

Temperature and Concentration Effects on the Rheological Properties of Polymer Solutions

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SUMMARY The effects of temperature and concentration on the rheological properties of polymer solutions are investigated. The fluids studied are three aqueous solutions of Separan (polyacrylamide) and four blends of Separan with corn syrup at different polymer concentrations. The temperature range used in the study is from 20° to 50°C. Shear stress and first normal stress difference are measured as a function of shear rate on a Weissenberg Rheogoniometer. Both shear stress and first normal stress difference obey power law relationship over the shear rate range $1 \leq \dot{\gamma} \leq 1000 \text{ sec}^{-1}$. The effects of temperature and concentration can be adequately described by an Arrhenius-type exponential function and a power function respectively.

1 INTRODUCTION

There is a vast amount of literature dealing with the rheological characterisation of polymer solutions and melts. Most of the reported data is in the form of shear stress vs. shear rate, and to a lesser extent, first normal stress difference as a function of shear rate. Very seldom are the effects of temperature and concentration on fluid properties being considered, despite their importance in many engineering design problems. For example, in many polymer processing operations, proper selection of system temperature and concentration is important not only for processability purposes but also for controlling final product quality. A number of workers (e.g. 1-4) have studied the effect of temperature on the apparent viscosity of polymer solutions and melts but few have investigated its effect on fluid elasticity. Recently, Meissner⁽⁵⁾ studied the temperature effect on fluid elasticity of low density polyethylene melt, and concluded that the effect is only moderate to slight, about a factor of ten smaller than the corresponding effect on melt viscosity. By contrast, Han⁽⁶⁾ found a larger effect of temperature using the high density polyethylene and polypropylene melts.

In this work the effects of temperature and concentration on rheological properties of dilute polymer solutions are investigated. A polyacrylamide polymer was chosen as the test material because it exhibits a strong elastic characteristic even at very low concentration. Furthermore, it has a very broad scope of industrial applications. This type of polymer has been used effectively as flocculant, thickening agent, and film former in industrial waste treatment, in mining and ore processing, in petroleum industry and in many other process industries. It has also been proved to be a very effective drag-reducing agent.

2 EXPERIMENTAL

Separan MG-500 is a medium viscosity, high molecular weight (order of 10^6) polymer of polyacrylamide manufactured by Dow Chemical. The polymer is readily soluble in water and exhibits excellent stability under normal conditions of storage. The polymer solution is also highly resistible to shear degradation. Seven Separan solutions were used in the experiment: three aqueous solutions of concentration

0.50, 0.75 and 1.0 percent by weight Separan; and four Separan-water-corn syrup (SWC) blends made up of 0.03, 0.08, 0.10 and 0.15 percent Separan, 4.0 percent water, and the rest corn syrup, respectively.

The aqueous solutions were prepared by slowly adding the required amount of Separan powder, over a period of 15 minutes into the vortex of an agitated container filled with distilled water. Mixing speed was kept very low to minimise the mechanical degradation of polymer and to avoid excessive entrainment of air. When the powder had dissolved completely, the solution was transferred and stored in air-tight screw-top bottles for 48 hours before being characterised. In the preparation of SWC blends, the aqueous Separan solution of fixed concentration was first made up and then blended with the corn syrup in a mixing tank. Agitation was continued for about 2 hours until the mixture became homogeneous.

The test fluids were characterised over a temperature range from 20°C to 50°C on an R-16 cone-and-plate Weissenberg Rheogoniometer. The shear stress τ and the first normal stress difference $P_{11} - P_{22}$ were measured over the shear rate range of $4 \leq \dot{\gamma} \leq 1100 \text{ sec}^{-1}$ for the aqueous solutions and $1 \leq \dot{\gamma} \leq 300 \text{ sec}^{-1}$ for the SWC blends. The reproducibility of the experimental results were within $\pm 2\%$ and $\pm 5\%$ for the shear stress and the first normal stress difference respectively. An electrically heated chamber surrounding the cone-and-plate assembly was used to control the temperature of the test fluid to within $\pm 0.4^\circ\text{C}$ of the set temperature. Evaporation of sample during shear was prevented by the application of a film of an inert silicone oil, of similar viscosity as the test fluid, around the circumference of the assembly⁽⁷⁾. The normal stress data were all corrected for inertial effects⁽⁸⁾.

3 RESULTS AND DISCUSSION

All test fluids were found to be pseudoplastic (shear-thinning) and highly elastic. The SWC blends were considerably more viscous and elastic than the aqueous solutions. Figure 1 presents a plot of shear stress and first normal stress difference as a function of shear rate for the 1.0% aqueous Separan solution and for the 0.15% SWC blend at 20°C. It can be seen that all flow curves are linear on logarithmic scales over the shear rate ranges used in this investigation. The shear stress and the

first normal stress difference for the SWC blend are at least an order of magnitude larger than the aqueous solution at the same shear rate. However, both fluids have similar order of stress ratio, which is defined as the ratio of first normal stress difference to shear stress. The stress ratio is a dimensionless group related to Weissenberg number, a parameter frequently used to characterise polymer flow behaviour.

