$$Nu_x = Ra_x^{1/4} Pr^{1/4} (4.361 + 9.953 Pr)^{-1/4} \qquad (13)$$

for uniform heat flux.

The corresponding empirical correlations suggested by Churchill and Ozoe (1973) to represent the data obtained by the numerical solution of the governing transport equations are

$$Nu_x = 0.503 Ra_x^{1/4} / [1 + (0.492/Pr)^{9/16})^{4/9} \qquad (14)$$

for the isothermal wall and

$$Nu_x = 0.563 Ra_x^{1/4} / [1 + (0.437/Pr)^{9/16}]^{4/9} \qquad (15)$$

for the uniform heat flux. Equations (12) and (14), and (13) and (15) are compared in Table 1 and 2, respectively.

The algebraic method is obviously an approximate one and must not substitute the exact solutions. It provides, however, extremely simple expressions which lead to results which are in reasonable agreement with the exact solutions.

NOTATION

a = thermal diffusivity
A, B, A', B', C' = numerical constants
g = acceleration of gravity
h_x = local heat transfer coefficient
k = thermal conductivity
Nu_x = $h_x x/k$ (Nusselt number)
Pr = ν/a (Prandtl number)
Ra_x = $g\beta\Delta T x^3/\nu a$ (Rayleigh number)
T = temperature
T_w = wall temperature
T_∞ = ambient temperature
ΔT = $T_w - T_\infty$
u = x component of velocity
u_0 = x velocity scale
v = y component of velocity
v_0 = y velocity scale
x = distance up the plate
y = distance to the plate
β = volumetric coefficient of expansion
δ = k/h_x (thickness of the thermal boundary layer)
ν = kinematic viscosity

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Low Shear Viscosity of Dilute Polymer Solutions

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A modification of a viscometer originally proposed by Zimm and Crothers in 1962 is presented, which may be used to measure ultra low shear viscosity for highly dilute polymer solutions. This may provide useful *information on polymer coil dimensions* and relaxation time. Use of the low shear viscosity data leads to very large values of relaxation time induced by polymer addition to a concentration of only 2 to 3 wppm. This finding is consistent with the marked viscoelastic effects exhibited by these solutions.

Interest in the flow behavior of highly dilute polymer solutions has increased greatly in recent years as many potential applications of these systems have emerged. Examples include tertiary oil recovery, turbulent drag reduction and cavitation suppression. Basic to the correlation and interpretation of data for any of these applications is measurement of the solution viscosity η. A closely related quantity is the intrinsic viscosity $[\eta]$ which provides additional useful information on polymer coil dimensions and relaxation time. $[\eta]$ is obtained directly from measurement of solution viscosity η and solvent viscosity η_s by the equation

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

From knowledge of $[\eta]$, the primary solution relaxation time Θ, and root-mean-square end to end distance $\bar{h}$ may then be calculated (Ferry, 1970; Flory, 1969):

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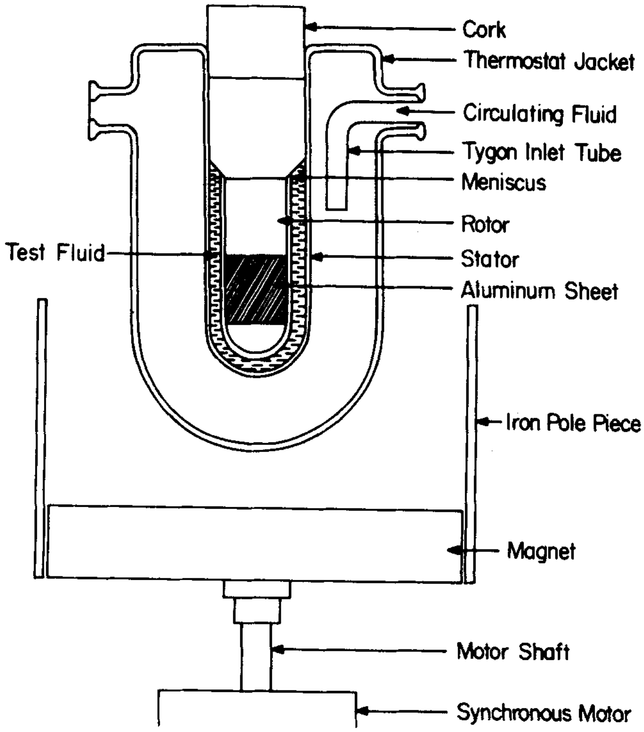

