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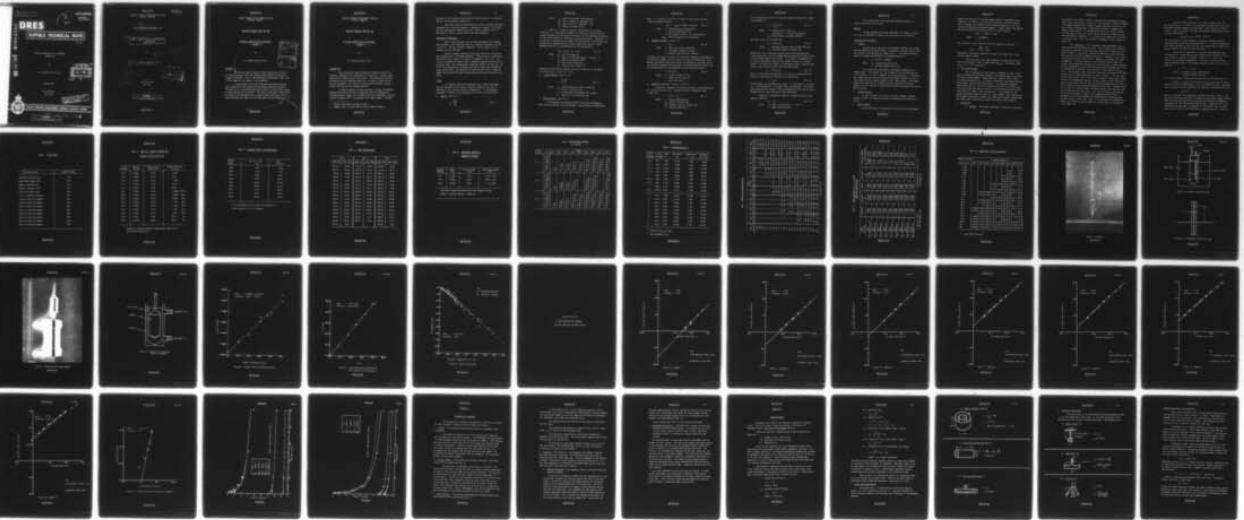
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by

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ABSTRACT

The density, vapor pressure, surface tension and viscosity
of thickened Dowanol, DPM, were measured experimentally according to
standard techniques. Each of the techniques is explained in detail and
a brief summary of the theory is also presented.

A new parameter called the 'dissolved density' was defined
which promises to allow differentiation between thickening polymers.
The addition of an acrylate polymer had no effect on the surface tension
or vapor pressure of the solvent. The effect of thickener concentration
on viscosity was determined over a range of shear rates where the thic-
kened solutions were found to follow the power-law fluid model.

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INTRODUCTION

There are several important physical properties that can be
measured to determine the characteristics of materials. Primary among
these are the chemical purity and toxicity. The vapor hazard and flow
properties are also frequently important. In order to quantify these
last two parameters, such things as density, vapor pressure, surface
tension and viscosity are commonly measured.

In chemical defence training exercises, solvents are commonly
employed which have low toxicity properties and can be detected on
three-way detector paper[+] or by standard analytical techniques. One such
solvent is Dowanol, DPM[++] (dipropylene glycol methyl ether). The manu-

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+   Federal Stock Number FSN 6665-21-0309

++   Dowanol, DPM is a trade name of the Dow Chemical Company.

facturer of this solvent provides exhaustive data on most of its chemical, physical and toxicological properties.

When small amounts of Rohm and Haas K-125 (an acrylate thickener) are added, the viscosity of Dowanol is observed to increase. This report provides quantitative information on this viscosity change as well as the effect on density, surface tension and vapor pressure.

EXPERIMENTAL PROCEDURES

Most of the techniques used in these experiments are standard and available in many laboratory manuals or chemistry textbooks (see Refs. 1, 2 and 3). They are included in Appendix I of this report for convenience and easy reference.

Several standard, Newtonian fluids were chosen for calibrating the equipment used in the above procedures. These fluids are commercially available and are listed in the Tables as Standards A, B, C, etc. The fluid to be tested was Dowanol, DPM, a commercial solvent available only in 45 gallon drums. Gas chromatography showed our sample to be 88% pure, the other 12% being basically propylene glycol methyl ether and tripropylene glycol methyl ether. The thickener was Rohm and Haas K-125, a commercial powder consisting of 80% methyl methacrylate and 20% butyl and ethyl acrylates.

THEORY

The theories behind the techniques used in these experiments are well described in most books on physical chemistry (e.g. Ref. 3). A good book on the field of rheology is Reference 4. In the following paragraphs, formulas will be presented with little or no derivations.

a.   Density (see Fig. 1)

$$\rho_s = \frac{M_s \rho_w}{M_w} \qquad \text{(Eq. 1)}$$

where: ρ_s = density of unknown species (g/cm^3)

M_s = mass of species in pycnometer (g)

M_w = mass of water in pycnometer   (g)

ρ_w = density of water (g/cm^3)

Equation 1 is used to calculate the density of the polymer solutions. If a high density substance is mixed with a low density substance, the density of the resulting material will lie between the densities of the starting materials (assuming no chemical reactions). Therefore, if the density of the solution increases with the addition of the polymer, the polymer can be assumed to have a higher density than the pure liquid. Mathematically this is expressed by the following equation.

$$m_p \rho_s = \rho_p(m_p + m_L - V_L \rho_s) \qquad \text{(Eq. 2)}$$

where: m_p = mass of polymer (g)

ρ_s = density of solution (g/cm^3 ... from Eq. 1)

ρ_p = density of polymer (g/cm^3)

m_L = mass of pure liquid (g)

V_L = volume of pure liquid (cm^3)

Equation 2 can be used to evaluate the dissolved density of the polymer by plotting $(m_p \rho_s)$ vs $(m_p + m_L - V_L \rho_s)$.

b.   Surface Tension   (see Fig. 2)

$$\gamma_s = \frac{r \rho_s\, gh}{2} \qquad \text{(Eq. 3)}$$

where: γ_s = surface tension of species (dynes/cm)

r = radius of capillary (cm)

g = gravitational acceleration (981 cm/sec^2)

h = length of rise of meniscus (cm)

c.   Vapor Pressure   (see Fig. 3)

This parameter was measured directly with mercury manometers and a precision mercury, glass thermometer. With pressure and temperature

data, it is possible to calculate the heat of vaporization from the Clausius-Clapeyron equation:

$$\log P = -\Delta H_{vap}/(2.303RT) + Constant \quad (Eq.\ 4)$$

where: P = measured pressure (dynes/cm^2)

T = measured temperature (°K)

R = gas constant (8.314×10^7 ergs/g mole/°K)

ΔH_{vap} = heat of vaporization (ergs/g mole)

d.   <u>Ostwald Viscosity</u>   (see Fig. 4)

$$\eta = K\rho_s t \quad (Eq.\ 5)$$

where: η = shearing viscosity (g/cm/sec)

K = instrument constant (cm^2/sec^2)

t = measured time interval (> 200 sec)

The shear rate cannot be controlled with these viscometers but depends on the capillary diameter and the viscosity of the fluid being used. Also, because the pressure head varies during the experiment, the shear rate is not constant throughout the experiment. An average, Newtonian shear rate can be calculated for each experiment from the following formula:

$$\dot{\gamma} = 4V/(\pi r^3 t) \quad (Eq.\ 6)$$

where: V = volume of bulb (3.2 cm^3)

r = radius of capillary (cm)

$\dot{\gamma}$ = shear rate (sec^{-1})

e.   <u>Brookfield Viscosity</u>   (see Figs. 5 and 6)

Using this instrument, the shearing viscosity can be determined as a function of shear rate. The shear rate for a Newtonian fluid is (Ref. 4):

$$\dot{\gamma} = 2\Omega/(1 - s^2) \quad (Eq.\ 7)$$

where: $s = R_i/R_o$ (dimensionless)

R_i = radius of spindle (cm)

R_o = radius of housing cylinder (cm)

Ω = rotation rate (sec^{-1})

For a non-Newtonian fluid this expression becomes slightly more complex (see Appendix II):

$$\dot{\gamma} = 2\Omega \sum_{p=0}^{\infty} s^{2pm} m \qquad \text{(Eq. 8)}$$

where: m = slope of log Ω vs log τ_{Ri}
evaluated at $\tau = s^{2p}\tau_{Ri}$ (dimensionless)

τ_{Ri} = shear stress on spindle (dynes/cm^2)

The shear stress is calculated from:

$$\tau_{Ri} = T/(2\pi R_i^2 Le) \qquad \text{(Eq. 9)}$$

where: T = measured torque on inner cylinder (dyne-cm)
Le = equivalent length of spindle (cm)

Because the inner spindle has surface area at both top and bottom, viscous drag occurs not only between the two cylindrical faces but also at the top and bottom of the spindle. This effect is compensated for by using an equivalent length for the spindle instead of its actual length. This equivalent length is calculated by using a standard, Newtonian fluid of known viscosity and using the formula:

$$Le = T/(2\pi R_i^2 n\dot{\gamma}) \qquad \text{(Eq. 10)}$$

Once $\dot{\gamma}$ is determined from equation 6 or 7 and τ_{Ri} is determined from equation 8, the shearing viscosity is calculated from:

$$n = \tau_{Ri}/\dot{\gamma} \qquad \text{(Eq. 11)}$$

Unfortunately, for non-Newtonian liquids n is a function of $\dot{\gamma}$, so when τ_{Ri} is plotted against $\dot{\gamma}$ a straight line is not obtained. The type of curve which results, however, helps to characterize the fluid as being a Bingham plastic, shear-thinning or shear-thickening.

Generally, non-Newtonian behavior is modelled by the simple power-law equation:

$$\tau_{Ri} = n_0 \dot{\gamma}^n \qquad \text{(Eq. 12)}$$

where: n_0 = shear viscosity when $\dot{\gamma} = 1$ sec^{-1}
n = power-law coefficient

This study did not investigate time dependent behavior or elastic properties of the fluids.

RESULTS

The data obtained from these experiments are listed in Tables 1 to 10 and are depicted in Figures 7 to 21 for ease of visualization.

DISCUSSION OF THE RESULTS

a. Density

As expected, the densities of the polymer solutions were greater than the density of the pure solvent. The density increased linearly with the increase in concentration as shown by Fig. 7. An equation relating density to polymer concentration for thickened Dowanol is:

$$\rho_s = 0.959 + 0.000199c$$

where: ρ_s = solution density (g/cm^3)
c = polymer concentration (g/ℓ)

Fig. 8 shows that the relation represented by Equation 2 is indeed linear. The slope of the line is equal to the dissolved density of the polymer. For K-125 in Dowanol the dissolved density is 1.209 g/cm^3. This number could be used for characterizing unknown polymers or determining the similarity between batches of the "same" polymer. This number might not be identical for different solvents because the dissolved density will be a function of the molecular association between the solvent and the polymer.

b. Surface Tension

As seen in Table 2, the surface tension of Dowanol remained constant at 29.3 ± 0.2 dynes/cm and was not affected by the addition of K-125.

c. Vapor Pressure

Table 4 and Figure 9 present data for two runs with unthickened

Dowanol and one run with thickened Dowanol (DO-4) on the Ramsey-Young apparatus. In Figure 9 it can be clearly seen that within the experimental accuracy no difference could be measured between the vapor pressures of thickened and unthickened Dowanol. A least squares line through the data yielded the following equation for vapor pressure:

$$\log P = -2457/T + 7.942$$

where: P = kilopascals
          T = °K

The accuracies on the constants at the 90% confidence limits are:

$$-2457 \pm 275$$
and $$7.942 \pm 0.106$$

Experimental inaccuracies appeared to be due to the impurities in the original Dowanol samples.

From the value of the slope, Equation 4 can be used to calculate the corresponding heat of vaporization (ΔH_{vap}). For Dowanol, DPM, ΔH_{vap} is 4.7×10^{11} ergs/g mole.

d.   Equivalent Lengths

The five Newtonian fluids listed as standards in Table 1 were used to evaluate the equivalent lengths of the spindles used in the Brookfield Small Sample Adaptor. These values are listed in Table 5 after calculation by Equation 10. It should be noted that even though spindle 3 had an actual length longer than spindle 1, its equivalent length was significantly smaller. The actual length to gap ratio for spindle 3 was five times larger than that of spindle 1, thus the end effects were more significant for spindle 1 than for spindle 3. This accounts for the greater equivalent length of spindle 1. Both spindles 1 and 2 had equivalent lengths significantly greater than their actual lengths, showing that end effects were contributing to the viscous drag on these spindles.

e.   Viscosities

(1)   Ostwald - The Ostwald experimental viscosities calculated

by Equation 5 are listed in Table 2 along with the corresponding average shear rates (calculated by Equation 6). The viscosity is seen to increase with polymer concentration. However, because the shear rate differs for each viscosity determination, it would not be proper to compare these numbers quantitatively. For non-Newtonian fluids the viscosity changes with the shear rate and this factor could influence any comparison made from the Ostwald viscometers. It is necessary to compare the viscosities at identical shear rates and the Ostwald viscometers are not capable of doing this.

(2) Brookfield - This instrument gives experimental data relating revolutions per minute to torque. Using Equation 9 of the Theory, this data is converted to revolutions per minute versus shear stress as shown in Table 6. One needs to convert the RPM data to shear rate data. There are two alternative methods of doing this. Equation 7 can be used to calculate the shear rate directly. However, this assumes the liquid is Newtonian. The other method is to use Equation 8 which takes into account the non-Newtonian characteristics of the fluid. Because extremely viscous, non-Newtonian fluids were being used, both techniques were tried. To use Equation 8, one must first evaluate 'm', the slope of log τ_{Ri} vs log Ω. Least squares linear regression lines were calculated for the data of Table 6 and yielded the values of m shown in Table 7. The fact that m differs significantly from 1.0 for some of the more viscous liquids demonstrates the non-Newtonian behavior of these liquids. Using these values of m, the true shear rates for each fluid were evaluated and are listed in Table 8 along with the approximate Newtonian shear rates. Although values of m as high as 1.36 were found, the Newtonian shear rates varied at most only 2% from the true shear rates. This small deviation cannot justify the extra calculations. Figures 10 to 18 demonstrate that there is essentially no difference between the non-Newtonian and Newtonian plots of shear stress vs shear rate. Thus, it is concluded that the Newtonian shear rate formula is accurate enough for fluids whose 'm' coefficient is less than 1.4.

From the linear regression lines shown in Figures 10 to 18, the viscosities at $\dot{\gamma} = 1.0$ sec^{-1} and the power law coefficients are easily evaluated from the intercept and slope data. These values are listed in Table 9. Thus, for example, the power law equation relating shear stress to shear rate for DO-7 is:

$$\tau = (6.08 \pm 0.42)\ \dot{\gamma}^{\ (0.882 \pm 0.021)}$$

The error limits for these constants are based on the 90% confidence limits described by Neville and Kennedy (Ref. 5). It should be mentioned that these equations are valid only over the limited range of shear rates shown in Table 8 for which the data were taken.

A quantitative comparison of viscosity can be made for each thickened fluid. Figure 19 shows the viscosity ratio (viscosity of solution divided by viscosity of solvent ... both at $\dot{\gamma} = 1$ sec^{-1}) as a function of the polymer concentration. The curve is similar to those shown by Middleman (Ref. 4) and at high viscosity ratios (> 20) it can be seen that:

$$n_r \propto c^{4.9} \ ... \ (n_r > 20) \ ....$$

where n_r = viscosity ratio (dimensionless)
c = polymer concentration (g/ℓ)

This relation agrees closely with that observed by many others (Ref. 4).

