DILUTE SOLUTION PROPERTIES OF
DRAG REDUCING POLYMERS

by
N. D. Sylvester and J. S. Tyler

May, 1970

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FOREWORD

The technical report was prepared by the Thermal Systems Group under project THEMIS at the University of Notre Dame, College of Engineering. The co-authors, Dr. N. D. Sylvester and Mr. J. S. Tyler are respectively Assistant Professor and Research Assistant in the Department of Chemical Engineering.

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This technical report has been reviewed and approved for submittal to the sponsoring agency, May, 1970.

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Group Leader, Thermal Systems

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ABSTRACT

Experimental data on the dilute solution viscosity behavior of two effective drag reducing polymers (polyethylene oxide-Polyox and Separan - a partially hydrolyzed polyacrylamide) in various solvents (distilled water, salt water and simulated sea water) is presented and discussed. The unusual viscosity behavior observed for both polymers in the simulated sea water for concentrations less than thirty parts per million is explained by postulating an interchain ionic bonding effect for the Separan solutions and an ion-dipole, salt-polyether complex formation in the Polyox solutions. Tentative conclusions concerning the effectiveness of the polymers as drag reducers in the solvents and concentrations tested are presented.
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<td>a</td>
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<tr>
<td>c</td>
<td>polymer concentration (gram/deciliter)</td>
</tr>
<tr>
<td>d₂</td>
<td>polymer density (g/ml)</td>
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<tr>
<td>K</td>
<td>constant in Mark-Houwink equation (See Eq. (6))</td>
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<tr>
<td>k'</td>
<td>Huggins' hydrodynamic interaction parameter (dl⁻¹)</td>
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<td>[η]</td>
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I. INTRODUCTION

Drag reduction is an increase in the volumetric flow rate at a given pressure drop due to the addition, most commonly, of a small amount (e.g., 100 weight parts per million or less) of a linear, high molecular weight polymeric material to a low viscosity liquid, like water. Examples of polymers which have been used in aqueous solution include; polyethylene oxide (Polyox), Carboxymethylcellulose (CMC), guar gum, and Separan — a partially hydrolyzed polyacrylamide (see Patterson et al., 1969 for a complete bibliography). A very large number of experimental studies have been carried out (Patterson et al., 1969) to investigate this extremely interesting and perplexing phenomena. However, only a few of these have been theoretical (Savins, 1964; Astarita, 1965; Hershey and Zakin, 1967; Elata et al., 1966; Meyer, 1966; Seyer and Metzner, 1967 and 1969; Rodrigues et al., 1967; Patterson and Zakin, 1968; and Astarita, et al., 1969) and, although there are a number of semitheoretical correlations presently available, none of them are totally acceptable. Many researchers are agreed that the cause of drag reduction is some kind of interaction between the turbulent eddies and the dissolved macromolecules near the solid boundaries (Gadd, 1965; Goldstein et al., 1969; Squire et al., 1967; and Nicodemo et al., 1969) whether or not viscoelasticity is considered.

As part of our studies to elucidate the mechanism of drag reduction, we have investigated the viscosity behavior of dilute
solutions of drag reducing polymers. Since the expected naval use of the drag reduction phenomena is in the ocean, we have taken data not only in pure water but also in salt water and simulated sea water. Dilute solution viscosity behavior gives one a semi-quantitative feel for the solvent-polymer and polymer-polymer intra and inter-molecular interactions in solution. The intrinsic viscosity of a solution is an indication of these interactions and the greater its magnitude the greater the interactions.

The intrinsic viscosity, which represents the capacity of a polymer to enhance the viscosity of a solvent, is defined by

\[
[\eta] = \lim_{c \to 0} \frac{\eta - \eta_s}{c \eta_s} = \lim_{c \to 0} \frac{\eta_{sp}}{c} 
\]

where \( \eta \) is the solution viscosity, \( \eta_s \) is the solvent viscosity and \( c \) is the concentration of polymer. The specific viscosity, \( \eta_{sp} \), represents the incremental viscosity attributable to the polymeric solute. The ratio \( \eta_{sp}/c \) is a measure of the specific capacity of the polymer to increase the relative viscosity and has been called the reduced viscosity.

The viscosity behavior at low concentrations can be described by the Huggins' equation (Huggins, 1958)

\[
\frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c + ... 
\]

The intrinsic viscosity is a characteristic function of the single macromolecule in a particular solvent. The Huggins' constant, \( k' \),
is a measure of the hydrodynamic interaction between macromolecules. Values of \( k' \) between 0.4 and 0.6 have been registered (Huggins, 1958 and Flory, 1953) for uncharged flexible coils. However, in solutions of ionized colloids strong electrostatic interactions exist between the charged particles and between their mutually interpenetrating atmospheres and accordingly much higher values of \( k' \) are expected and have been observed (Huggins, 1958 and Stromberg, 1966).