Figure 1. Schematic diagram of modified Zimm-Crothers viscometer. The presence of the aluminum sheet leads to greater stability at low shear rates than the steel pellet of Zimm and Crothers. Dimensions: rotor outer diameter = 1.00 cm; stator inner diameter = 1.20 cm; rotor height 5.00 cm; stator height = 9.0 cm.

TABLE 1. POLYMER TESTED

Polymer	Designation and manufacturer	Concentration (ppm)
Partially hydrolyzed polyacrylamide	Separan AP273 (S-273) Dow Chemical	3, 10
Polyacrylamide	Separan MG200 (S-200) Dow Chemical	40
Polyacrylic acid	Versicol S-25 (V-25) Allied Colloids	2, 40

$$\Theta = \frac{\eta_s[\eta]M}{RTS} \tag{1}$$

$$\bar{h} = \kappa\left([\eta]M\right)^{1/3} \tag{2}$$

Strictly speaking, $[\eta]$ in Equations (1) and (2) should be the limiting or zero shear intrinsic viscosity. This fact is often ignored, however, and $[\eta]$ calculated from values of η obtained in a high shear capillary type of viscometer. Such a practice may lead to large errors for the markedly shear thinning polymers of most commercial interest. Unfortunately, accurate low shear viscosity measurements for highly dilute polymer solutions are not easily accomplished with available equipment. In this work, a modification of a viscometer originally proposed by Zimm and Crothers (1962) is presented, which may be used to readily obtain such measurements.

EXPERIMENTAL

The three polymers used in the present study are known to exhibit marked drag reduction in turbulent pipe flow. They are listed in Table 1. The viscometer design is illustrated in Figure 1. It consists of a freely floating inner cylinder or rotor, supported by buoyancy and held in place by surface forces of the test fluid contained in the space between the inner and outer cylinder (stator). A constant torque is applied by interaction of a rotating magnetic field with an aluminum sheet inside the rotor. The sheet of aluminum was cut to a width closely approximating the inside rotor diameter. The sheet was then rolled loosely lengthwise over a glass rod and guided into the rotor. The tendency of the aluminum sheet to uncurl resulted in a barely noticeable seam. In Zimm and Crothers' original design, a steel pellet was used instead of the aluminum, but we found that this arrangement led to serious instabilities in operation of the equipment. Unless the pellet were perfectly round in shape and permanently fixed in the center of the bottom of the rotor, the rotor would wobble violently as it rotated, leading to erratic speeds.

The relative viscosity was calculated from the ratio of the rotational periods of the rotor (measured with a cathetometer) for the test solution and solvent. The viscometer was used to study the various polymers over a pH range from 2 to 13, both with and without 0.5% by weight sodium chloride. It was observed that gellike particles were present in the solutions of S-200 and V-25. The particles remained even after periods of 1 wk or greater. They were often so large as to cause serious wobble of the rotor axis and at times even blocked the annular gap and caused the rotor to stop. To eliminate this problem, the 40 wppm solutions of S-200 and V-25 were filtered prior to use. Although this procedure leads to uncertainty as to the actual solution concentration, the trends in viscosity with pH and salt addition should be unaffected. The relaxation time calculations in Table 2, however, required accurate estimates of solution concentration. For these calculations, data on unfiltered solutions of V-25 at 2 wppm were used. Those runs in which the rotor experienced serious wobble or ceased movement altogether were discarded. For the S-200 solution at 4 wppm, consistent data could not be obtained.