Finally, in Table 10 and Figures 20 and 21, the effect of shear rate on viscosity is demonstrated for all the thickened fluids. The curves shown on Figures 20 and 21 represent the theoretical relationship given by:

$$n = n_o / \dot{\gamma}^{(1-n)} \ ....$$

where n is the power law coefficient computed and listed in Table 9. We see that the data and the curves on Figures 20 and 21 show a shear thinning effect for the high concentration solutions and essentially a Newtonian relationship for the low concentration solutions. Figures 20 and 21 also demonstrate that the power law equation is inaccurate at very low shear rates where it predicts the viscosity will approach infinity. The Ellis

model could be used to overcome this problem but was avoided here because it necessitates the determination of an extra constant (Ref. 4).

CONCLUSIONS

1. The density of thickened Dowanol is a linear function of the concentration of polymer K125 up to 50 g/ℓ. The dissolved density of polymer K125 in Dowanol is 1.209 g/cm^3.

2. The surface tension is unaffected by polymer addition.

3. The vapor pressure is unaffected by polymer addition. The heat of vaporization of Dowanol is 4.7 x 10^{11} ergs/g mole.

4. Although Dowanol is a Newtonian liquid, the addition of polymer K125 produced non-Newtonian, shear thinning solutions.

5. The relationship between log viscosity ratio vs log polymer concentration is linear at high viscosity ratios with a slope of 5.

6. The viscosity of all solutions could be modelled by the power law equation over shear rates of 0.5 sec^{-1} to 500 sec^{-1}.

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TABLE 1: FLUIDS USED

Fluid Description	Report Acronym
Brookfield Standard 100	ST-A
Brookfield Standard 1000	ST-B
ASTM Oil Standard, S20	ST-C
ASTM Oil Standard, S200	ST-D
ASTM Oil Standard, S600	ST-E
0.0　g K-125/litre Dowanol	DO-1
9.92 g K-125/litre Dowanol	DO-2
20.00 g K-125/litre Dowanol	DO-3
30.05 g K-125/litre Dowanol	DO-4
30.13 g K-125/litre Dowanol	DO-5
36.61 g K-125/litre Dowanol	DO-6
39.94 g K-125/litre Dowanol	DO-7
49.97 g K-125/litre Dowanol	DO-8
50.20 g K-125/litre Dowanol	DO-9

TABLE 2: DENSITIES, SURFACE TENSIONS AND

OSTWALD VISCOSITIES AT 25°C

Liquid Acronymn	Density (g/cm^3)	Surface Tension (dynes/cm)	Ostwald Viscosity (poise)	
ST-A	0.9626	20.55	0.949	
ST-B	0.9699	21.54	9.92	
ST-C	0.8669	30.31	0.3313	
ST-D	0.8758	31.87	4.073	
ST-E	0.8834	32.90	12.46	
DO-1	0.9505	29.36	0.03585	(576)[†]
DO-2	0.9524	29.22	0.1396	(168)
DO-3	0.9537	29.18	0.4683	(64)
DO-4	0.9562	29.36	1.612	(24)
DO-5	0.9570	29.20	1.556	(29)
DO-6	0.9573	29.78	3.475	(16)
DO-7	0.9577	29.32	5.144	(13)
DO-8	0.9612	29.45	18.32	(3)
DO-9	0.9599	28.93	18.41	(3)

[†] Numbers in brackets represent average shear rates (sec^{-1}) calculated by Equation 6.

TABLE 3: <u>DISSOLVED DENSITY OF POLYMER DATA</u>

Dowanol Sample	$m_p + m_L - V_L \rho_s$ [†] (g)	$m_p \rho_s$ [†] (g^2/cm^3)
DO-1	0.00	0.00
DO-2	8.02	9.45
DO-3	16.80	19.07
DO-4	24.35	28.73
DO-5	23.63	28.83
DO-6	29.80	35.05
DO-7	32.74	38.25
DO-8	38.27	48.03
DO-9	40.80	48.19

[†] for an explanation of variables see Equation 2 ...

data plotted as X vs Y in Figure 8

TABLE 4: VAPOR PRESSURE DATA

DO-1		DO-1		DO-4	
Temp (°K)	Pres (kPa)	Temp (°K)	Pres (kPa)	Temp (°K)	Pres (kPa)
411.95	91.86	413.25	84.53	413.95	93.46
403.15	87.86	408.25	78.79	412.15	89.73
401.95	82.66	404.35	73.19	409.75	84.26
399.65	77.06	401.45	68.13	407.55	78.66
398.75	71.59	401.35	63.06	405.15	73.33
395.05	65.86	396.75	57.46	403.65	67.46
392.55	60.26	394.25	52.13	400.35	61.86
391.75	54.53	390.25	46.80	397.95	56.26
388.35	49.06	389.95	41.20	395.35	50.66
386.85	43.06	388.95	35.86	391.55	44.80
383.55	38.00	387.55	30.80	390.15	39.46
379.75	32.40	380.95	25.06	385.75	33.86
376.45	26.80	376.15	20.00	379.65	28.13
368.65	21.06	369.15	14.53	374.45	22.53
361.15	15.60	354.75	9.47	366.45	17.07
349.85	10.00	353.15	6.93	354.55	11.47
335.15	4.40			341.35	5.87

TABLE 5:   EQUIVALENT LENGTHS OF

BROOKFIELD SPINDLES

Spindle Acronym	Radius (cm)	Actual Length (cm)	Equivalent Length (cm)
SP-1	0.8382	3.150	3.52 ± 0.03
SP-2	0.8382	6.299	6.58 ± 0.05
SP-3	0.9322	3.162	3.19 ± 0.08

Equivalent Lengths Determined With Three Standard Liquids

Radius of Cylinder Housing - 0.9525 cm

TABLE 6: SHEAR STRESS DATA FOR DOWANOL

τ_{Ri} (dynes/cm²)

Spindle (acronymn)	Ω (sec⁻¹)	Sample								
		DO-1	DO-2	DO-3	DO-4	DO-5	DO-6	DO-7	DO-8	DO-9
SP-1	0.0524	-	-	-	-	-	-	-	-	-
	0.1047	-	-	-	-	-	-	4.632	-	18.06
	0.2618	-	-	-	-	-	8.801	12.51	44.46	43.54
	0.5236	-	-	-	7.874	7.411	17.14	24.55	85.22	82.45
	1.047	-	1.390	4.632	15.75	14.82	33.35	47.71	148.2	148.2
	2.094	-	2.779	9.264	30.11	29.18	63.00	88.93	255.7	258.0
	5.236	1.390	7.411	22.23	69.48	69.02	140.4	193.2	503.9	500.2
	10.47	2.779	12.97	42.61	130.2	127.8	248.7	334.9	807.8	807.8
SP-2	0.0524	-	-	-	-	-	-	-	-	8.906
	0.1047	-	-	-	-	-	-	5.195	-	17.81
	0.2618	-	-	-	-	-	8.906	12.37	-	43.40
	0.5236	-	-	-	7.422	-	17.32	24.49	-	81.64
	1.047	-	1.484	4.701	14.84	-	33.15	46.76	-	159.1
	2.094	-	2.969	9.154	29.19	-	62.59	87.83	-	251.4
	5.236	1.732	6.680	22.27	68.53	-	139.3	190.2	-	492.9
	10.47	3.464	13.36	42.30	126.4	-	246.6	322.6	-	801.6
SP-3	0.0524	-	-	-	-	-	9.906	12.79	46.48	47.46
	0.1047	-	-	-	8.667	7.885	18.57	26.41	86.32	87.50
	0.2618	-	-	-	20.64	19.92	44.16	62.32	179.3	186.5
	0.5236	-	-	11.97	40.45	39.01	82.55	114.3	305.4	316.6
	1.047	-	6.604	23.52	75.12	73.87	149.0	201.4	507.9	538.2
	2.094	3.302	14.03	45.81	137.0	135.3	260.0	347.5	820.0	861.8
	5.236	9.080	34.26	105.2	296.3	293.0	521.7	683.5	1504	1516
	10.47	17.75	66.45	195.2	531.6	521.6	924.5	1179	2350	2371

TABLE 7: DETERMINATION OF m

Spindle Acronymn	Fluid Acronymn	Slope[†] x	Deviation[††] dx	Coefficient m = 1/x	Accuracy[††] dm = dx/x^2
1 & 2	DO-1	1.000	±0.657	1.000	±0.657
1 & 2	DO-2	0.964	±0.036	1.037	±0.039
1 & 2	DO-3	0.959	±0.009	1.043	±0.010
1 & 2	DO-4	0.940	±0.018	1.064	±0.020
1	DO-5	0.951	±0.028	1.052	±0.031
1 & 2	DO-6	0.904	±0.014	1.106	±0.017
1 & 2	DO-7	0.914	±0.023	1.094	±0.028
1	DO-8	0.781	±0.042	1.280	±0.069
1 & 2	DO-9	0.840	±0.031	1.190	±0.044
3	DO-1	1.048	±0.242	0.954	±0.220
3	DO-2	0.999	±0.057	1.001	±0.057
3	DO-3	0.931	±0.033	1.074	±0.038
3	DO-4	0.892	±0.024	1.121	±0.030
3	DO-5	0.923	±0.042	1.083	±0.049
3	DO-6	0.855	±0.028	1.170	±0.038
3	DO-7	0.844	±0.039	1.185	±0.055
3	DO-8	0.736	±0.031	1.359	±0.057
3	DO-9	0.735	±0.038	1.361	±0.070

[†] Slope of log τ_{Ri} vs log Ω

[††] 90% confidence limit

TABLE 8: COMBINED SHEAR RATE AND STRESS DATA

Sample

Newtonian Rate (sec^{-1})	DO-1 sec^{-1}	DO-1 d/cm^2	DO-2 sec^{-1}	DO-2 d/cm^2	DO-3 sec^{-1}	DO-3 d/cm^2	DO-4 sec^{-1}	DO-4 d/cm^2	DO-5 sec^{-1}	DO-5 d/cm^2	DO-6 sec^{-1}	DO-6 d/cm^2	DO-7 sec^{-1}	DO-7 d/cm^2	DO-8 sec^{-1}	DO-8 d/cm^2	DO-9 sec^{-1}	DO-9 d/cm^2
0.465																	0.475	8.91
0.928													0.939	4.63			0.950	18.1
0.928													0.939	5.20			0.950	17.8
2.32											2.35	8.80	2.35	12.5	2.40	44.5	2.38	43.5
2.32											2.35	8.91	2.35	12.4			2.38	43.3
2.49											2.49	9.91	2.49	12.8	2.50	46.5	2.50	47.5
4.64							4.68	7.87	4.67	7.41	4.70	17.1	4.70	24.6	4.80	85.2	4.75	82.5
4.64							4.68	7.42			4.70	17.3	4.70	24.5			4.75	81.6
4.97							4.98	8.67	4.97	7.89	4.98	18.6	4.98	26.4	5.00	86.3	5.00	87.5
9.28			9.32	1.39	9.33	4.63	9.35	15.8	9.34	14.8	9.40	33.4	9.39	47.7	9.60	148	9.50	148
9.28			9.32	1.48	9.33	4.70	9.35	14.8			9.40	33.2	9.39	46.8			9.50	159
12.4							12.4	20.6	12.4	19.9	12.5	44.2	12.4	62.3	12.5	179	12.5	187
18.6			18.6	2.78	18.7	9.26	18.7	30.1	18.7	29.2	18.8	63.0	18.8	87.8	19.2	256	19.0	258
18.6			18.6	2.97	18.7	9.15	18.7	29.2			18.8	62.6	18.8	88.9			19.0	251
24.8					24.9	12.9	40.5	24.9	24.9	39.0	24.9	82.6	24.9	114	25.0	305	25.0	317
46.4	46.4	1.39	46.6	7.41	46.7	22.2	46.8	69.5	46.7	69.0	47.0	140	47.0	193	48.0	504	47.5	500
46.4	46.4	1.73	46.6	6.68	46.7	22.3	46.8	68.5			47.0	139	47.0	190			47.5	493
49.7			49.7	6.60	49.7	23.5	49.8	75.1	49.7	73.9	49.8	149	49.8	201	50.0	508	50.0	538
92.8	92.8	2.78	93.2	13.0	93.3	42.6	93.5	130	93.4	128	94.0	249	93.9	335	96.0	808	95.0	808
92.8	92.8	3.46	93.2	13.4	93.3	42.3	93.5	126			94.0	247	93.9	323			95.0	802
99.3	99.2	3.30	99.3	14.0	99.5	45.8	99.6	137	99.5	135	99.6	260	99.6	348	100	820	100	862
248	248	9.08	248	34.3	249	105	249	296	249	293	249	522	249	684	250	1504	250	1516
497	496	17.8	497	66.5	497	195	498	532	497	522	498	925	498	1179	500	2350	500	2371

... see Figures 10 to 18

TABLE 9: SHEAR VISCOSITY AT $\dot{\gamma} = 1.0$ AND

POWER LAW COEFFICIENTS

Sample Acronymn	Intercept[†] a	Accuracy[††] da	Slope[†] n	Accuracy[††] dn	Viscosity (poise) $\eta_0 = 10^a$ (accuracy)	
DO-1	-1.546	±0.200	1.039	±0.096	0.0284	±0.017
DO-1 (Newtonian)[†††]	-1.545	±0.200	1.038	±0.096	0.0285	±0.017
DO-2	-0.772	±0.037	0.961	±0.021	0.169	±0.015
DO-2 (Newtonian)	-0.768	±0.037	0.960	±0.021	0.171	±0.015
DO-3	-0.236	±0.017	0.944	±0.009	0.581	±0.023
DO-3 (Newtonian)	-0.233	±0.017	0.943	±0.010	0.585	±0.023
DO-4	0.302	±0.025	0.913	±0.015	2.00	±0.12
DO-4 (Newtonian)	0.305	±0.024	0.913	±0.015	2.02	±0.11
DO-5	0.287	±0.035	0.917	±0.021	1.94	±0.16
DO-5 (Newtonian)	0.289	±0.035	0.916	±0.021	1.95	±0.16
DO-6	0.660	±0.023	0.876	±0.016	4.57	±0.25
DO-6 (Newtonian)	0.664	±0.023	0.875	±0.016	4.61	±0.25
DO-7	0.784	±0.029	0.882	±0.021	6.08	±0.42
DO-7 (Newtonian)	0.788	±0.030	0.881	±0.021	6.14	±0.44
DO-8	1.416	±0.035	0.746	±0.023	26.1	±2.2
DO-8 (Newtonian)	1.424	±0.037	0.744	±0.024	26.5	±2.4
DO-9	1.339	±0.037	0.800	±0.026	21.8	±1.9
DO-9 (Newtonian)	1.346	±0.036	0.799	±0.027	22.2	±1.9