Many theoretical studies have been conducted (Huggins, 1968 and Flory, 1953) to predict the intrinsic viscosity. Einstein (1906 and 1911) treated the case of a dilute solution of spherical solute particles which were large relative to the size of the solvent molecules. These large spheres block the motion of some of the solvent molecules and so produce an increase in viscosity. The quantitative relation is

\[
\frac{n_{sp}}{c} = \frac{5}{2d_2}
\]  

(3)

where \( d_2 \) is the density of the solute. Guth et al. (1936 and 1938), extending Einstein's hydrodynamic treatment to allow for the mutual interference of the solute particles, obtained the relation

\[
\frac{n_{sp}}{c} = \frac{5}{2d_2} + \frac{14.1c}{d_2^2} + \ldots
\]  

(4)
These relations depend on the assumption of large, impervious, spherical solute particles. For solute and solvent particles of the same size, with solvent-solvent, solvent-solute and solute-solute attractions equal, the viscosity of the solution should obviously be identical with that of the pure solvent; hence

$$\eta_{sp} = 0 \text{ and } [\eta] = 0$$

(5)

For spherical solute particles of intermediate size the viscosity behavior should be intermediate between that corresponding to Equation (4) and that of Equation (5); i.e., $[\eta]$ should be between about two and one-half and zero. However most high molecular weight $[M-O(10^6)]$ polymer solutions have intrinsic viscosity values greater than two and one-half which may be due to a number of factors depending on the particular polymer and solvent and including large solute-solvent interactions (very "good" solvents), structural factors (chain stiffness), chain entanglements or association and intra-molecular repulsions (polyelectrolytes). The relationship between the intrinsic viscosity and molecular weight for long chain molecules is given by Mark-Houwink (Mark, 1938 and Houwink 1940) equation

$$[\eta] = KM^a$$

(6)

where $K$ and $a$ are constants dependent on the particular polymer and solvent. The exponent $a$ is generally found between one-half and one, although, theoretically it should have the values
a = 0 for impervious spheres

a = 2 for extended rodlike molecules

The hydrodynamic size of a macromolecular coil in solution can be related to the polymer molecular weight by the relation (Tanford, 1965; Tompa, 1956; Morawetz, 1965; and Birshtein and Ptitysn, 1966)

\[ r_o = \left( \frac{K M^{a+1}}{\phi} \right)^{1/3} \]  

where \( r_o \) is the hydrodynamic radius of the coil, \( M \) is the molecular weight, \( K \) and \( a \) are the constants in the Mark-Houwink intrinsic viscosity equation, and \( \phi \) depends on solvent power and molecular weight. From Equation (7) it can be shown that for a given polymer-solvent system the higher \( M \) the larger \( r_o \). Also for a polymer of given \( M \) the "better" the solvent the larger \( r_o \). Conversely, the smaller the attractions between like and unlike molecules the more tightly coiled the average chain will be and the smaller \([\eta]\) for a given molecular weight. Thus the magnitude of \([\eta]\) for a given molecular weight is a measure of the size of the macromolecular coil which is determined for flexible, linear high polymers primarily by the relative importance of like-like and like-unlike intermolecular and intra-molecular interactions between the solvent and polymer segments.
II. EXPERIMENTAL RESULTS

Two polymers, known to be effective drag reducers (Patterson et al., 1969), were studied. They were polyethylene oxide (Polyox-P301-Union Carbide) and Separan AP30 (SAP30-Dow Chemical) a partially hydrolyzed polyacrylamide. The chemical structures of these flexible, high molecular weight, linear polymers can be represented by

\[
\text{Polyox-P-301} \quad \left[ \text{CH}_2-\text{CH}_2-\text{O} \right]_n \quad M = 4 \times 10^6
\]

\[
\text{Separan-SAP30} \quad \left[ \left( \text{CH}_2-\text{CH}-\text{CH}_2 \right) \left( \text{CH} \right) \right]_m \quad M = 2 \times 10^6
\]

where \( m = 3 \) and \( n \) large

The spatial relationship of the ether linkages in P301 is favorable for forming association complexes. It has been suggested (Sylvester, 1968) that two water molecules are associated with each ether oxygen by hydrogen bonding in the dissolved polymer chain. Such hydration contributes some measure of stiffness to the molecules since they are not as flexible in solution as might be expected and this has been born out by intrinsic viscosity measurements. It is also likely that P301 molecules associate with each other which also would cause higher [\( \eta \)] values. SAP30 is an anionic polyelectrolyte. It is well known that polyelectro-
lyte molecules are much more extended in solution due to the electrostatic repulsion of the chain ionic groups which leads to much higher \( [\eta] \) values (Flory, 1953 and Morawetz, 1965).