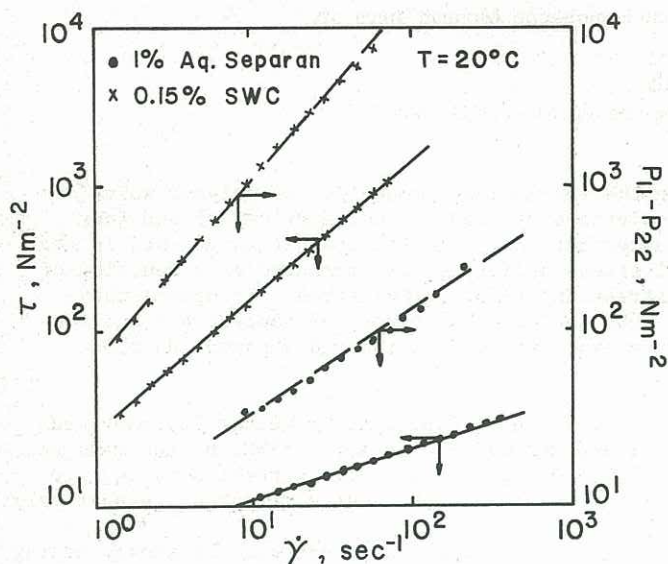


Figure 1 Flow curves for 1.0% Aqueous Separan and 0.15% SWC at 20°C

Several simple non-Newtonian fluid models have been used to describe the pseudoplastic behaviour of a fluid. The simplest of these is the power-law or Ostwald-de Waele model

$$\tau = K\dot{\gamma}^n \quad (1)$$

where n and K are the flow behaviour and fluid consistency indices respectively. When $n = 1.0$, Eq.(1) reduces to the Newtonian fluid model, and K becomes the viscosity of the fluid. At other values of n , the apparent viscosity, defined as

$$\eta_{ap} = K\dot{\gamma}^{n-1} \quad (2)$$

is a function of shear rate. The linearity of the flow curves shown in Fig. 1 indicates that the shear stress-shear rate data for both aqueous solution and SWC blend can be adequately describe by Eq. (1). Equation (1) has been successfully applied to all test fluids at various concentrations and temperatures, with an average deviation of less than $\pm 3\%$. It is interesting to compare the slopes of the two τ vs. $\dot{\gamma}$ flow curves shown in Fig. 1. An n value of 0.85 was obtained for the SWC blend, and 0.34 for the aqueous solution. This implies that the effect of shear thinning for the blend is much smaller than the aqueous solution. For example, the apparent viscosity of the aqueous solution reduces by 79%, from 1.12 to 0.234 Ns/m², over a shear rate range $10 \leq \dot{\gamma} \leq 100 \text{ sec}^{-1}$; whereas the blend experiences a reduction of only 28%, from 20.2 to 14.5 Ns/m².

It can be seen from Fig. 1 that the variation of the first normal stress difference with shear rate also obeys a power-law relation. Hence, an expression similar to Eq. (1) may be written for the first normal stress difference

$$P_{11} - P_{22} = \sigma\dot{\gamma}^s \quad (3)$$

The parameters σ and s have similar physical significance as K and n in Eq. (1). Han⁽⁶⁾ used a similar expression in describing his polyethylene and polypropylene data. In this work all the normal stress data have been correlated using Eq. (3). The average deviation between the experimental data and Eq. (3) is about $\pm 5\%$.

Figure 2 shows the flow curves for the 0.5% aqueous solution obtained at four different temperatures. The flow curves represent the best-fit lines through the experimental points, with the same degree of accuracy as those shown in Fig. 1. The experimental points have not been drawn to avoid crowding of the figure. It can be observed that the four shear stress curves are nearly parallel to each other, as are the four normal stress curves. This indicates that indices n and s are insensitive to changes in temperature, and can be assumed to be independent of temperature. Average values of n and s for all test fluids are tabulated in Table I. Since n represents the degree of shear-thinning or the deviation from Newtonian behaviour, it is expected that its value will decrease with increasing polymer concentration.