[†] Log τ_{Ri} vs Log $\dot{\gamma}$

[††] 90% confidence limit

[†††] $\dot{\gamma}$ determined from $\dot{\gamma} = 2\Omega/(1 - s^2)$

... see Figure 19

TABLE 10: SHEAR RATE EFFECT ON VISCOSITY

Newtonian Shear Rate (sec^{-1})	Viscosity (poise)								
	DO-1	DO-2	DO-3	DO-4	DO-5	DO-6	DO-7	DO-8	DO-9
0.465									18.8
0.928							4.93		19.1
0.928							5.54		18.7
2.32						3.74	5.32	18.5	18.3
2.32						3.79	5.28		18.2
2.49						3.98	5.14	18.6	19.0
4.64				1.68	1.59	3.64	5.23	17.8	17.4
4.64				1.59		3.68	5.21		17.2
4.97				1.74	1.59	3.73	5.30	17.3	17.5
9.28		0.149	0.496	1.69	1.58	3.55	5.08	15.4	15.6
9.28		0.159	0.504	1.58		3.53	4.98		16.7
12.4				1.66	1.60	3.54	5.02	14.3	15.0
18.6		0.149	0.495	1.61	1.56	3.35	4.67	13.3	13.6
18.6		0.160	0.489	1.56		3.33	4.73		13.2
24.8			0.482	1.63	1.57	3.32	4.58	12.2	12.7
46.4	0.0300	0.159	0.475	1.49	1.48	2.98	4.11	10.5	10.5
46.4	0.0373	0.143	0.478	1.46		2.96	4.04		10.4
49.7		0.133	0.473	1.51	1.49	2.99	4.04	10.2	10.8
92.8	0.0300	0.144	0.457	1.39	1.37	2.65	3.57	8.42	8.51
92.8	0.0373	0.139	0.453	1.35		2.63	3.44		8.44
99.3	0.0333	0.141	0.460	1.38	1.36	2.61	3.49	8.20	8.62
248	0.0366	0.138	0.422	1.19	1.18	2.10	2.75	6.02	6.06
497	0.0359	0.134	0.392	1.07	1.05	1.86	2.37	4.70	4.74

... see Figures 20 and 21
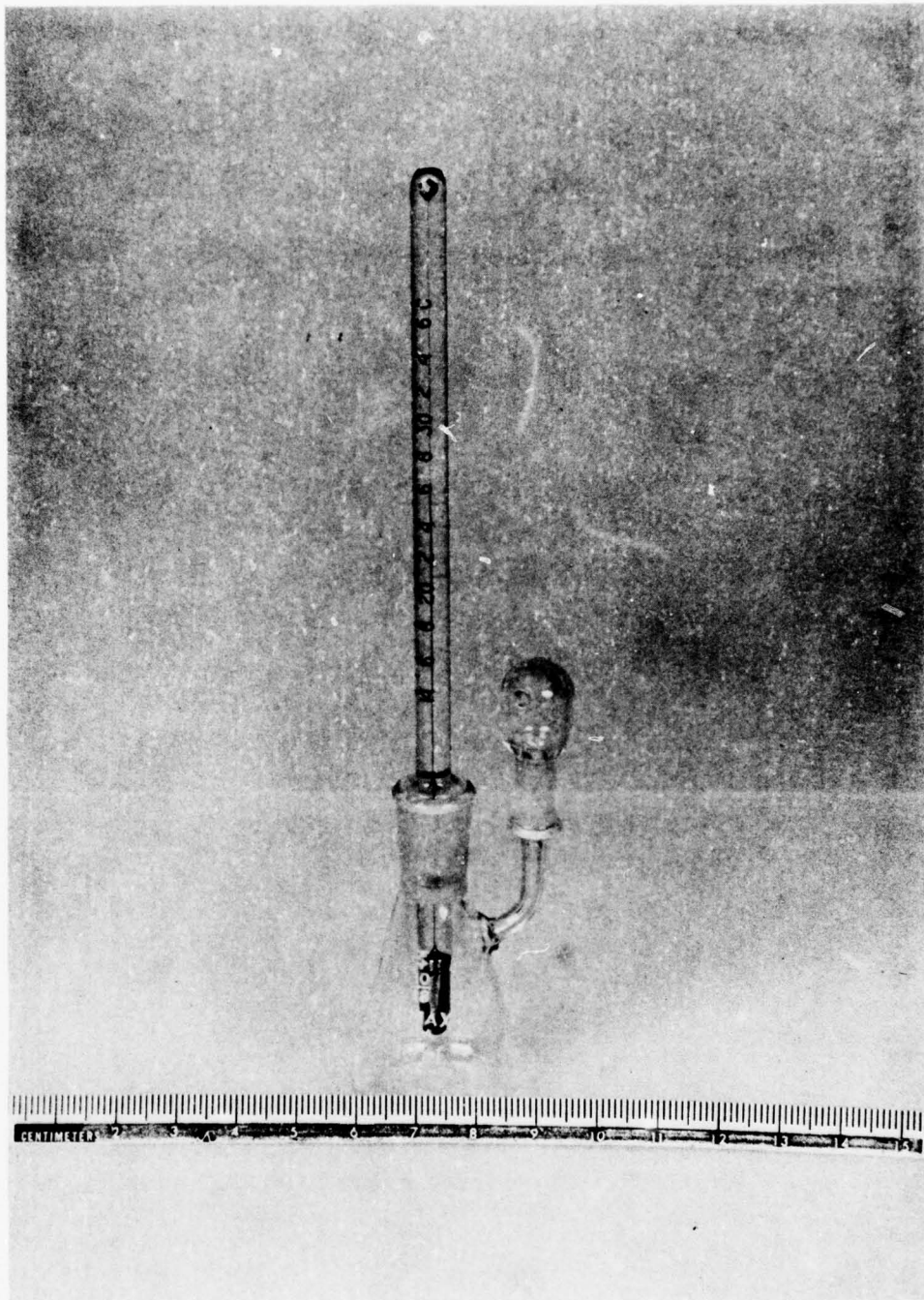
Figure 1: Pycnometer
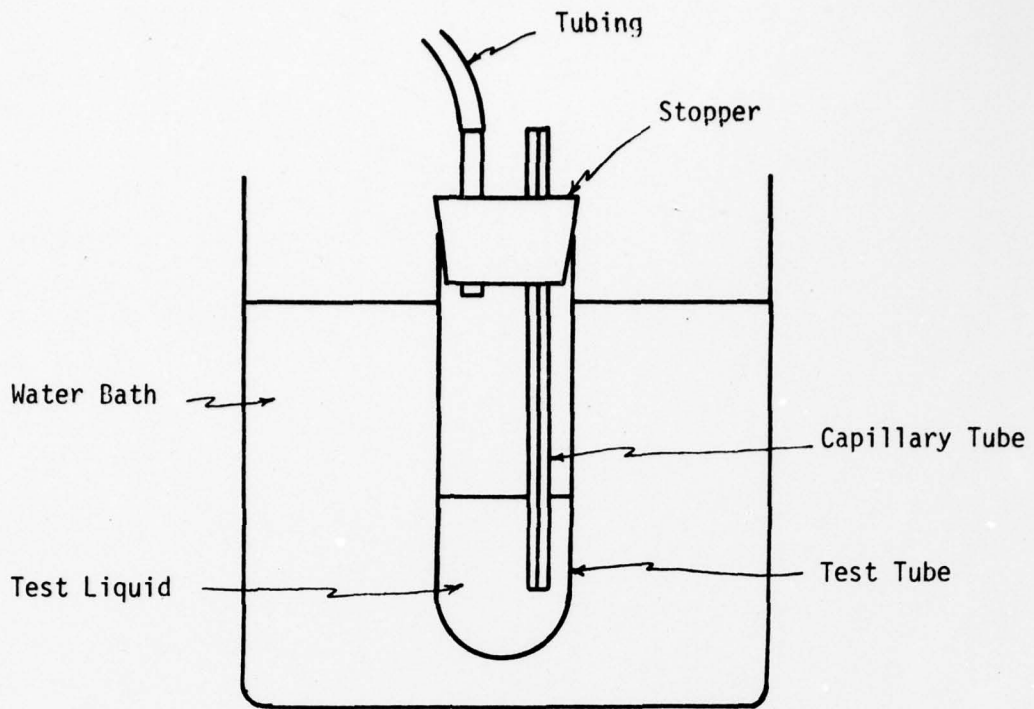
Figure 2a: Surface Tension Apparatus
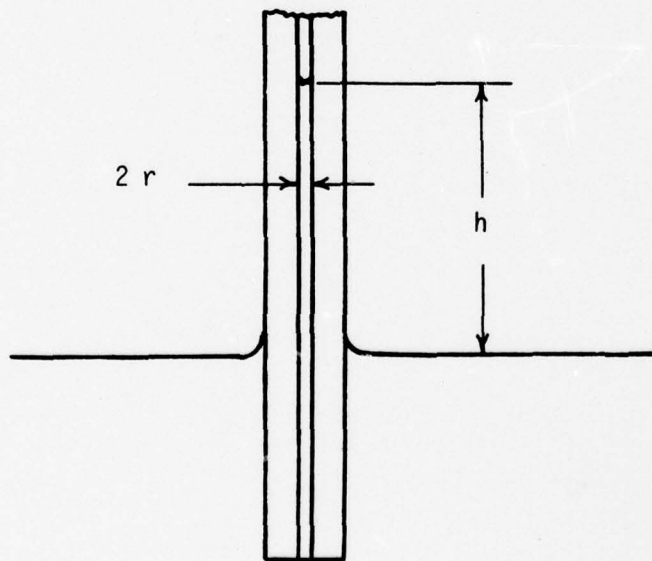
Figure 2b: Enlargement of Capillary Tube

Water In →

Water Out ←

→ To Manometer

To Vacuum
Tank and Pump

Condensor

Copper "S"
Hook

Precision
Thermometer

Muslin
Cloth

Flash
Guard

200 ml
Flask

Heating
Mantle
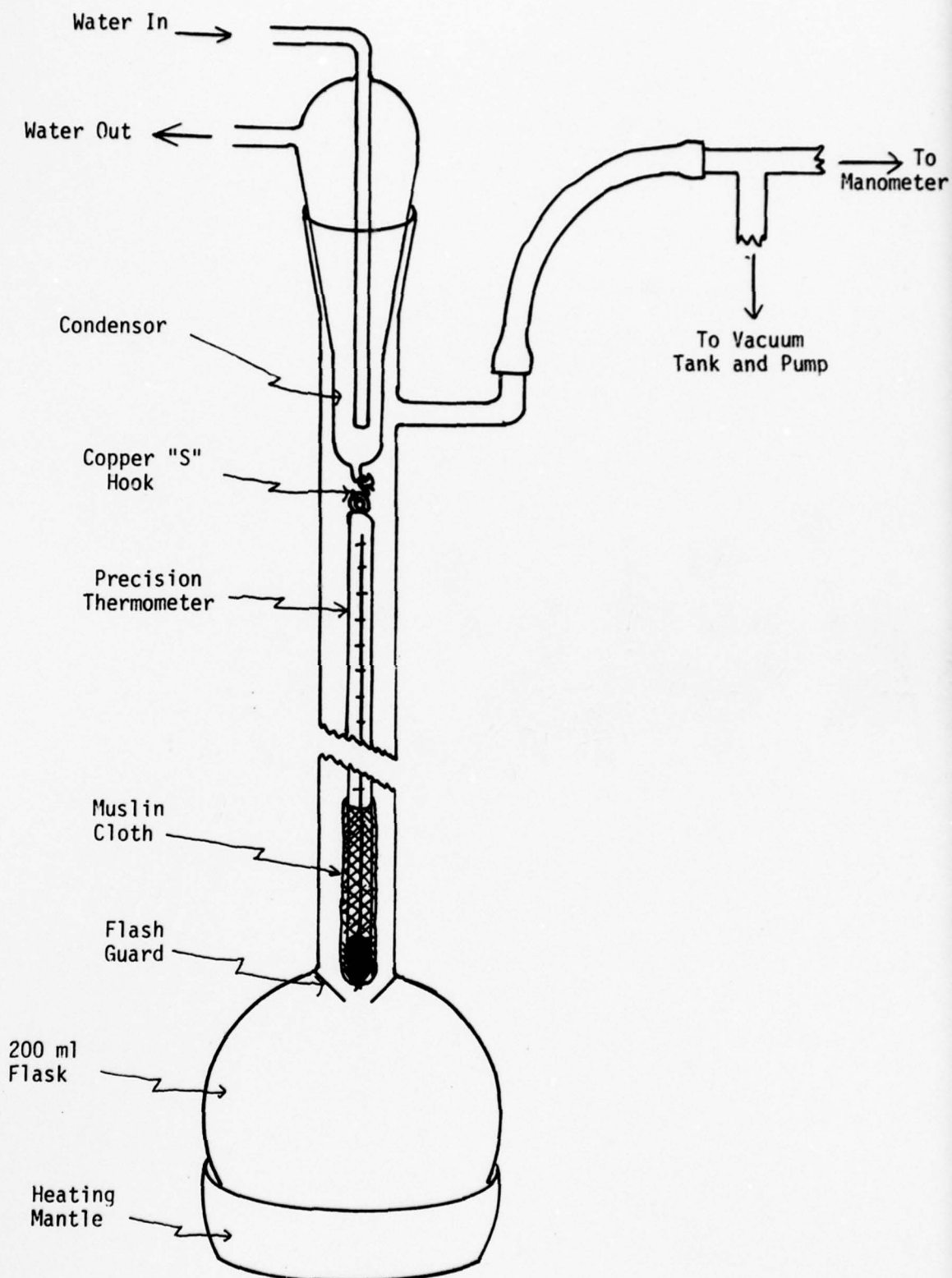
Figure 3:   Vapor Pressure Apparatus
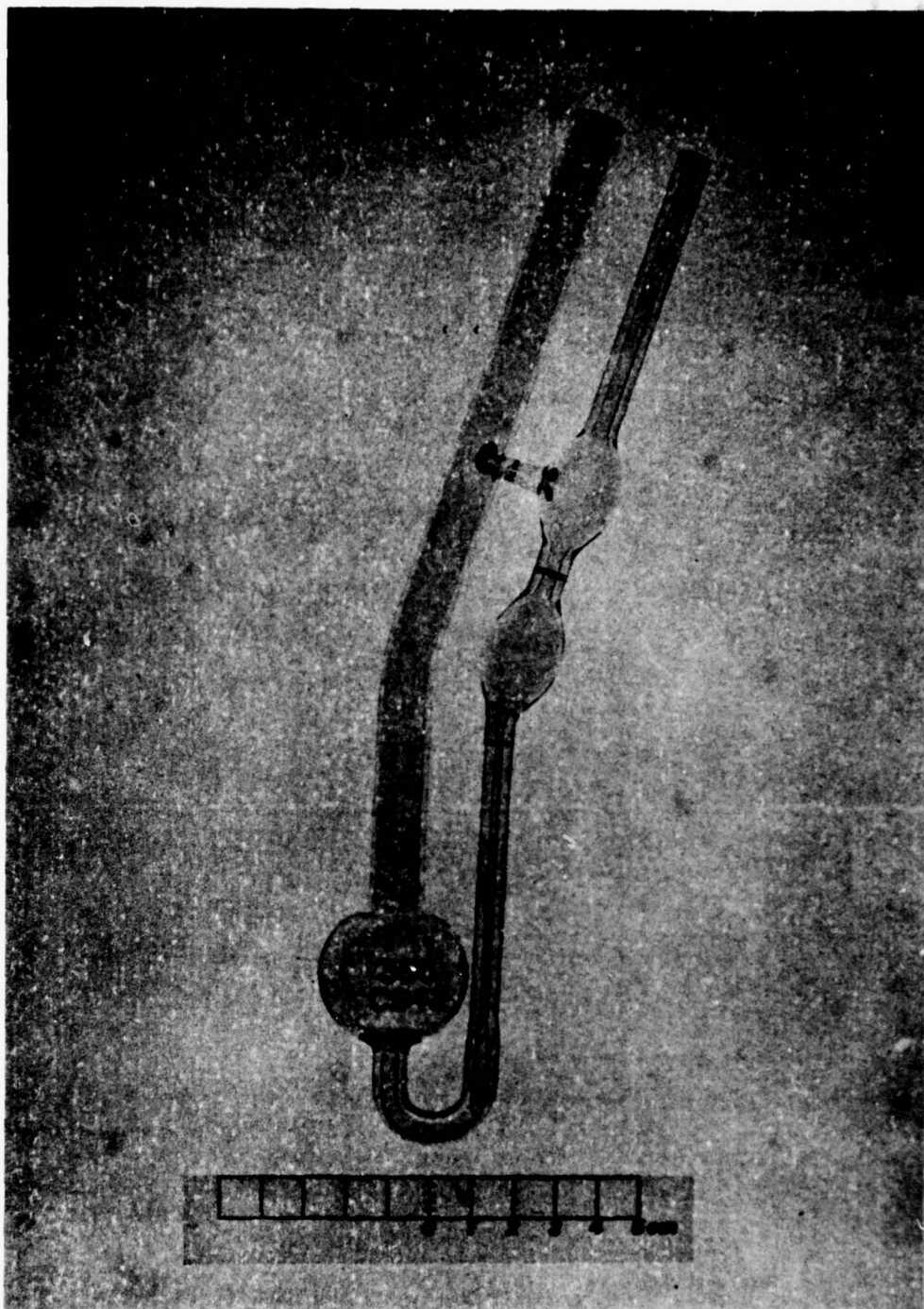
Figure 4: Ostwald Viscometer