For P301, two different solvents were tested, distilled water and simulated sea water. Viscosity data were measured at 30°C using Ubbelohde dilution viscometers, over a concentration range from 1 to 500 weight parts per million. For SAP50, three different solvents were used, distilled water, salt water (0.55M NaCl) and simulated sea water. The composition of the simulated sea water shown in Table 1 is essentially that given by the Office of Saline Water. The experimental data is represented by plotting both \( \eta_{sp}/c \) and \( \ln \eta_r/c \) versus \( c \), where \( \eta_r = \eta_{sp} + 1 \) is the relative viscosity. Extrapolation of the two resulting curves to zero concentration yields the same value of the intrinsic viscosity.

Figure 1 is the required plot for P301 in distilled water and Figure 2 for P301 in sea water. The plots are very similar and there is apparently little difference between the solutions for concentrations between 30 and 500 ppm. The \([\eta]\) values are 10.6 and 9.6 \( \text{dl} \)/g respectively. Little (1969) found a value of 20.0 for Polyox coagulant (M=6x10^6). The data are replotted in Figure 3 as in \( \eta_{sp}/c \) vs. \( c \) to show the behavior at concentrations less than 30 ppm. As in Figures 1 and 2 linear extrapolation yields the corresponding \([\eta]\) values. However, a striking difference is noted between the two solutions. The reduced viscosity curve for P301-sea water rises as \( c \to 0 \) while the reduced viscosity curve for
<table>
<thead>
<tr>
<th>Component</th>
<th>Molarity (moles/liter)</th>
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<tr>
<td>NaCl</td>
<td>0.4756</td>
</tr>
<tr>
<td>KCl</td>
<td>0.00923</td>
</tr>
<tr>
<td>XBr</td>
<td>0.00084</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.01034</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>0.05417</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>0.55018</strong></td>
</tr>
</tbody>
</table>

**TABLE 1**
Composition-Simulated Sea Water
Figure 1  Plots of $\eta_{SP}/c$ and $\ln \eta_r/c$ for P301 in distilled water at 30.0°C.
Figure 2: Plots of $\eta_{sp}/c$ and $\ln \eta_r/c$ vs. $c$ for P301 in sea water at 30°C.
Figure 3  Plots of $\ln \left( \frac{\eta_{SP}}{c} \right)$ vs $c$ for P301 in sea water and in distilled water at 30.0°C.
P301-distilled water falls. The sharp curvature represents a rather sudden change in the intermolecular interactions. The sudden decrease is not unexpected, even though it has rarely been reported because concentrations this low are not normally studied and is possibly due to either the existence of entanglements between chains or macromolecular association above 30 ppm. The sudden increase, however, is curious. It quite possibly means that a significant chain expansion is taking place.