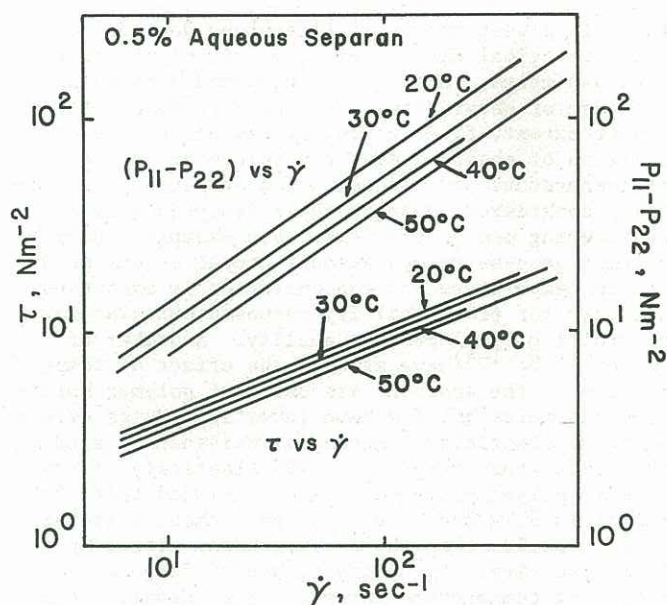


Figure 2 Flow curves for 0.5% Aqueous Separan at four different temperatures

The consistency coefficients K and σ , obtained from the intercept of the τ vs. $\dot{\gamma}$ and $(P_{11} - P_{22})$ vs. $\dot{\gamma}$ plots respectively at shear rate equal to unity, are strongly temperature dependent. The effect of temperature on these parameters can be successfully represented by the following exponential (Arrhenius-type) relations :

$$K = \alpha \exp(\beta/T) \quad (4)$$

and

$$\sigma = \phi \exp(\xi/T) \quad (5)$$

The Arrhenius-type expression has been used for many years to represent the effect of temperature on fluid viscosity. The parameters β and ξ can be related to the "viscous" and "elastic" flow activation energies, respectively. The correlations based on Eqs. (4) and (5) are presented in Fig. 3 for the three aqueous Separan solutions. Values of

the parameters evaluated from Fig. 3 are tabulated in Table II. Although values of β and ξ appear to decrease with increasing concentration, the fluid actually becomes more viscous and elastic at higher polymer concentration, as indicated by the magnitudes of α and ϕ . Contrary to the findings of Meissner⁽⁵⁾, the effect of temperature on fluid elasticity appears to be larger than its effect on fluid viscosity for aqueous Separan solutions.

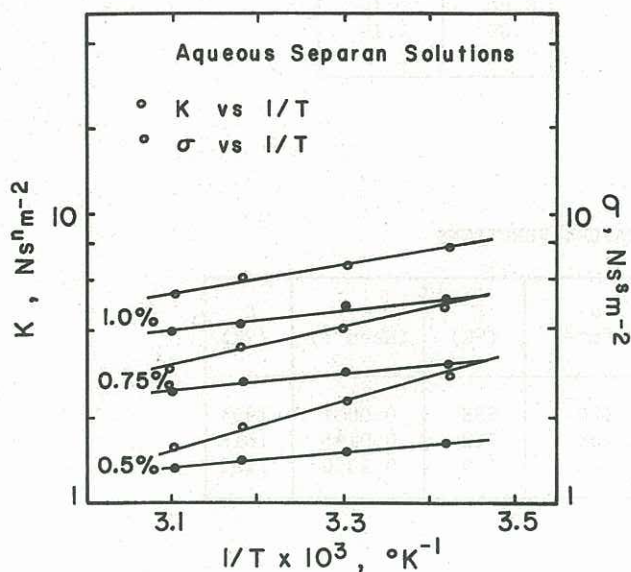


Figure 3 Effects of temperature on parameters K and σ for the Aqueous Separan Solutions

The effect of polymer concentration on rheological properties can be seen in Fig. 4, which depicts the flow curves for the three aqueous solutions at 20°C. Both slope and intercept of the flow curve vary with concentration. While n and s decrease with increasing polymer concentration, the fluid becomes more viscous and elastic as the concentration increases, as reflected from the values of K and σ . No attempt was made to correlate n and s with concentration, since the effect of concentration on these two parameters was relatively insignificant compared to its effect on K and σ . The variation of K and σ with concentration can be empirically described by a power function

$$K = K_0 C^p \quad (6)$$

and

$$\sigma = \sigma_0 C^q \quad (7)$$

where C is the polymer concentration in weight percent, and K_0 , σ_0 , p and q are empirical parameters which may be functions of temperature. Equations (6) and (7) imply that a plot of $\log K$ vs. $\log C$, and $\log \sigma$ vs. $\log C$ is linear with the slope equal to p or q , and intercept K_0 or σ_0 respectively. The validity of these equations is illustrated in Fig. 5 for all test fluids at 20°C. Similar plots have also been constructed for fluids at other temperatures. Values of the parameters evaluated from these figures are tabulated in Table III.