UNCLASSIFIED
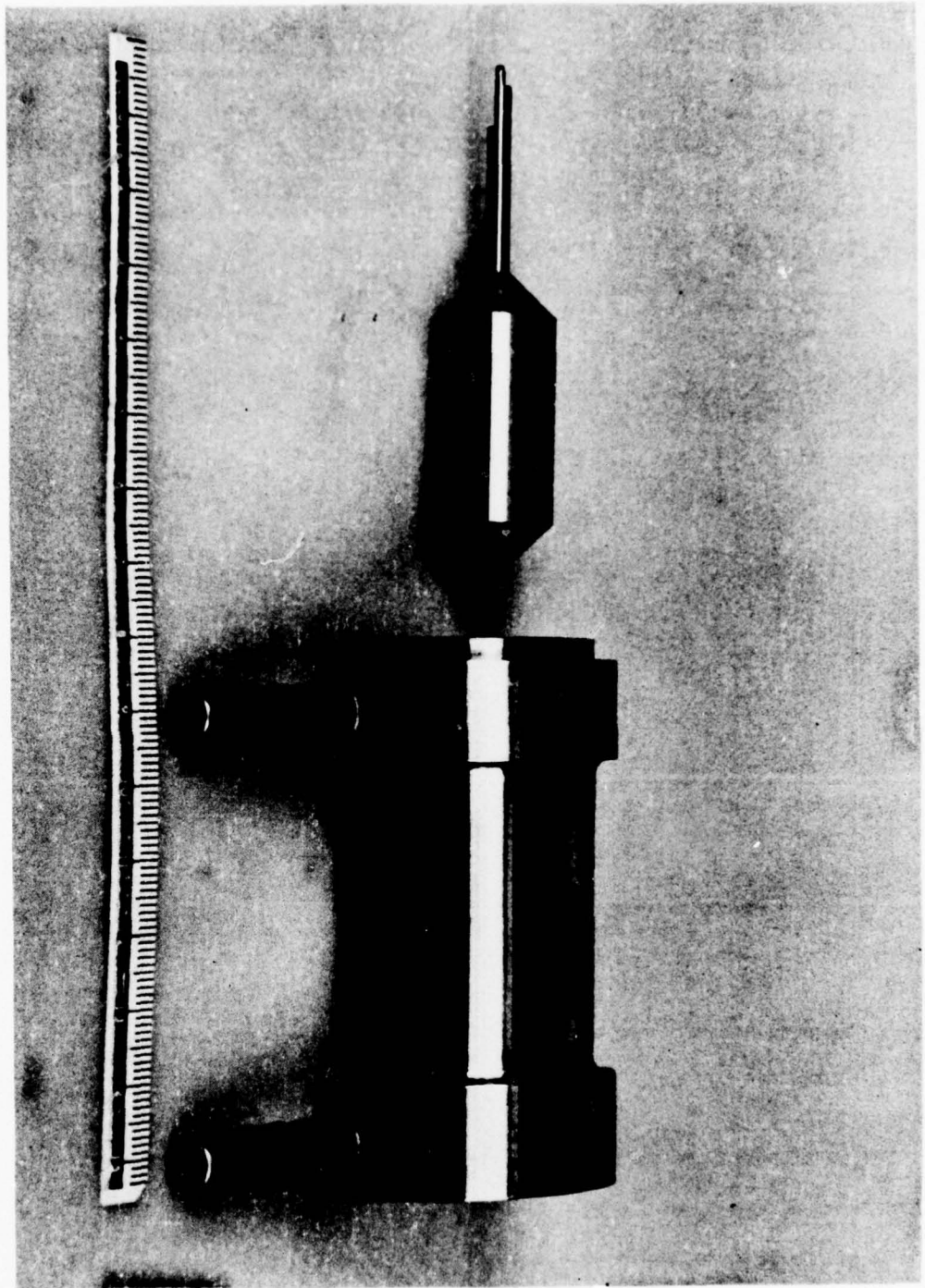
Figure 5:   Brookfield Small Sample Adaptor

Test Liquid

Spindle

Housing

Water Out

Water In
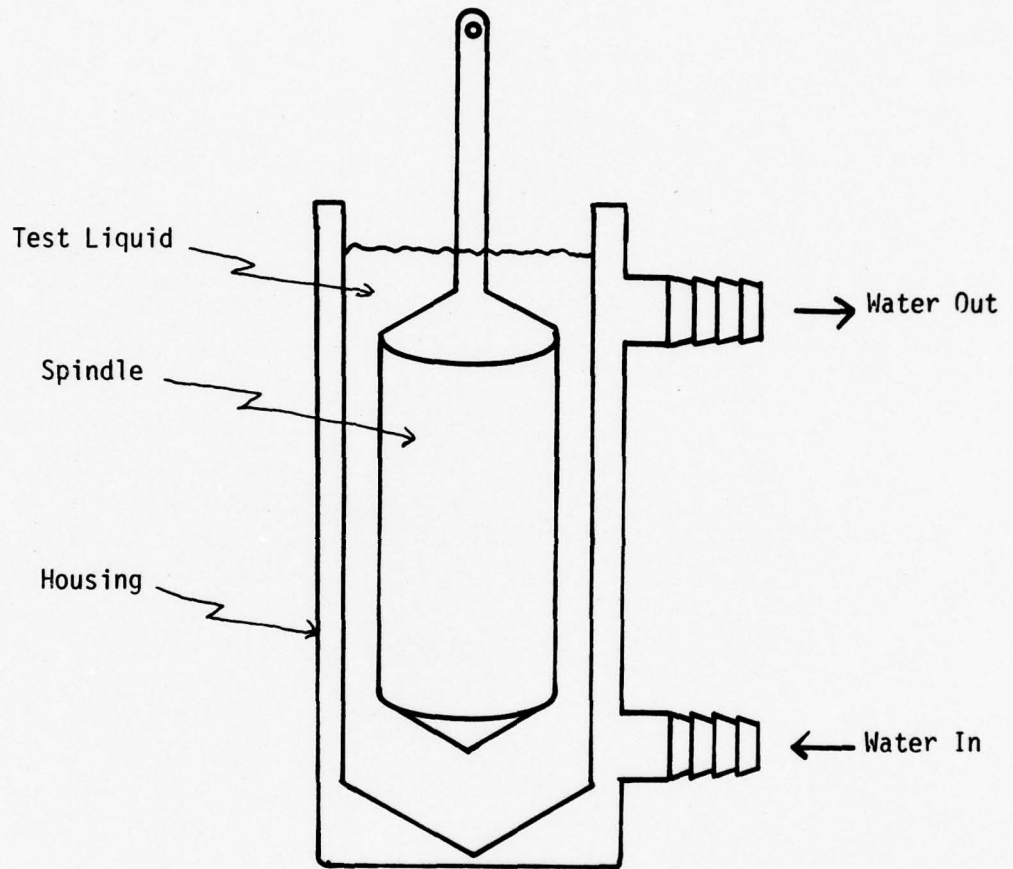
Figure 6:   Schematic of Brookfield
            Coaxial Viscometer
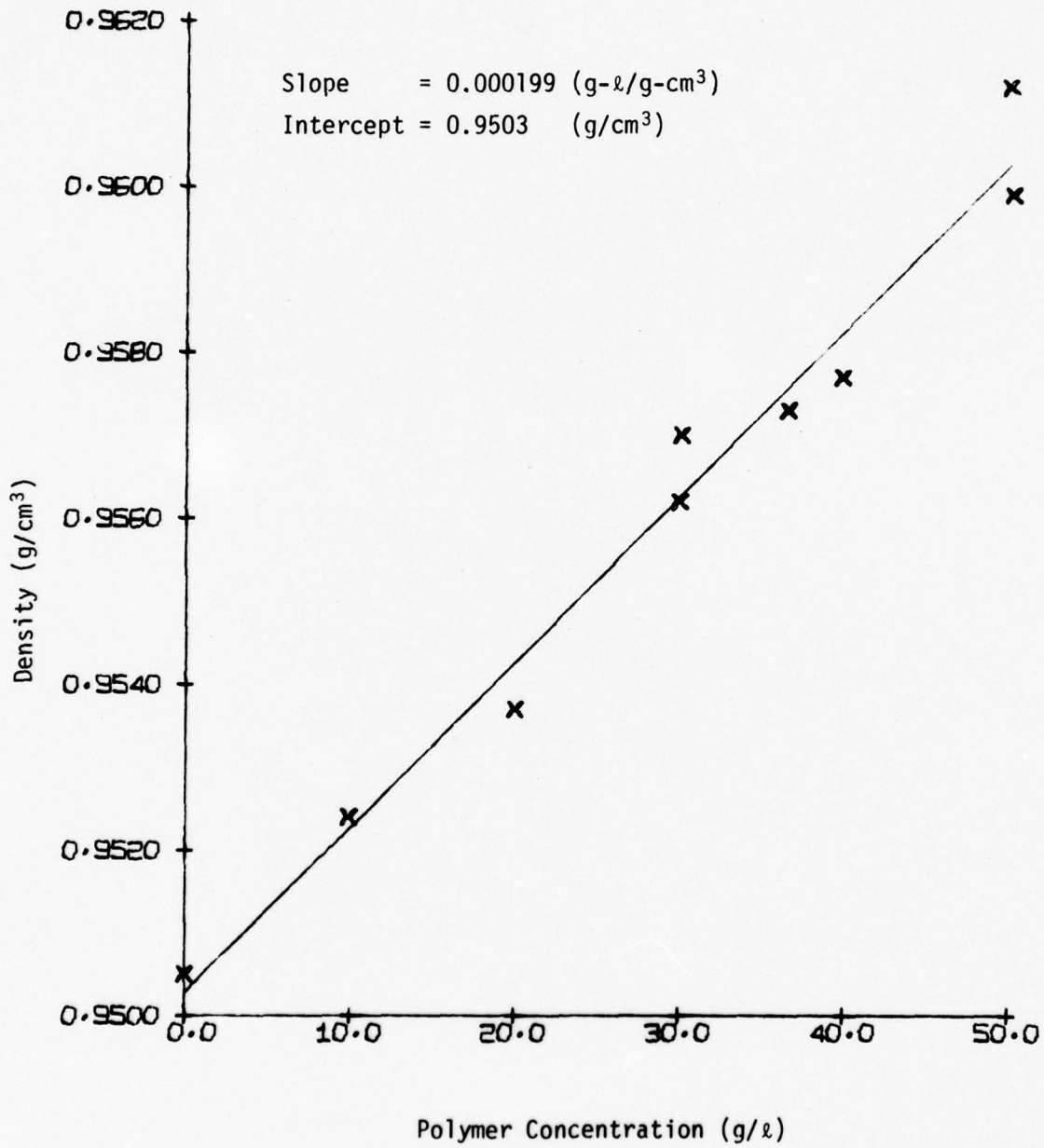
Figure 7:   Polymer Effect on Solution Density
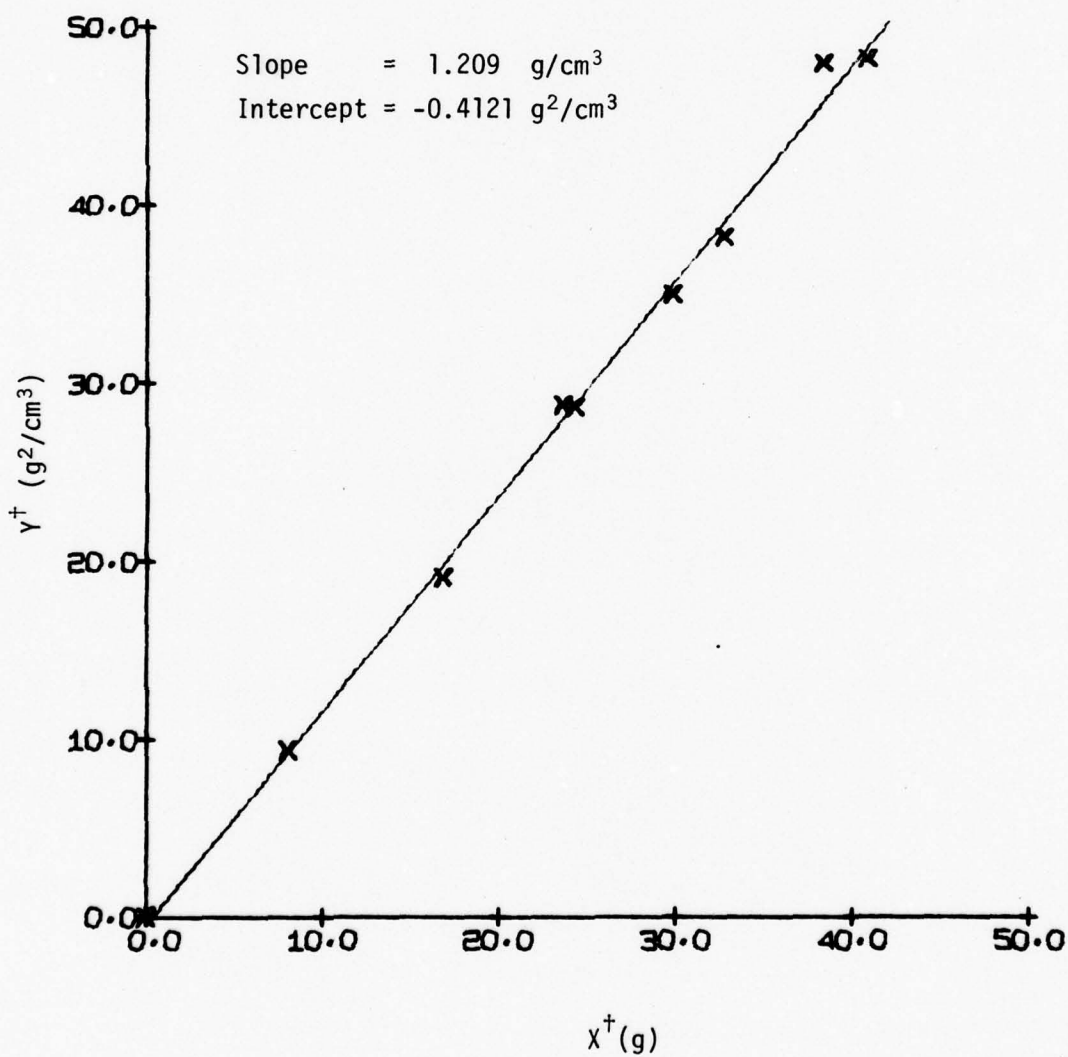
Figure 8: Dissolved Density Determination
[†](See Equation 2 of the Theory)
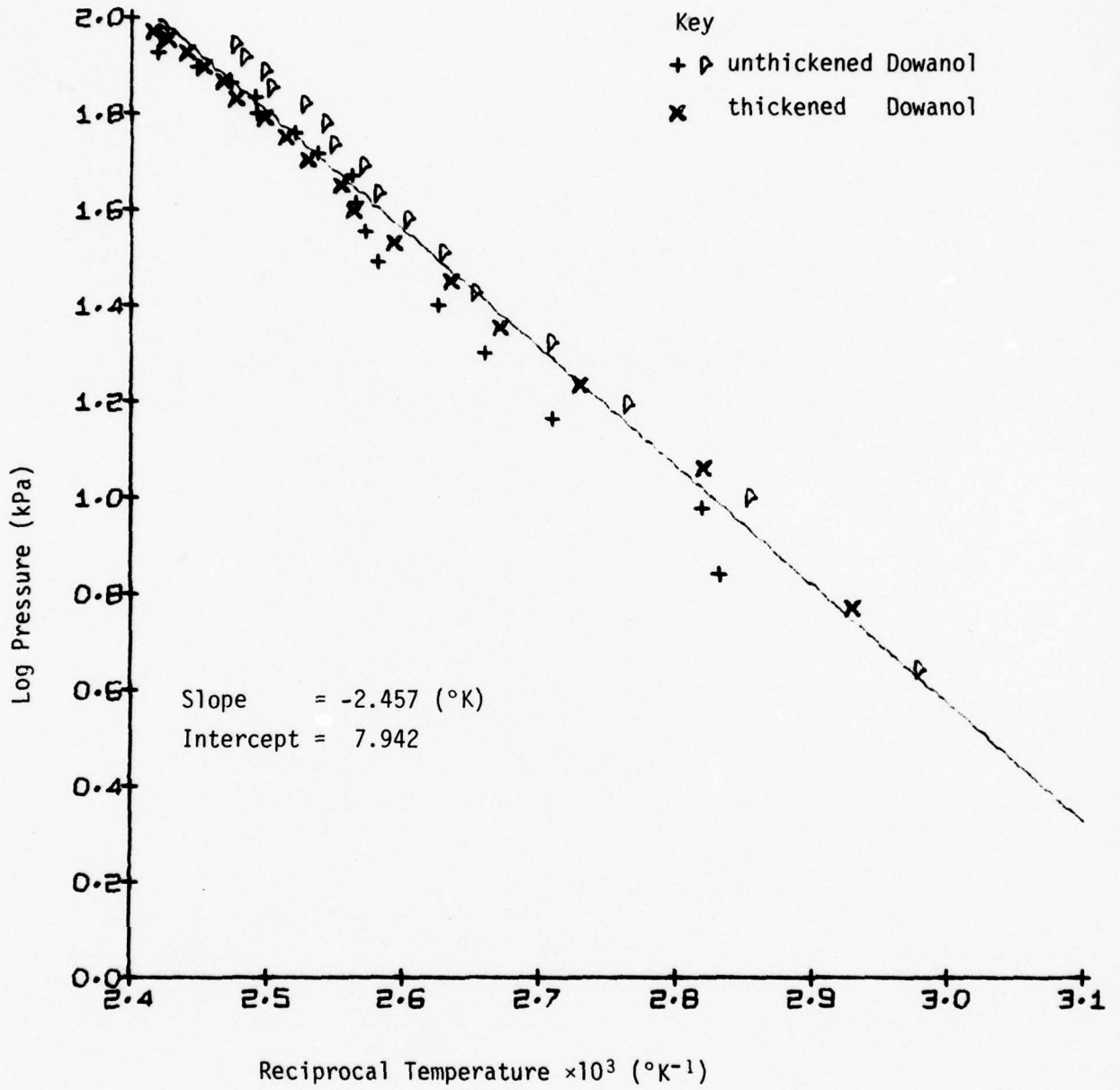
Figure 9: Vapor Pressure Data