The SAP30-water data shown in Figure 4 presents somewhat of a problem. If the standard concentration range of 100-500 ppm is investigated, the intrinsic viscosity is found to be 106 (dl/g) an extremely high value. Williams (1970) obtained the same value for \([\eta]\). It is seen that \(\eta_\text{sp}/c\) decreases sharply for \(c\) less than 25 ppm. A smooth curve drawn through all the data appears to intersect the ordinate at approximately \([\eta] = 64\) dl/g, also quite high. Figure 5 shows \(\eta_\text{sp}/c\) vs. \(c\) for SAP30-simulated sea water, the ln \(\eta_\text{p}/c\) data are not shown as all the points are nearly coincident with the ones shown at their respective concentrations. If the data for \(c > 30\) ppm are extrapolated to \(c = 0\), \([\eta] = 6.0\) (dl/g), more than an order of magnitude lower than for distilled water. However for \(c < 30\) ppm a spectacular increase in \(\eta_\text{sp}/c\) occurs as \(c\) decreases. Figure 6 shows \(\eta_\text{sp}/c\) and ln \(\eta_\text{p}/c\) vs. \(c\) for SAP30-salt water. The value of \([\eta]\) found by dual extrapolation, 10.4 (dl/g), is somewhat higher than the SAP30-sea water value and nearly an order of magnitude less than the SAP30-distilled
water value. A comparison between the SAP-10-sea water and the SAP30-distilled water reduced viscosity behavior which clearly shows the low concentration behavior is presented in Figure 7. The intrinsic viscosity values of the particular solutions are summarized in Table 2.
Figure 4. Plots of $\eta_{sp}/c$ and $\ln \eta_{w}/c$ vs. $c$ for SAP30 in distilled water at $30.0^\circ$C.
Figure 5 Plot of $\eta_{sp}/c$ vs. $c$ for SAP30 in sea water at 30.0°C.
Figure 6 Plots of $\eta_{sp}/c$ and $\ln \eta_r/c$ vs. $c$ for SAP50 in 0.35M NaCl at 30.0°C.
Figure 7: Plots of $\ln (\eta_{sp}/c)$ vs. $c$ for SAP30 in sea water and distilled water at 30.0°C.
<table>
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<th>Polymer</th>
<th>Solvent</th>
<th>[η] dl/g</th>
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<tbody>
<tr>
<td>Polyox-P301</td>
<td>distilled water</td>
<td>10.6</td>
</tr>
<tr>
<td>Polyox-P301</td>
<td>simulated sea water</td>
<td>9.6</td>
</tr>
<tr>
<td>Separan-SAP30</td>
<td>distilled water</td>
<td>106.0</td>
</tr>
<tr>
<td>Separan-SAP30</td>
<td>0.55M NaCl-Salt water</td>
<td>10.4</td>
</tr>
<tr>
<td>Separan-SAP50</td>
<td>simulated sea water</td>
<td>6.0</td>
</tr>
</tbody>
</table>
III. DISCUSSION OF RESULTS

First some overall comparisons can be made between the Polyox and Separan distilled water solutions. Since the molecular weights of the two polymers are nearly the same although the distributions are unknown and \([\eta]_{\text{SAP30}}\) is nearly an order of magnitude greater than \([\eta]_{\text{P301}}\) it is obvious that the SAP30 chains are considerably more expanded in solution. This of course is expected since SAP30 is a polyelectrolyte and the electrostatic repulsions between the ionic groups on the chains will cause significant expansion. Upon comparing the SAP30-distilled water results with the SAP30-sea water and SAP30-salt water results, it is apparent that the added electrolyte has essentially neutralized the electrostatic repulsions between chain ionic groups and caused a considerable contraction of the chains. This type of behavior is well known for polyelectrolytes (Flory, 1953; Morawetz, 1965 and Stromberg, 1966). Similar data have been obtained by Williams (1970) for SAP30 at various NaCl concentrations. Figure 7 shows that for \(c < 10\) ppm the SAP30 intermolecular interactions are the same order of magnitude in the sea water as in the distilled water. This curious behavior can be explained as follows: In the SAP30-distilled water system the expansion of the polyions eventually reaches an upper limit and the decrease of \(\eta_{sp}/c\) upon further dilution merely reflects the decreasing interference between the expanded chains. For the SAP30-sea water solutions the increase in \(\eta_{sp}/c\) as \(c\) decreases is believed to be due to an interchain bonding effect.
caused by the presence of the divalent ions (Ca$^{++}$, Mg$^{++}$). That is, the negative charges on two separate polymer molecules are bridged by a divalent ion causing increased intermolecular interaction. The interchain bonding should be a relatively unimportant factor at higher concentrations, but leads to aggregate structures at low concentrations, with the resulting increase in $n_{sp}/c$. The fact that no such reduced viscosity increase was noted in the SAP30-salt water solutions, which have no divalent ions, lends support for the given explanation.

The curious behavior of the P301-sea water solutions, for C < 25 ppm shown in Figure 3 can be explained on the basis of the extensive investigation of Pedersen (1967). Pedersen showed that many cyclic polyethers (Polyox is a polyether) form complexes with the salts of the elements belonging to the following groups of the periodic table: all in 1A and 1B, most in 11A; some in 11B and a few in 111A, 111B and IVB. These compounds are salt-polyether complexes formed by ion-dipole interaction between the cation (e.g., sodium) and the oxygen atoms symmetrically placed in the polyether ring. The preferred rings are those containing five or six oxygen atoms each separated from the next by two carbon atoms which is the spacing of the oxygen atoms in the Polyox chains. Pedersen listed the following conditions necessary for the formation and the factors influencing the stability of the complexes.
1) The relative sizes of the ion and the hole in the polyether ring.
2) The number of oxygen atoms in the polyether ring.
3) The coplanarity of the oxygen atoms.
4) The symmetrical placements of the oxygen atoms.
5) The basicity of the oxygen atoms.
6) Steric hindrance in the polyether ring.
7) The tendency of the ion to associate with the solvent.
8) The electrical charge of the ion.