RESULTS AND DISCUSSION

Viscosity data for a typical test run are shown in Figure 2 for two glycerine-water solutions over a range of shear rates from 0.03 to $0.3s^{-1}$. As noted, these were obtained from the ratio of the measured period of revolution for the solution to that for pure water. The solid lines represent

TABLE 2. RELAXATION TIME CALCULATIONS AT CONCENTRATION CORRESPONDING TO ONSET OF VENA CONTRACTA INHIBITION*

(RELAXATION TIME CALCULATED FROM ZIMM THEORY, $\Theta = \frac{0.42\,(\eta - \eta_s)M}{cRT}$ (FERRY, 1970))

Polymer	Concentration (ppm)	Viscosity ($Pa{\cdot}s$)		Relaxation time (s)	
		$113s^{-1}$	$0.1s^{-1}$	$113s^{-1}$	$0.1s^{-1}$
S-273	3	0.0012.	0.0035	0.1	1.0
V-25	2	0.0013	0.0023	0.7	2.2
S-200	4	0.0012		0.1	

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*(Chiou and Gordon, 1977). Data at $113s^{-1}$ were obtained in a Wells-Brookfield cone and plate microviscometer. Data at $0.1s^{-1}$ were obtained in the present apparatus, using unfiltered solutions. For S-200, this led to such a problem with gel types of particles that low shear measurements could not be obtained.

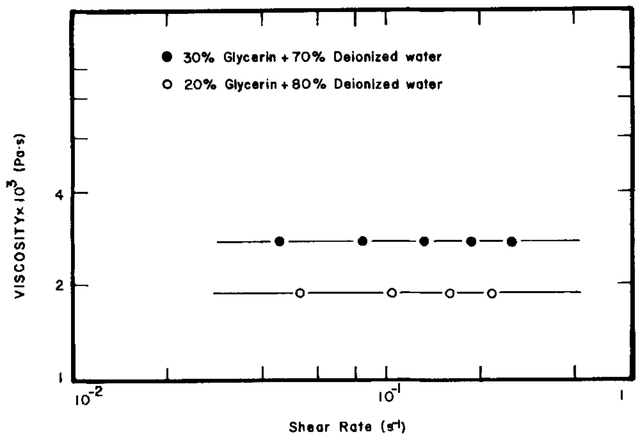

Figure 2. Results for Newtonian solutions - reference solvent water. Temperature 25°C. The solid lines refer to the viscosity value calculated from a Cannon Fenske capillary viscometer.

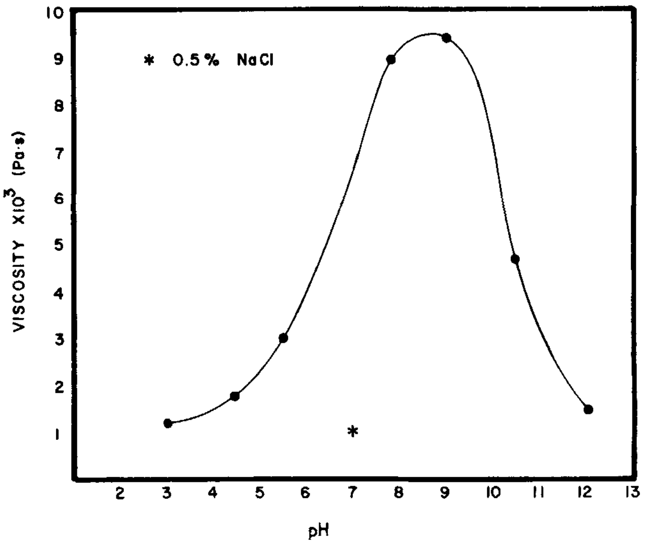

Figure 3. Effect of pH and 0.5% sodium chloride on viscosity of S-273 solution in deionized water. Concentration 10 wppm. Shear rate range: 0.03 to 0.3s^{-1}. The pH was varied by hydrochloric acid or sodium hydroxide addition.