Figures 10 to 18

Linear Relationships Between

Log Shear Rate and Log Shear Stress
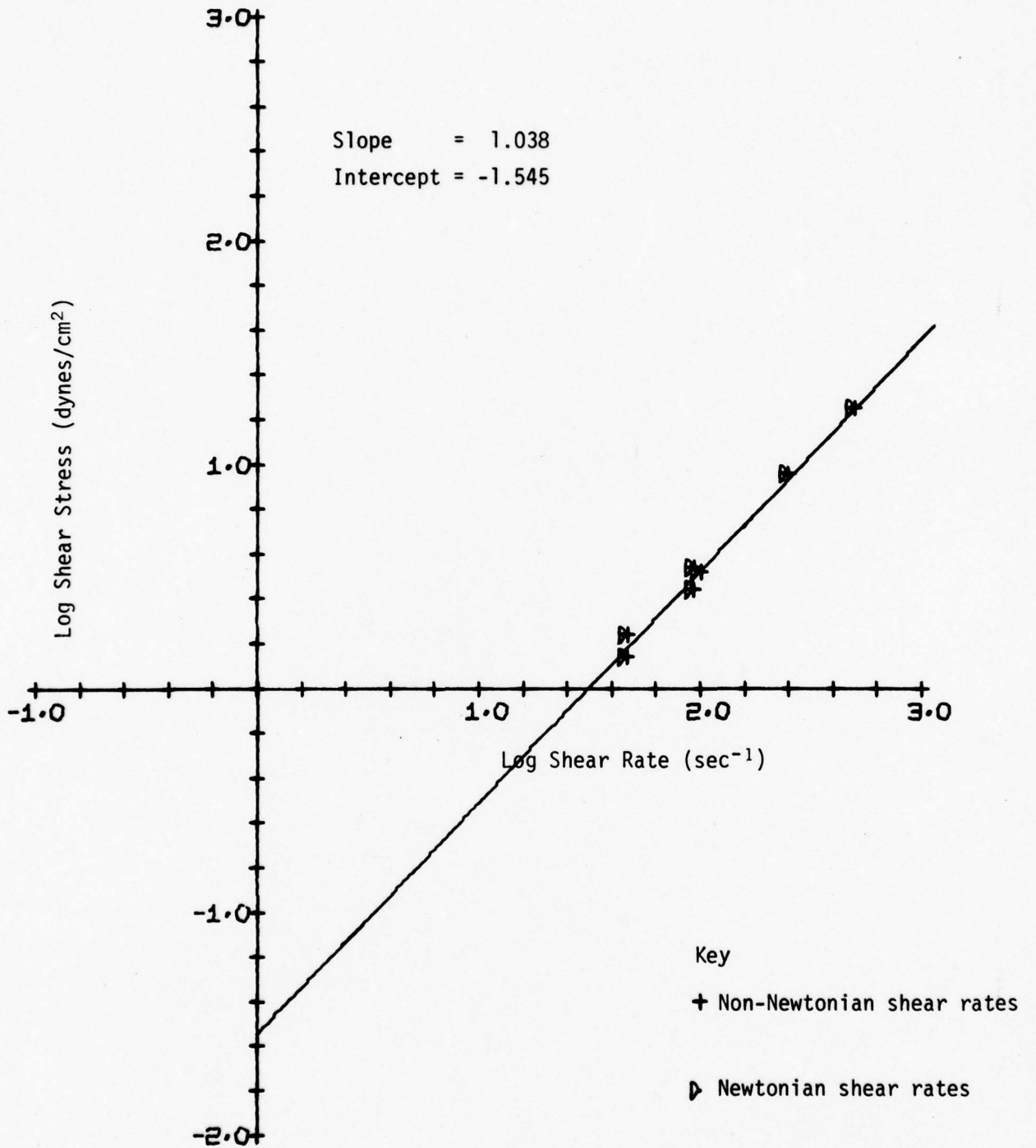
Figure 10:   Dowanol 1
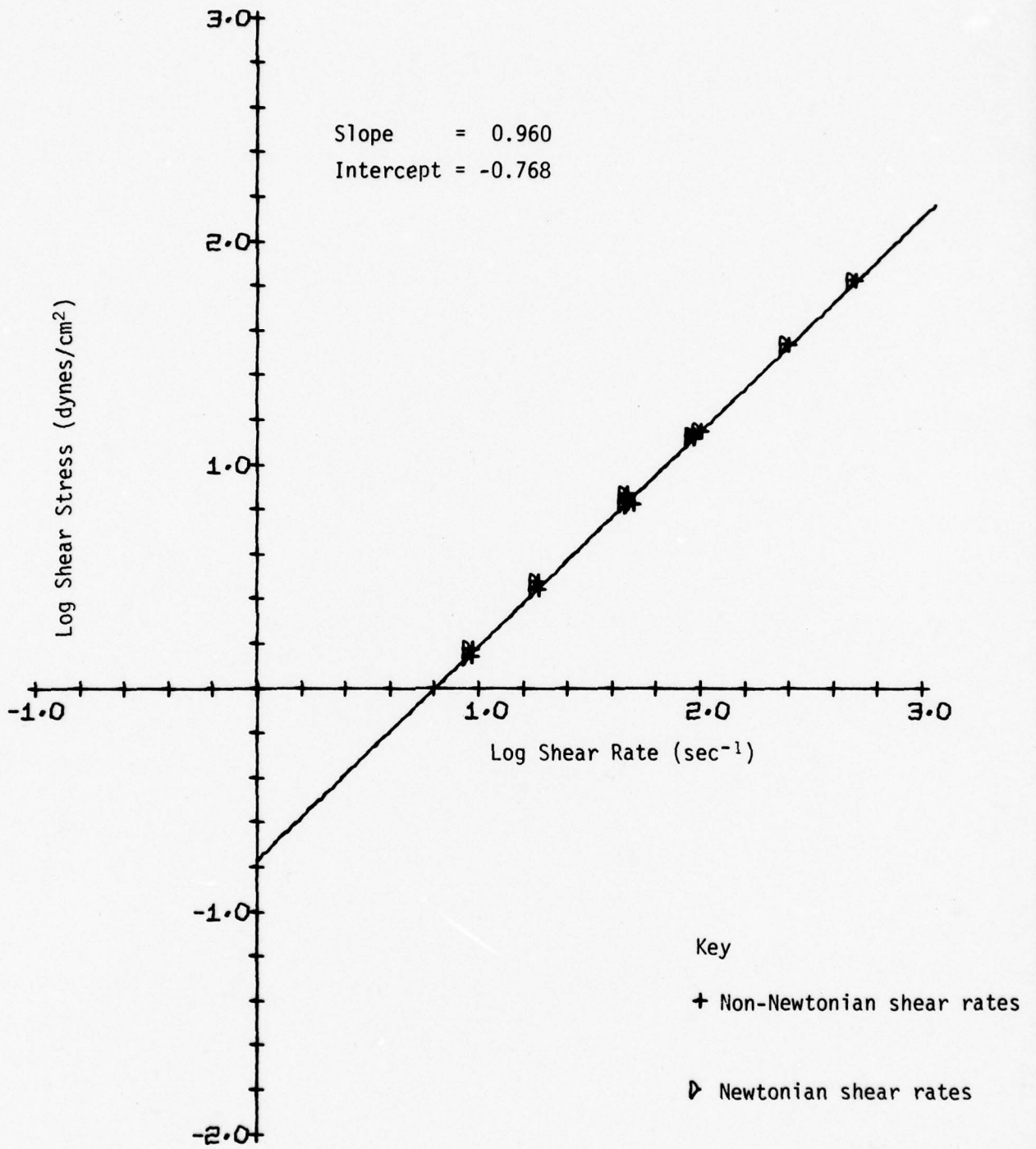
Figure 11: Dowanol 2
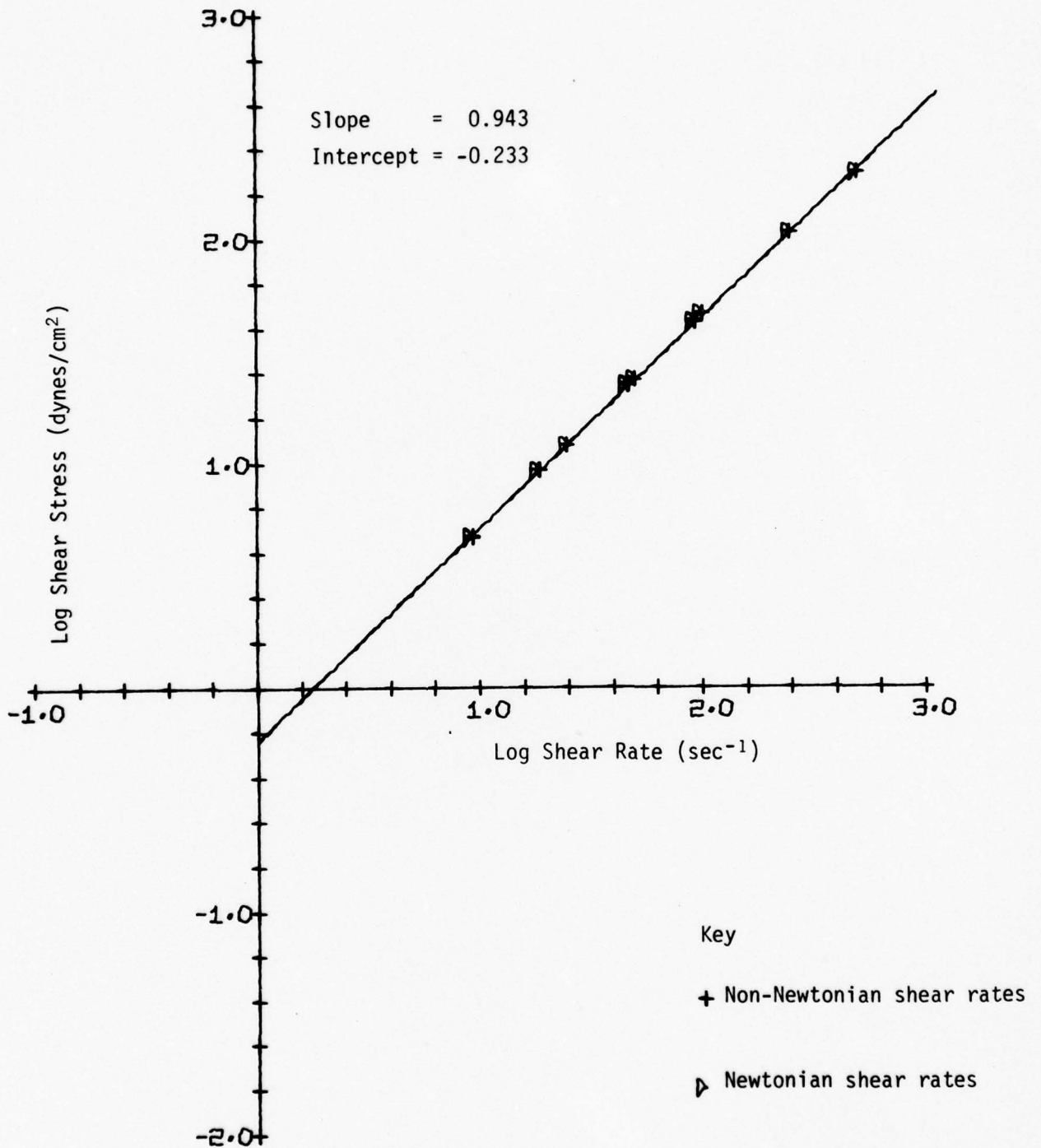
Figure 12: Dowanol 3