Except for parameter p , the other three parameters are temperature dependent. Value of q increases slightly with temperature, whereas K_0 and σ_0 decrease when temperature increases. The latter signifies a reduction in apparent viscosity and apparent elasticity with increasing temperature

holding the concentration constant. Figure 5 indicates that the influence of polymer concentration on fluid elasticity appears to be much stronger than its effect on apparent viscosity for SWC blend, and about the same degree for the aqueous Separan solutions.

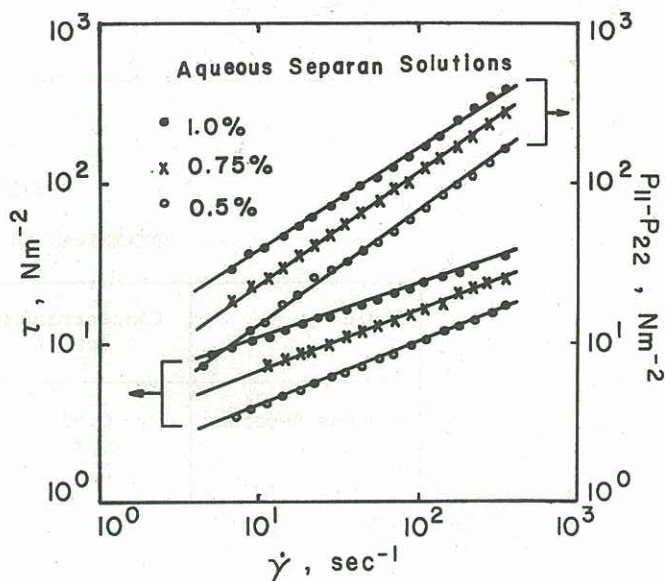


Figure 4 Flow curves for three Aqueous Separan Solutions of varying concentration at 20°C

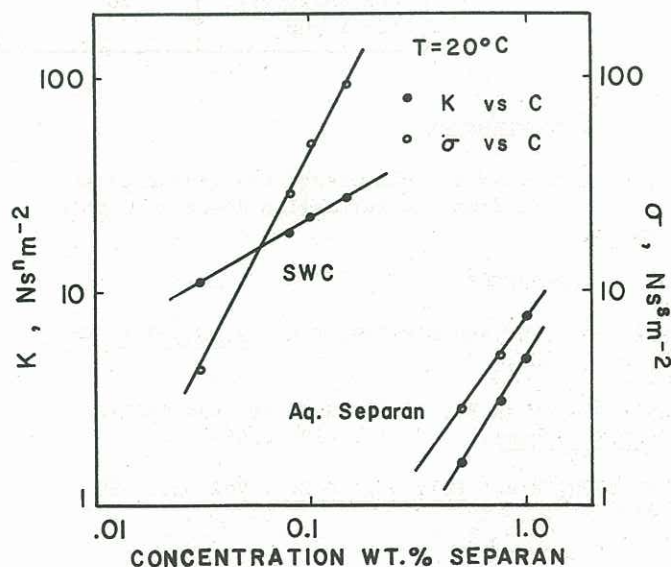


Figure 5 Effects of concentration on parameters K and σ for the Aqueous Separan Solutions and the SWC blends at 20°C

TABLE I
POWER LAW INDICES n AND s

Fluid	Concentration (wt %)	n	s
Aqueous Separan	0.50	0.42	0.70
	0.75	0.36	0.68
	1.00	0.34	0.67
Separan/Water/ Corn syrup	0.03	0.94	1.30
	0.08	0.90	1.16
	0.10	0.89	1.10
	0.15	0.85	1.09

TABLE II
PARAMETERS IN TEMPERATURE FUNCTIONS

Fluid	Concentration (wt %)	α (Ns^nm^{-2})	β ($^{\circ}\text{K}$)	ϕ (Ns^sm^{-2})	ξ ($^{\circ}\text{K}$)
Aqueous Separan	0.50	0.180	638	0.0031	1994
	0.75	0.266	712	0.0195	1618
	1.00	0.363	769	0.1350	1182

TABLE III
PARAMETERS IN CONCENTRATION FUNCTIONS

Fluid	Temperature ($^{\circ}\text{C}$)	K_o (Ns^nm^{-2})	p	σ_o (Ns^sm^{-2})	q
Aqueous Separan	20	4.90	1.64	7.61	1.44
	30	4.57	1.65	6.36	1.57
	40	4.14	1.58	5.99	1.74
	50	3.90	1.60	5.05	1.78
Separan/Water/ Corn syrup	20	83.50	0.57	3888	1.94

4 ACKNOWLEDGMENT

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