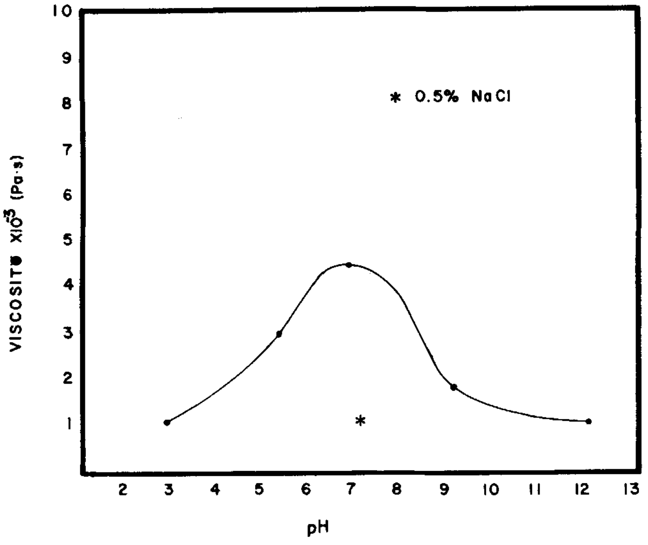

Figure 4. Effect of pH and 0.5% sodium chloride on viscosity of filtered S-200 solution in deionized water. Concentration 40 wppm. Shear rate range: 0.03 to 0.3s^{-1}. The pH was varied by hydrochloric acid or sodium hydroxide addition.

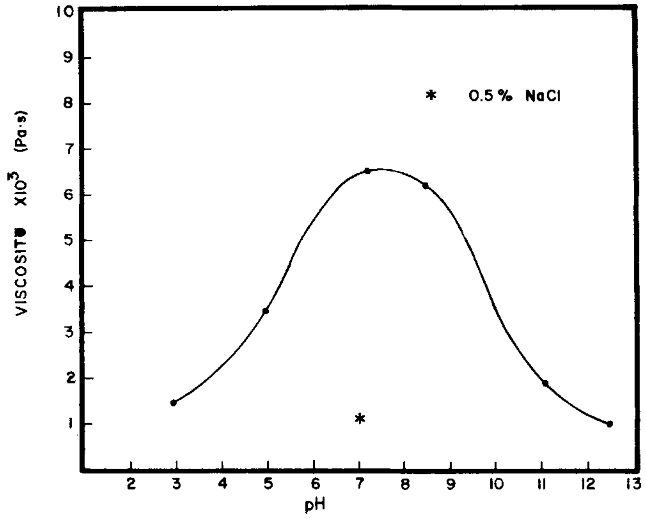

Figure 5. Effect of pH and 0.5% sodium chloride on viscosity of filtered V-25 solution in deionized water. Concentration 40 wppm. Shear rate range: 0.03 to 0.3s^{-1}. The pH was varied by hydrochloric acid or sodium hydroxide addition.

capillary tube data. The agreement is within 1% over the entire range of shear rates. Figures 3 to 5 illustrate the influence of pH on viscosity. The shear rate varies from approximately 0.03 to 0.3s^{-1}. For each polymer, a maximum in the viscosity-pH curve occurs at a pH of approximately 7. The addition of 0.5% (by weight) of sodium chloride is seen to lead to a marked drop in η.

It is of interest that very similar trends have been reported for the viscosity-pH behavior of these polymers at much higher concentrations (200 wppm) and shear rates (113s^{-1}) (Balakrishnan and Gordon, 1975). This confirms our previously held contention that the high concentration - high shear viscosity data does reflect the behavior of the individual macromolecule. In Table 2 we compare the calculated relaxation times from a prior study of vena contracta inhibition measured at 113s^{-1} with those of this study. We see that in each case use of the low shear viscosity value leads to a marked increase in calculated relaxation time. Perhaps even more informative is the enormous value of relaxation time induced by polymer addition to a concentration of only 2 to 3 wppm.

It is of interest to consider the potential role of the gellike particles or aggregates observed in this study. Recently, it has been postulated that such particles exist in many drag reducing solutions and may be a factor in some of the anomalous viscoelastic behavior reported for such systems (Hinch and Elata, 1979). In this study, the surprising large value of solution relaxation time observed for V-25 at 2 wppm could possibly be an artifact due to these aggregates. We would expect the viscosity data to be poorly reproducible, however, owing to variations in number and size of aggregates from batch to batch. This was not found to be the case here, although further work on the role of these aggregates is clearly indicated. Note that in the high shear cone and plate measurements, the presence of the aggregates could not readily be detected experimentally.