Figure 13:   Dowanol 4

Slope   = 0.916
Intercept = 0.289

Log Shear Stress (dynes/cm²)

Log Shear Rate (sec⁻¹)

Key

+ Non-Newtonian shear rates

▷ Newtonian shear rates

Figure 14:   Dowanol 5

Slope   = 0.875
Intercept = 0.664

Log Shear Stress (dynes/cm²)

Log Shear Rate (sec⁻¹)

Key

+ Non-Newtonian shear rates

▷ Newtonian shear rates

Figure 15: Dowanol 6

Slope   = 0.881
Intercept = 0.788

Log Shear Stress (dynes/cm²)

Log Shear Rate (sec⁻¹)

Key

+ Non-Newtonian shear rates

▷ Newtonian shear rates
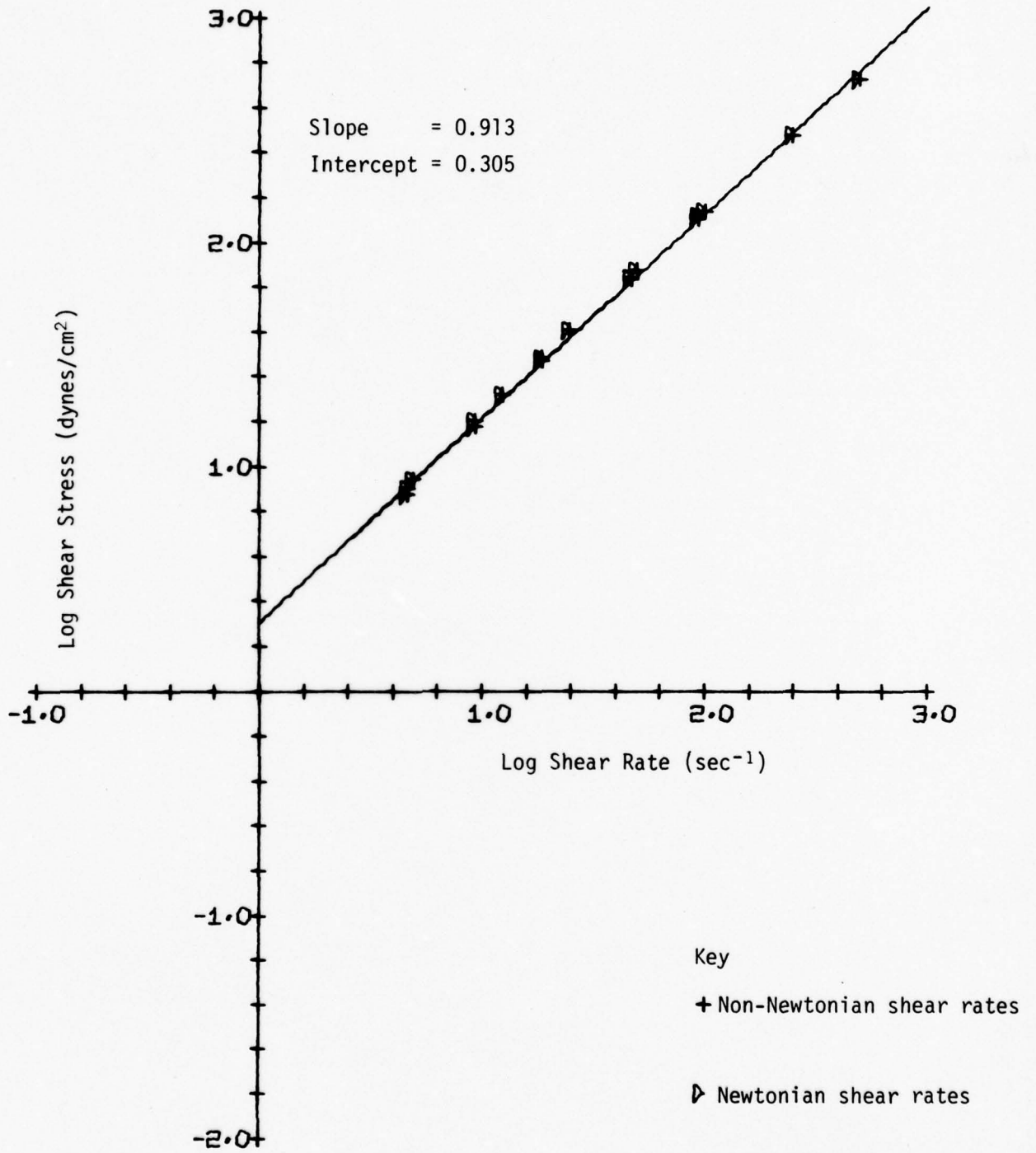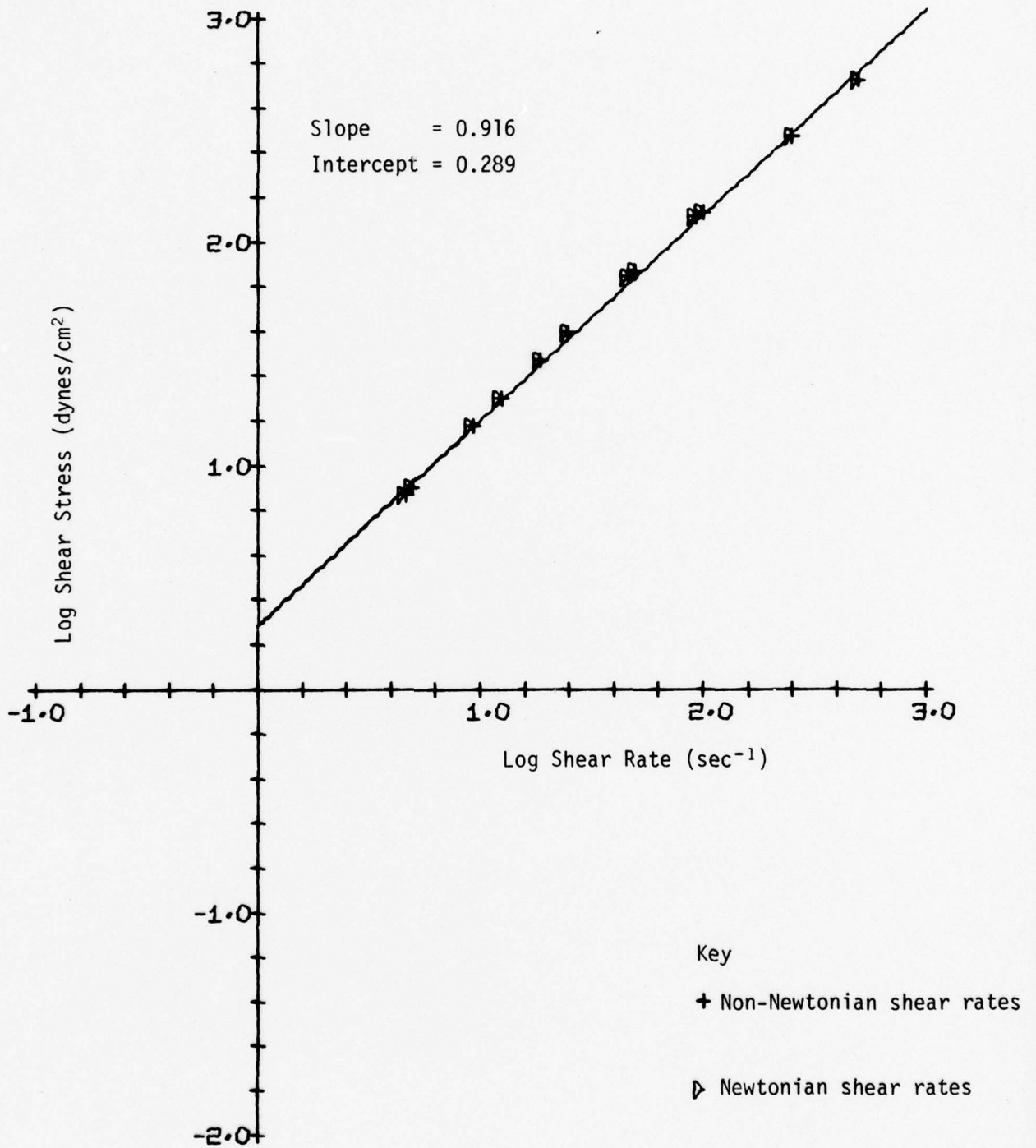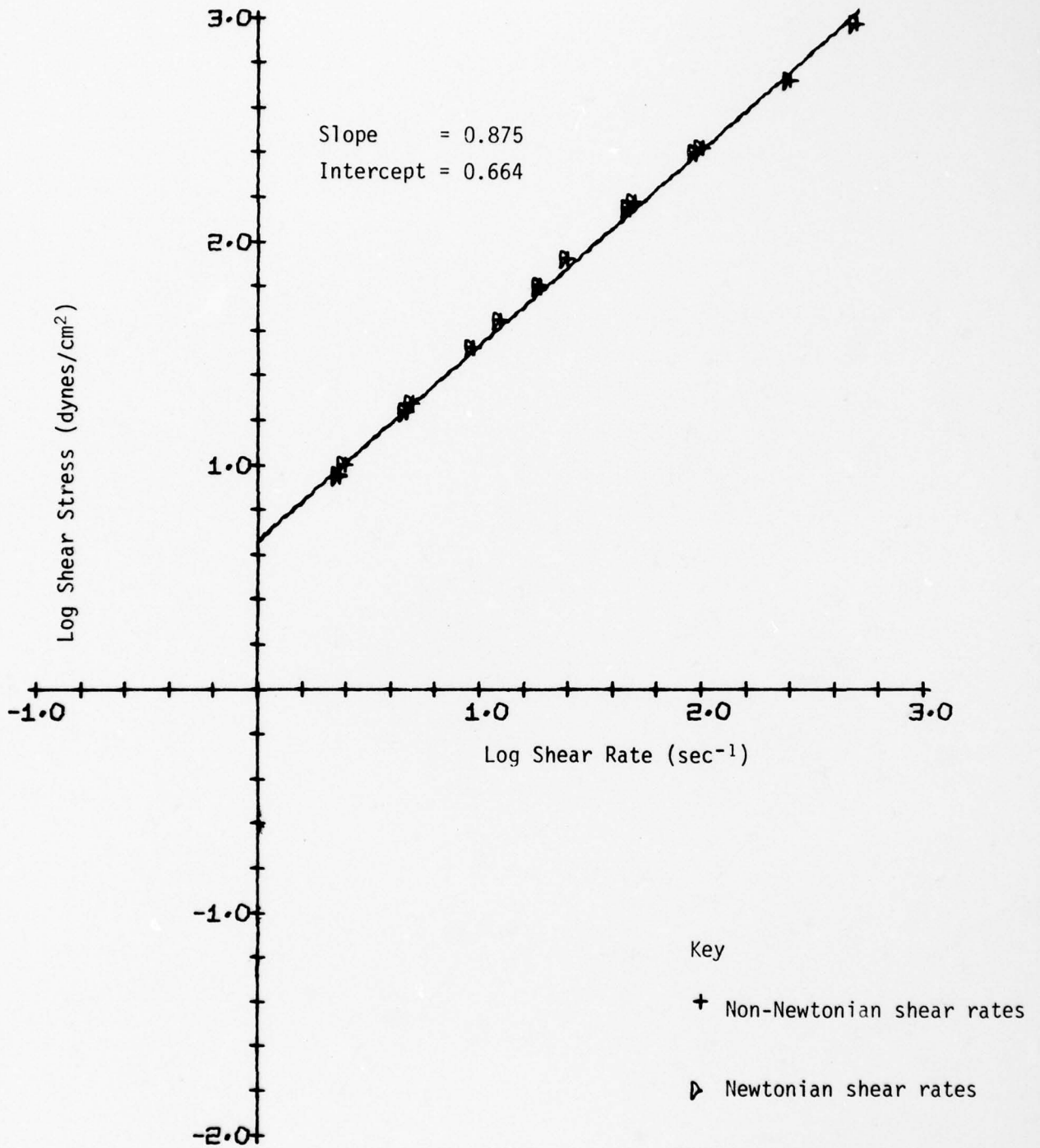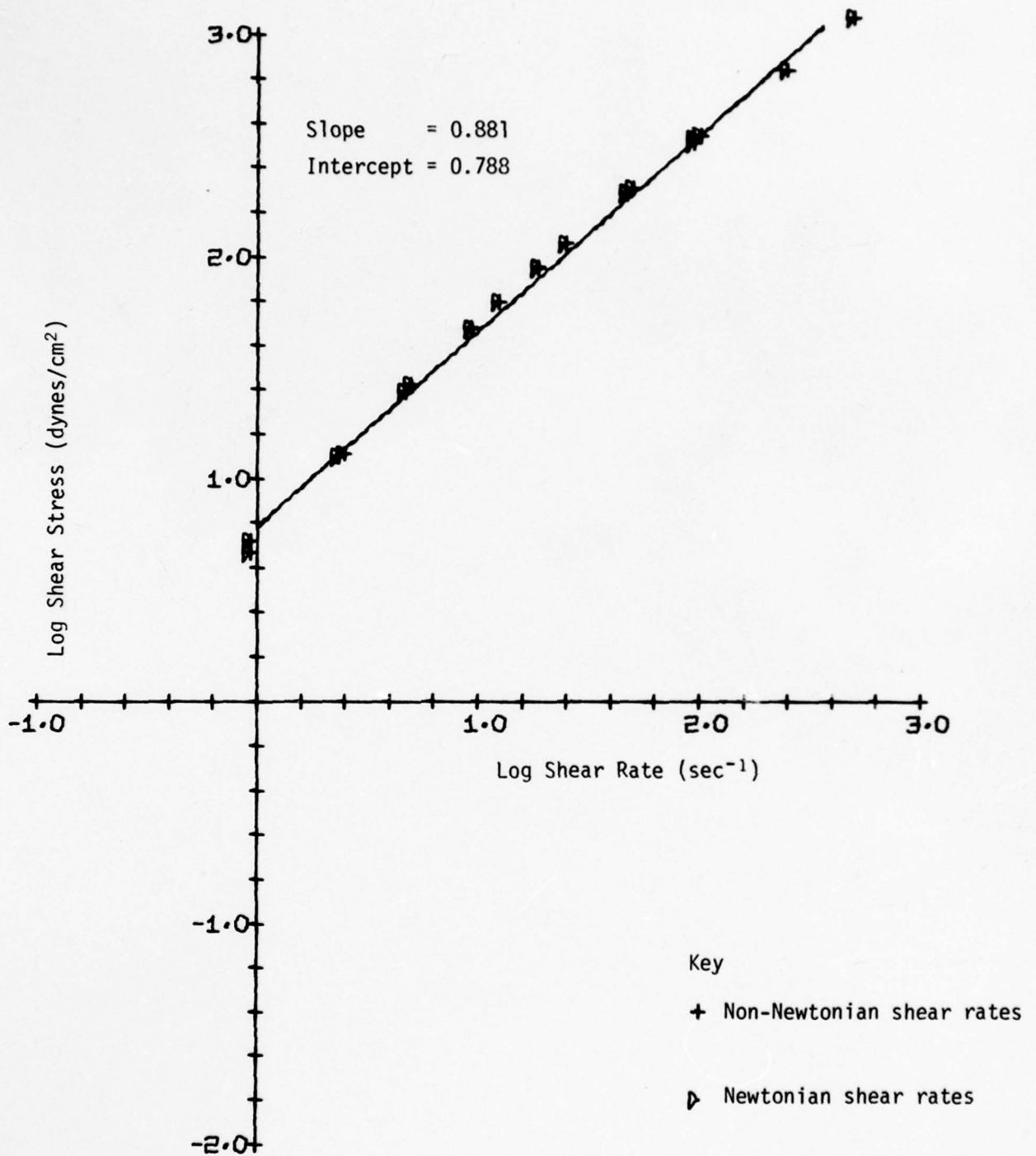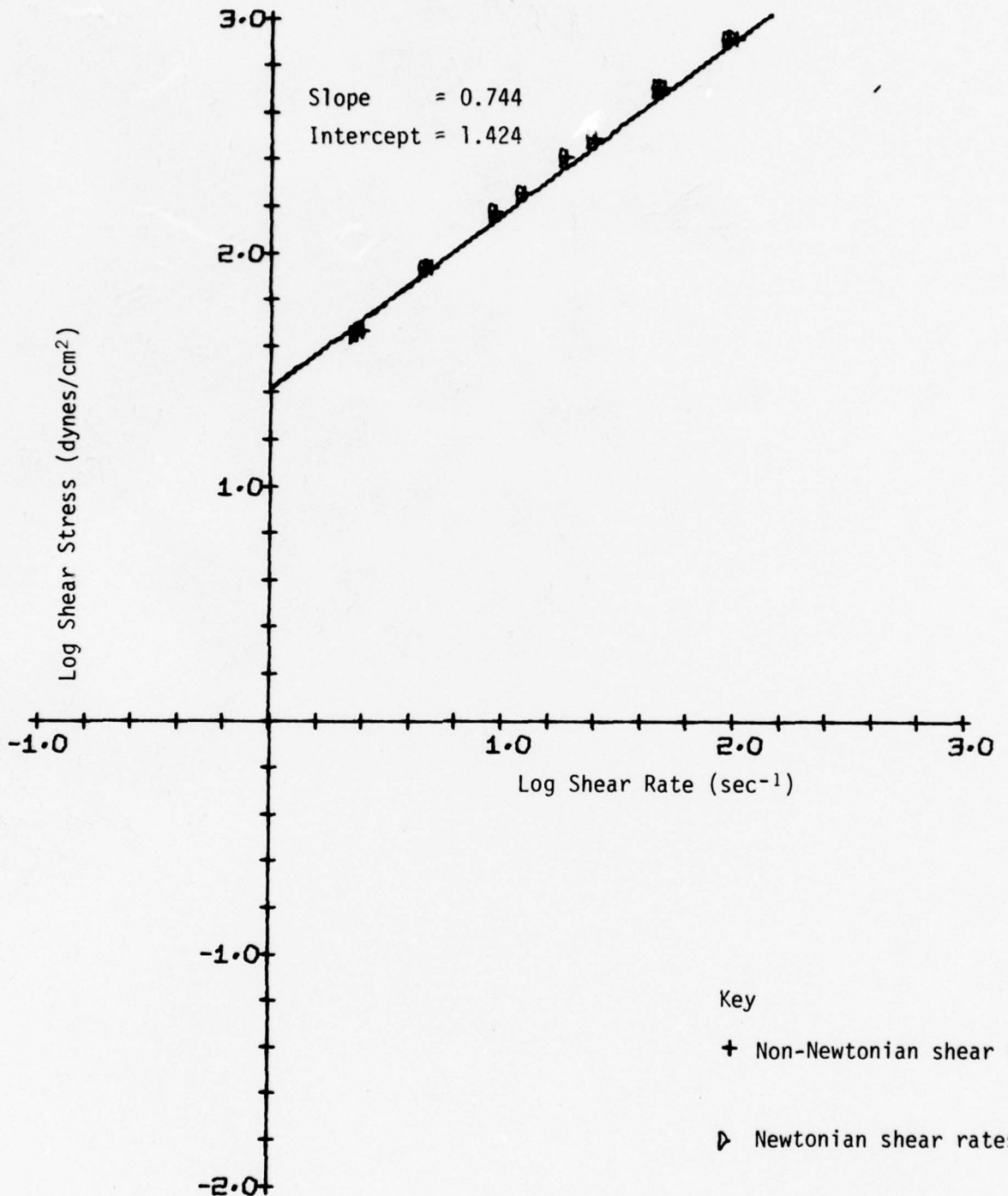
Figure 16:   Dowanol 7

