maximum swelling $Q$ of the gel in excess diluent of the known $\tau$ value. When this swelling is measured, the ionic strength $\mu$ of the swollen gel can be calculated and the final result gives a single $Q$-$\mu$ point on the appropriate line of Figure 6.

The high viscosity of an H-SPAN($Na^+$) powder dispersed in water and neutralized with base can be attributed to swelling of the powder in water to give a system of closely packed, swollen gel particles with essentially no interstitial-free solvent. Viscosity does not depend on the size of the initial powder particles. In a few tests of dried H-SPAN powders, screened to various sizes, the finer powders, while producing smoother suspensions gave rheological properties invariant with powder size. Three samples were examined: (a) the original powder of broad particle size distribution; (2) powder passing through a 105-μ screen; and (3) powder passing through a 30-μ screen.

Analysis of the Dilution Process

The physical process occurring in the thickening action of such materials as H-SPAN and Carbopol is envisaged as follows: When the initial mix-
ture is made up, the powdered polymer swells in the solvent to a limit determined by the amount of solvent available and by the ionic strength of the polyelectrolyte-solvent system. As dilution occurs from the initial 1.5% level of Figure 3, the extent of polyelectrolyte swelling changes to a level determined by the total ionic strength of the diluted system. In dilution with pure water (open circles of Fig. 3), the ionic strength is due only to the polyelectrolyte and, of course, drops steadily as diluent is added. The extent of swelling of the polyelectrolyte gel particles at any dilution is known; and from Figure 6, the extent to which the polymer would swell in the presence of excess solvent at the appropriate total ionic strength level can be calculated. The same argument applies for dilution with salt of known concentration. This argument suggests that the curves of Figure 3 should be replotted in a way reflecting the extent to which the gel would swell at any dilution level if excess solvent were available.

The concentration \(c\) can be multiplied by the factor \(Q\) (obtained from Fig. 6) for the appropriate ionic strength. The reduced viscosities are then recalculated as \(\eta_{\text{re}}/cQ\), and the concentration axis points recalculated as \(cQ\). Normalizing to 1.5% as a reference standard leads immediately to the result shown in Figure 7. All the points of Figure 3 (for \(\dot{\gamma} = 100\ \text{sec}^{-1}\)) fall on a single curve, which drops slowly as \(cQ\) decreases and then plummets rapidly as the concentration level is approached at which the diluting solvent is in excess.

The same result for Carbopol is shown in Figure 8 which is superimposable to the limit of the experimental data on Figure 7.

These last two figures show master curves representing the viscosity behavior of a gel/solvent system in the concentrated suspension region where the volume fraction of gel is large. It is instructive here to draw attention to a fine paper by Sieglaff, who constructed master curves describing
the viscosity behavior of dilute (low volume fraction) gel suspensions. His method and results appear closely related to ours, though his gel was a non-electrolyte (styrene-divinylbenzene) in organic solvents.

Sieglaff chose for each solvent a reference concentration \( c_1 \) at which \( \eta_{sp} = 1 \), assuming very reasonably that solutions having the same specific viscosity contained the same volume fraction of gel. When he replotted his viscosity data using a reduced concentration, \( c = (c/c_1) \), his plots of \( (\eta_{sp}/c) \) versus \( c \) were independent of solvent.

Although the systems we investigated and those by Sieglaff are quite different and although the reference concentrations in the two are quite arbitrary, results suggest that a master curve covering the whole concentration range may well be feasible and independent of either the gel or solvent system. This possibility is being pursued with particular attention to the problem of choosing more logical reference concentrations suitable for both the dilute and concentrated regions. These may well be the critical concentrations, indicated in our system by the vertical lines of Figure 3, at which the gel is fully swollen but with no excess solvent present.

Attention should also be drawn here to analogous considerations discussed by Simha and Zakin in relation to the solution viscosities of linear, flexible high polymers. They found that, in good solvents, curves of \( \eta_{sp}/[\eta]c \) versus the reduced variable \( c/c_0 \) were approximately superimposable. The reducing parameter \( c_0 \) for the concentration axis \( c \) is the concentration of incipient molecular overlap, as derived from molecular dimensions at infinite dilution. The reduced variable on the viscosity axis, \( [\eta]c \), is closely related to the reduced concentration scale, \( c/c_0 \). "Both," in the terms of Frisch and Simha, "express the average mass of polymer per unit volume relative to the same quantity within the molecular coil." This approach to corresponding state relations for the viscosity of moderately concentrated solutions has been extended by Utracki and Simha.
The analogy between the treatment of viscosity data for nonelectrolyte gel particle suspensions and electrolytic gel particle suspensions on the one hand and the treatment of nonelectrolytic polymer solution viscosity data on the other hand is extremely fascinating. In the case of cross-linked gel particles, and particularly in the H-SPAN system where there is evidence for charged groups on the swollen gel surface, no particle interpenetration or molecular entanglement seems possible. In the polymer solution systems, molecular interpenetration and entanglements would be expected to have significant effects. More detailed comparison of the rheology of concentrated gel suspensions and concentrated polymer solutions might be of considerable help in understanding rheological phenomena.

SUMMARY

Isoionic dilution of polyelectrolytes in solution leads to linear reduced viscosity-versus-concentration plots, as shown experimentally in the literature.\textsuperscript{13} Dilution conditions under which this behavior is observed could not be found for H-SPAN or Carbopol systems. Furthermore, centrifugation revealed that materials in these systems were present in liquid as macroscopic, swollen deformable gel particles. The mixtures are not solutions in any sense of the word. They are dispersions in which at high concentration levels no excess solvent is present. All solvent added serves to swell the gel. At a low enough concentration, dilution leads to a dispersion of fully swollen gel material in the excess solvent, the system under these conditions showing very low viscosity approaching that of the excess solvent alone.

At any ionic strength $\mu$, the amount of swelling which the gel would undergo in the presence of excess solvent was measured and is given by $Q$. The product of the concentration $c$ for a given mixture and $Q$, the gel swelling that would be experienced if solvent of the given ionic strength were present in excess, is a measure of how far the swollen gel in the mixture is from its equilibrium swelling. For a given shear rate, all dilution curves, independent of diluent, empirically reduce to a single curve when $cQ$ rather than $c$ is used as the concentration variable.

When a thickening agent, such as H-SPAN or Carbopol, is present in a mixture at a level such that the individual gel particles absorb all the solvent, the system consists only of closely packed and swollen gel with no free solvent. Under these conditions, the viscosity is high. On dilution or on increasing the ionic strength, a level is reached where solvent is in excess. The swollen gel particles are no longer in intimate contact, being separated by free solvent and the viscosity drops to low levels.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.
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