ACKNOWLEDGMENT

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NOTATION

c = polymer concentration, kg/m^3
M = polymer molecular weight
R = universal gas constant, 8.314 J/mole.$\cdot K$
S = numerical factor, dependent on solvent power
T = absolute temperature, °K
$\bar{h}$ = root-mean-square end to end distance of polymer molecule, m
η = solution viscosity, $PA \cdot s$ or $N \cdot s/m^2$
η_s = solvent viscosity, $Pa \cdot s$ or $N \cdot s/m^2$
Θ = relaxation time, s
κ = numerical factor, dependent on solvent power

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Multiplicity and Pollutant Formation for the Combustion of Hexane in a Refractory Tube

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This paper presents the results of a continuing study of the process of combustion in a refractory tube. Chen and Churchill (1972*a*) first demonstrated experimentally that flames of premixed propane vapor and air could be stabilized over a wide range of operating conditions. As contrasted with combustion stabilized by diffusion or backmixing, stabilization in the refractory tube by wall to wall radiation, and thermal conduction in the wall was found to minimize backmixing, to avoid oscillations and to yield a very thin, very stable and nearly invisible flame front. Chen and Churchill (1972*b*) also developed and solved numerically a theoretical model for the turbulent regime which yielded predictions of the wall temperature distribution and the limits of stable flow in good agreement with their experimental measurements. However, owing to the intervening irreversible modification of the experimental apparatus, they were unable to test the prediction by this model of the existence of six additional stationary states for the same external conditions.

Bernstein and Churchill (1976) constructed an essentially identical combustion chamber and experimentally confirmed the existence of many multiple stationary states. They also discovered that the NO_x concentrations from this process of combustion were only 5 to 40 ppm, depending on operating conditions.

Choi and Churchill (1978) demonstrated that flames from the evaporation and combustion of hexane droplets could also be stabilized in a refractory tube. The same combustion chamber was used as in the prior investigations, but an extended inlet section was added to provide sufficient distance for the evaporation. Very low concentrations of NO_x were again observed. Choi and Churchill (1979) improved the method of solution of the theoretical model of Chen and Churchill (1972*b*) and extended the model to include droplets as well as premixed gaseous fuel. Their solutions predicted the existence of at least two stationary states. Additional stationary states may have been eliminated by the approximation required to obtain convergence of the numerical calculations.

The objective of the current investigation was to investigate the possible existence and consequences of multiple stationary states for the evaporation and combustion of liquid droplets. To provide the necessary control and precision, the prior apparatus was completely rebuilt and recalibrated, and a system for online chemical analysis was added.

EXPERIMENTAL APPARATUS AND PROCEDURE

The investigation utilized an apparatus similar to that of Choi and Churchill (1978). The combustion chamber consisted of a round channel 9.7 mm in diameter and 864 mm long. The first 623 mm was a high purity aluminum oxide tube. The final 241 mm comprised the central hole in a cylindrical block of aluminum oxide, 75.5 mm in diameter. The central hole was surrounded by six identical outer holes which were used as guard heaters. The block was made from RTC-60 precision castable alumina ceramic. (The previous combustion chambers used by Churchill and co-workers were formed by cementing together pieces of channelled Wulff furnace elements.) The temperature distribution along the central hole and elsewhere in the cylindrical block was measured with platinum/platinum-10% rhodium thermocouples. The ceramic tube and block were both well insulated.

A single chain of uniformly sized and uniformly spaced droplets was generated by passing reagent grade hexane through 0.1143 mm ID (32 gauge) hypodermic tubing, vibrated at a controlled frequency of 543 Hz by the cone of a radio speaker. The observation that one droplet formed per oscillation permitted calculation of the droplet volume and, assuming a sphere, the droplet diameter from the rate of flow of hexane and the frequency. The droplet spacing was computed from a semitheoretical correlation of Choi and Churchill (1978). The inlet air stream was preheated sufficiently to assure complete evaporation of the droplets

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