Figure 17:   Dowanol 8
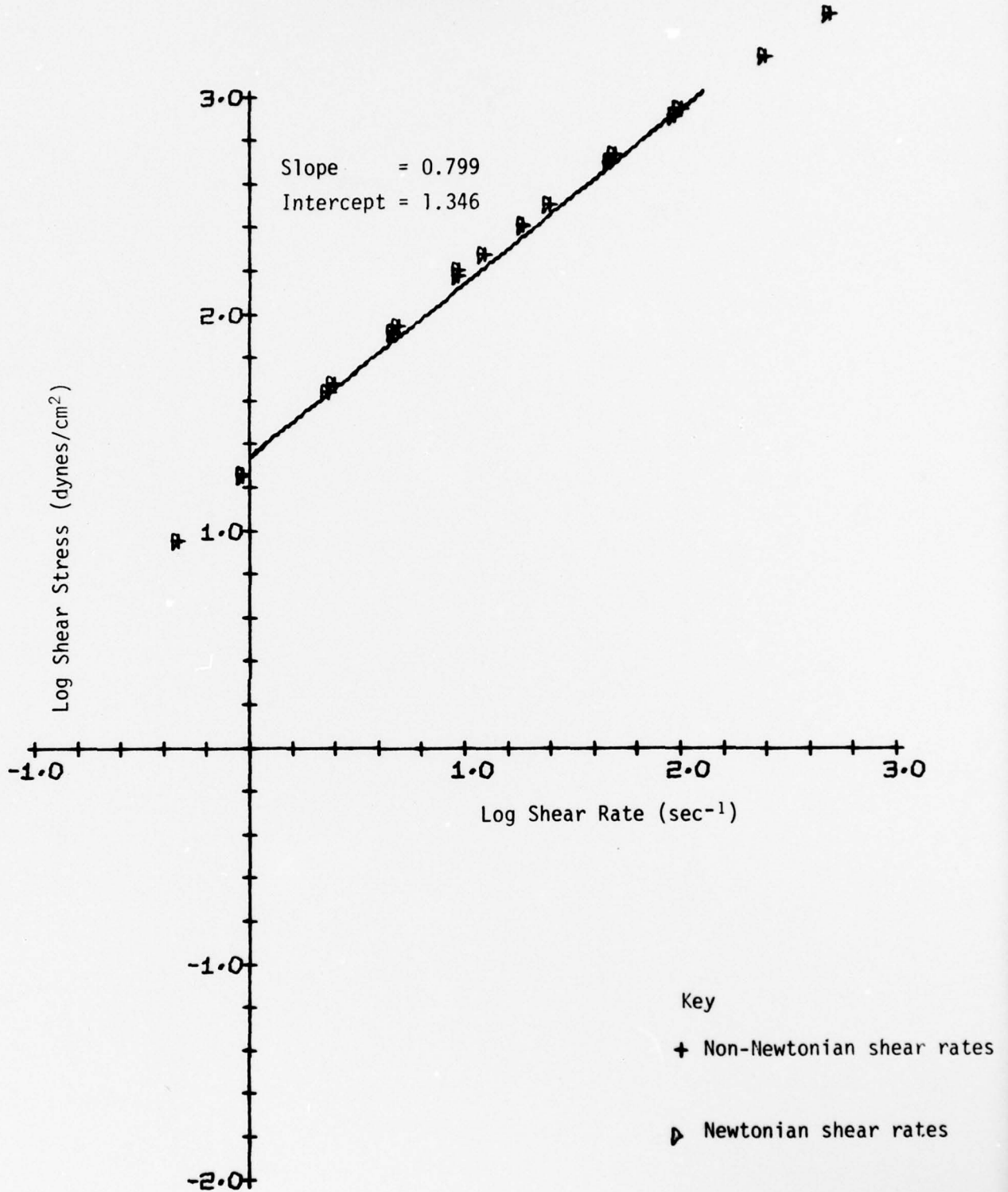
Figure 18: Dowanol 9

Slope   =   4.88 (ℓ/g)
Intercept = -5.41
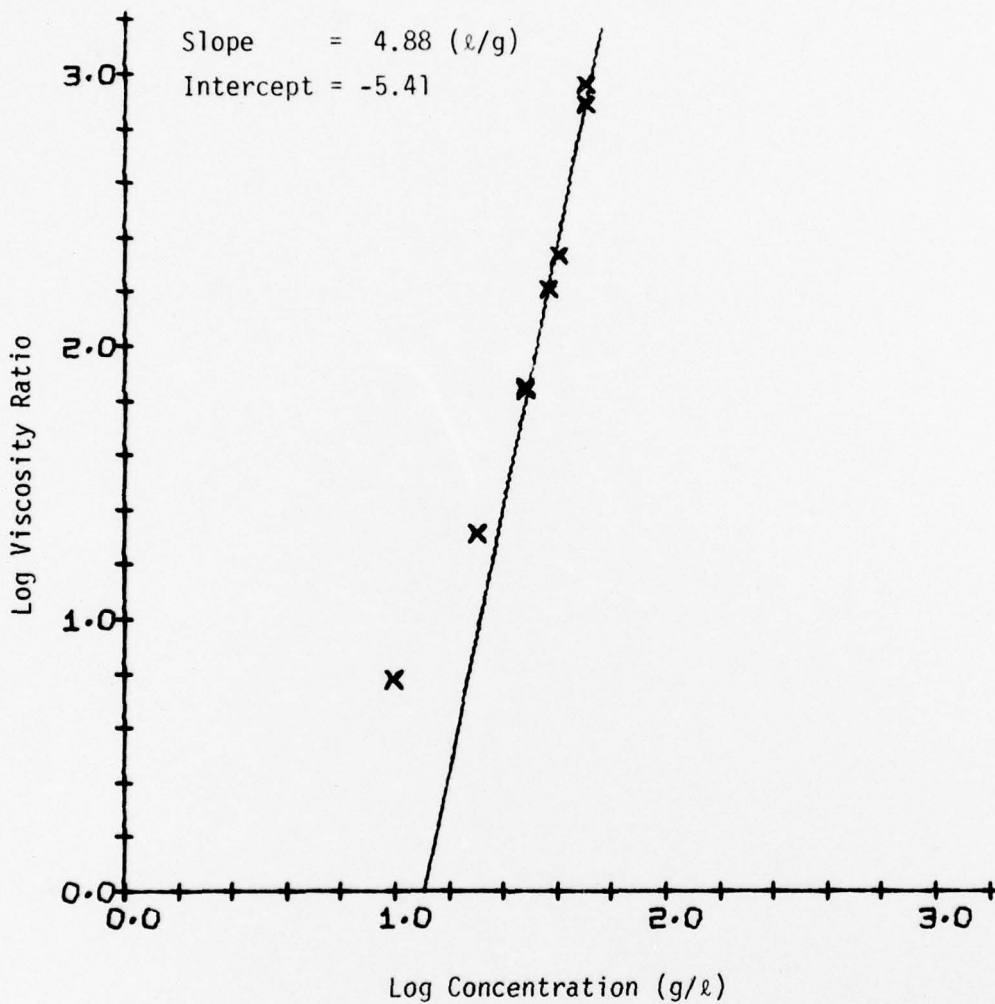
Figure 19: Effect of K-125 on Viscosity of Dowanol
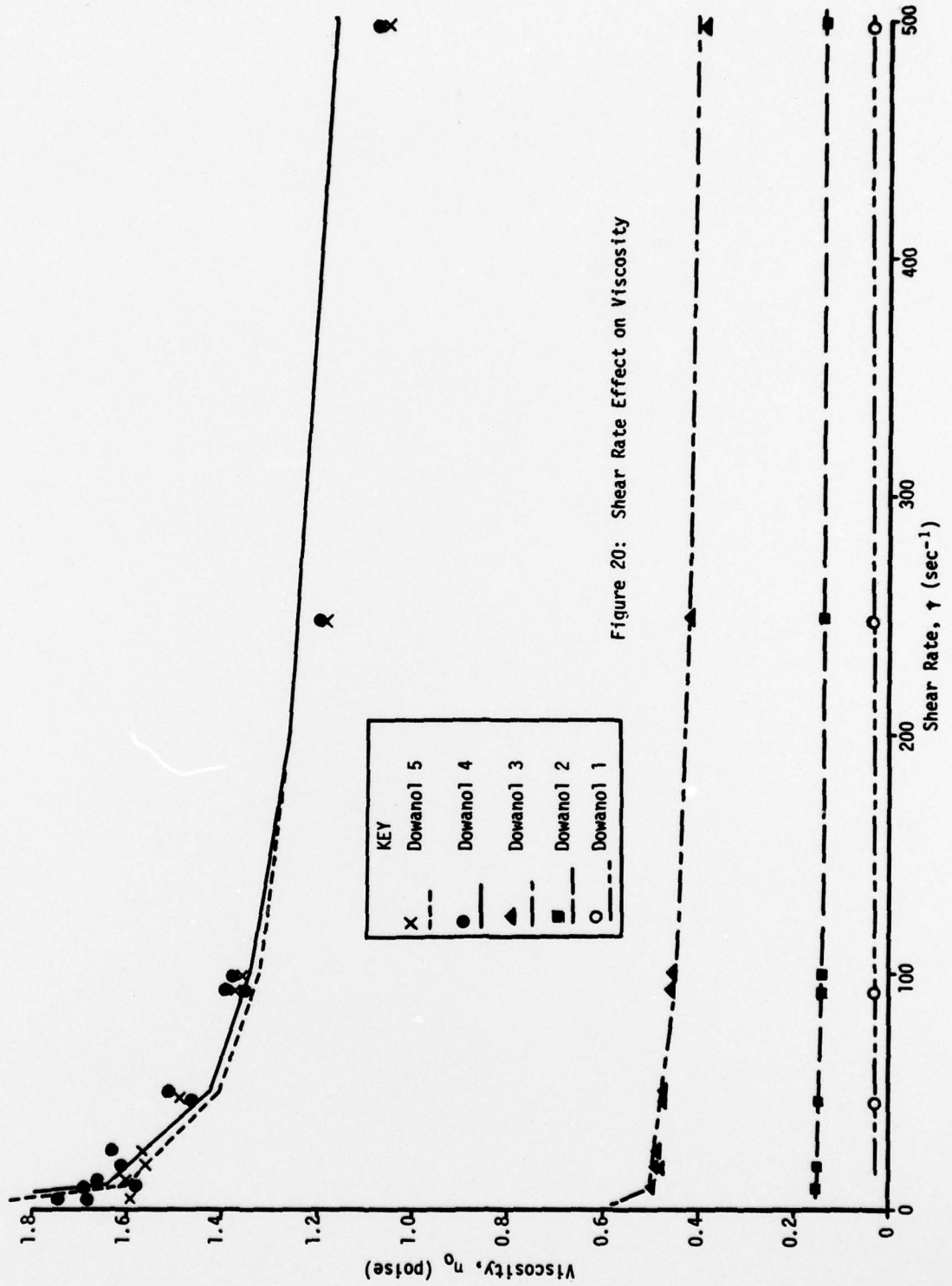
Figure 20: Shear Rate Effect on Viscosity