The polyethylene oxide polyether investigated here satisfies the necessary conditions listed. The flexible Polyox molecules can easily orient themselves to accommodate the available cations provided the solutions are dilute enough. The reorientation of the molecules to form complexes results in an expansion of the polymer chain. Pedersen also notes that a complex is more stable the greater the number of oxygen atoms (provided they are coplanar and symmetrically distributed in the polyether ring) and the more basic the oxygen atoms, one attached to an aromatic carbon being less basic than one attached only to an aliphatic carbon atom.

It can be visualized that the complexing causes a transformation of the polymer molecule from the "ball of twine" configuration to a partially extended and helical structure. That is, one can picture an imaginary hollow circular cylinder around which a part of the polymer molecule is wound in a tight helical coil and along whose center line lie the cations positioned to provide maximum
ionic-dipole attraction with the oxygen atoms and minimum charge repulsions between the cations. This type of configurational re-
arrangement, due to complexing with metal salts, results in not only extended molecules but also produces regions of rigidity along a given chain which also contributes to chain expansion. The ion-
dipole interaction induced chain expansion is only observed at the very low concentrations because its effect is masked at the higher concentrations by the intermolecular entanglements and association.

Since complexes are formed according to the equation,

\[ S \left[ (\text{metal}^{m+})_{n \text{ solvent}} \right] + \text{polyether}^z \]

\[ \text{polyether} - s(\text{metal}^{m+}) + s(n \text{ solvent}) \]

the formation of the complex of a particular ion will be minimized or prevented if the ion is too strongly associated with the solvent. However, Pedersen found that sodium readily formed stable complexes with his cyclic polyethers. Although the above hypothesis may not be the only explanation of the observed very dilute sea-water solution phenomena, it is qualitatively consistent with the experimental data.
IV. CONCLUSIONS

A number of tentative conclusions, requiring actual drag reduction measurements which are in progress, can be drawn in regard to the use of Polyox and Separan as drag reducing polymers. These conclusions are based on the belief that for a given polymer concentration it is primarily the size of polymer coil or group of polymer coils which determines the extent of the drag reduction for a given average velocity and tube diameter. This is born out by the results of Little (1969) and others (Hershey and Zakin, 1967; Virk et. al., 1966; and Hoyt and Soli, 1965) which show that the polymer concentration (for a given polymer) required to produce a given percentage drag reduction decreases as the molecular weight and thus the coil size of the macromolecules increases. First Polyox-P301 should be nearly as effective in sea water as it is in distilled water and on the basis of Figure 3 possibly considerably more effective in sea water at concentrations of less than 25 ppm. Separan SAP30 on the other hand should be much less effective in sea water except possibly at the very low concentrations (1 ppm) as shown in Figure 7. For concentrations greater than 25 ppm in sea water Polyox should be slightly more effective than Separan. However for C < 10 ppm both may become more effective with Separan somewhat better. Finally, it must be emphasized that actual drag reduction measurements must be made at the very low concentrations (<10 ppm) using the simulated sea water as the solvent to properly assess the effectiveness of Polyox and Separan.
One word of caution worth mentioning is that Polyox is much more susceptible to shear degradation than Separan (Sylvester, 1968). It is hoped that the results, discussion and conclusions given above will be of value to those evaluating the effectiveness of various drag reducing polymers and that the information presented will increase our understanding of this very complex phenomena.
V. BIBLIOGRAPHY

Guth, E. and Simha, R., Kolloid-Z., 74, 266 (1936).
Williams, H. C., Private Communication, 1970.
DILUTE SOLUTION PROPERTIES OF DRAG REDUCING POLYMERS

N. D. Sylvester and J. S. Tyler

May 1970

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In-House Account No. UND-99850

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Experimental data on the dilute solution viscosity behavior of two effective drag reducing polymers (polyethylene oxide-Polyox and Separana partially hydrolyzed polyacrylamide) in various solvents (distilled water, salt water and simulated sea water) is presented and discussed. The unusual viscosity behavior observed for both polymers in the simulated sea water for concentrations less than thirty parts per million is explained by postulating an interchain ionic bonding effect for the Separan solutions and a ion-dipole, salt-polyether complex formation in the Polyox solutions. Tentative conclusions concerning the effectiveness of the polymers as drag reducers in the solvents and concentrations tested are presented.
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