Figure 21: Shear Rate Effect on Viscosity
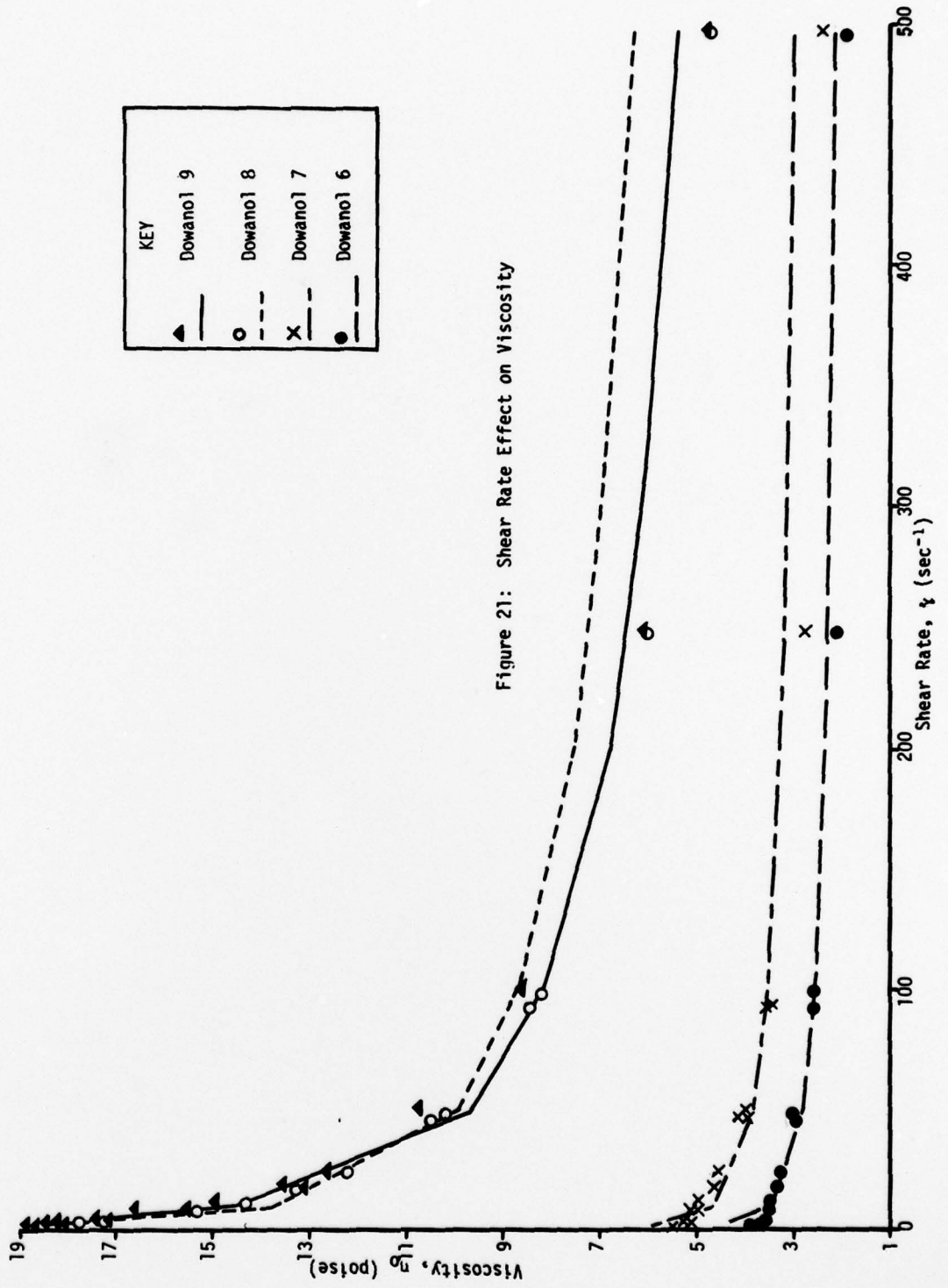
APPENDIX I

EXPERIMENTAL TECHNIQUES

All glassware was frequently cleaned with a chromic acid solution and then thoroughly rinsed with distilled water and acetone.

1. <u>Density</u> - This property was measured by means of a pycnometer with a thermometer.

The sample was cooled to 5 to 10°C below the test temperature and introduced into the clean pycnometer. The thermometer was then inserted into the pycnometer taking care not to trap any air bubbles. The pycnometer was then placed in a water bath for 10 to 15 minutes and allowed to come to thermal equilibrium. The excess fluid on the overflow arm was wiped off, being careful not to absorb any fluid from inside the arm. The pycnometer was then removed from the bath and the arm was capped. The pycnometer was wiped of excess water and left standing to dry for approximately 5 minutes, then weighed.

2. <u>Surface Tension</u> - This property was measured using glass, precision-bored capillary tubing (see Fig. 2).

The capillary rise apparatus was set up as in Figure 2. The test-liquid was poured into the test-tube to a depth of several centimeters in order for the capillary tubing to be partially immersed. The test-tube was then placed in a water bath and allowed to come to temperature (10 to 15 minutes). Pressure was then applied to the liquid to raise the level in the capillary, then released to allow the level to fall back to its equilibrium level. Suction was then applied to the liquid to lower the level in the capillary, then released to allow the level to climb back to its equilibrium level. Using a cathotometer, four or five readings of the capillary height at equilibrium were taken for each test-liquid.

3. <u>Vapor Pressure</u> - This property was measured by the Ramsey-Young technique using the Tobey modification (Ref. 1).

In this apparatus (Fig. 3) the liquid was vaporized from the round bottom flask using a heating mantle controlled by an autotransformer. The vapor would condense on the cold finger and flow down the thermometer to a hygrometer wick around the thermometer bulb.

The temperature measured was that of the liquid in equilibrium with the vapor.

Equilibrium was determined by a constant efflux time of 1 drop every 5 to 10 seconds off the thermometer bulb.

The pressure was controlled by a vacuum pump attached to a manometer and large ballast tank. The tank prevents sudden pressure surges from disturbing the equilibrium.

The pressure was successively reduced in steps, and a series of data points taken. The autotransformer was set in order to maintain a suitable rate of reflux at each reading.

4. <u>Viscosity</u> - This property is unfortunately more complex to measure than those previously described. Two different devices which work on different theoretical bases were used. The first apparatus is the Ostwald viscometer which works on the principle of capillary flow (see Fig. 4). The second apparatus is the Brookfield viscometer which works on the principle of coaxial flow (see Figs. 5 and 6).

  a. <u>Ostwald Viscosities</u> - The apparatus used was the Canon-Fenske type Ostwald viscometer.

To charge the viscometer, a rubber tube was connected to the large arm and the viscometer was inverted, dipping the small arm into the sample. Suction was applied to the rubber tube and the liquid was drawn up to the second etched line to fill both bulbs. The visco-meter was then turned back to its normal vertical position and the small arm was wiped clean. The viscometer was then placed in the constant temperature bath and allowed to come to thermal equilibrium (15 to 20 minutes). With a suction bulb attached to the small arm, the fluid was drawn up past the top etched line. The suction bulb

was then removed and the time was recorded for the fluid to pass both
etched lines. Measurements were taken for times greater than 200
seconds for which kinetic energy effects can be neglected as recom-
mended in the ASTM standards (Ref. 2).

Three readings were taken for each sample and averaged.

b. Brookfield Viscosities - The Brookfield viscometer was used with
    the Brookfield Small Sample Adaptor. This device uses the prin-
    ciple of coaxial rotation with the outer cylinder stationary.
    Temperature control is achieved by a jacket around the outer
    cylinder.

The required amount of sample was placed in the chamber and the
spindle was then inserted. The spindle and chamber were then attached
to the viscometer and the sample was allowed to come to temperature
(10 to 15 minutes) by circulating water through the jacket. The
clutch on the viscometer was depressed and the motor turned on, rota-
ting the spindle in the sample chamber. The clutch was then released
and the dial was allowed to rotate until the pointer stabilized at a
fixed position on the dial. The lowest possible speed to obtain a
reading was determined then further readings were recorded from the
lowest to the highest possible speed. Torque was then evaluated from
these readings.

Two slight modifications were built into this device. A longer
spindle and chamber were constructed to determine if end effects
were present in the smaller apparatus and to study liquids with lower
viscosities. Also, a thicker spindle was constructed for the small
device in order to extend the range of shear rates.

APPENDIX II

RHEOLOGY REVIEW

Rheology is the study of the reaction of materials to applied forces. This brief review is based extensively on the material in Middleman's book: The Flow of High Polymers (Ref. 4).

There are three basic categories used to describe materials. These are:

    i)   Hookean Elastic (ideal solid)

    ii) Newtonian Fluid (ideal liquid)

    iii) Anything Else

The first two categories are simple mathematical models which seem to describe many materials under normal atmospheric conditions. The third category consists of a multitude of mathematical models each claiming to represent a particular class of materials which do not fall into either of the first two categories. These rheological models (mathematical equations) are useful to help predict how a material will react under new or different environmental conditions.

The rheological equations take the form of relating the stress tensor (internal forces acting over an area) to the strain tensor (the actual displacement of the material relative to an initial, relaxed state). Some of the more commonly-used shear relations include:

    i)   Hookean Solid (elastic):

$$\tau_{ij} = G\gamma$$

        stress $\propto$ strain

    ii) Newtonian Liquid (viscous):

$$\tau_{ij} = \eta_0 \dot{\gamma}$$

        stress $\propto$ strain rate

iii) Power-Law Fluid:

$$\tau_{ij} = \eta_o \dot{\gamma}^n$$

iv) Bingham Plastic:

$$\tau_{ij} = G\gamma \ldots (\tau_{ij} < \tau_o)$$

$$\tau_{ij} = \tau_o + \eta_o \dot{\gamma} \ldots (\tau_{ij} > \tau_o)$$

v) Viscoelastic Fluid (Maxwell Model, Linear):

$$\tau_{ij} + \frac{\eta_o}{G} \frac{\delta \tau_{ij}}{\delta t} = \eta_o \dot{\gamma}$$

vi) Viscoelastic Fluid (Kelvin Model, Linear):

$$\tau_{ij} = \eta_o \dot{\gamma} + G\gamma$$

vii) Viscoelastic Fluid (Spriggs Model, non-Linear):

$$\tau_{ij} + \frac{\eta_o}{G} (F \tau_{ij}) = \eta_o \dot{\gamma}$$

.... where F is a special derivative.

The above seven relationships represent attempts to model real phenomena by equations of various degrees of complexity. Many other models exist. For some models, the constants can vary with time in order to simulate thixotropic or rheopectic fluids. Modern models use tensor notation thereby making the equation independent of any coordinate system.

When trying to fit experimental results to a rheological model, the flow situation must be kept simple. There are two basic types of experiments used to determine rheological coefficients for fluids:

1. Simple Shear Experiments

The coefficient, η, is determined by dividing the shearing stress, τ_{ij}, by the shearing strain rate, $\dot{\gamma}$. η may be a function of $\dot{\gamma}$. Three of the most commonly used techniques are illustrated in the following sketches.
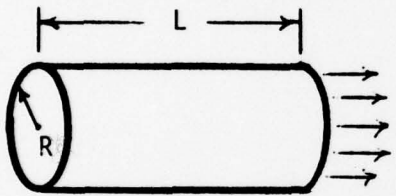
i) <u>Coaxial (Couette) Flow</u> (4)
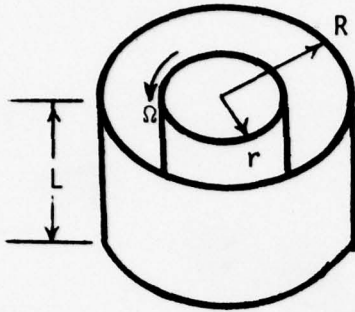
$$\dot{\gamma} = 2\Omega \sum_{p=0}^{\infty} s^{2p} m_m$$

$$\tau_r = T/(2\pi r^2 L)$$

.... where m evaluated at: $\tau = s^{2p}\tau_r$

$$s = r/R$$
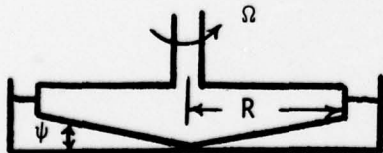
ii) <u>Capillary (Poiseuille) Flow</u> (4)

$$\dot{\gamma} = \frac{3Q}{\pi R^3} + \frac{\tau}{\pi R^3} \times \frac{dQ}{d\tau}$$

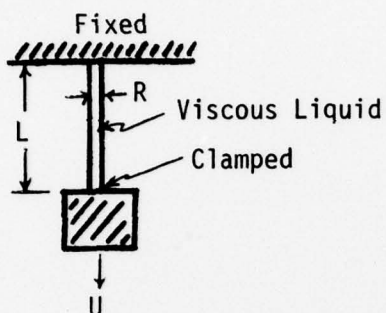$$\tau = R\Delta P/(2L)$$

iii) <u>Cone and Plate Flow</u> (4)

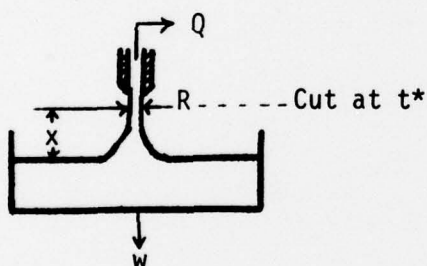$$\dot{\gamma} = \Omega/\psi$$

$$\tau = 3T/(2\pi R^3)$$

2. Elongation Experiments

The coefficient, η_e, is determined by dividing the normal stress, τ_{ii}, by the elongational strain rate, $\dot{\gamma}_e$. Very few experiments can be performed with low viscosity liquids in this area. Some examples are:
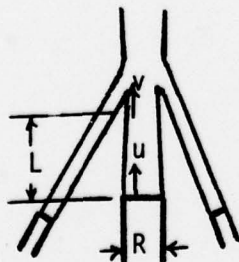
i) Simple Stretch (4)

$$\dot{\gamma}_e = U/L$$

$$\tau_{ii} = F/(\pi R^2)$$

ii) Open Syphon (6)

$$\dot{\gamma}_e = -2Q/(\pi R^3) \times \frac{dR}{dx}$$

$$\tau_{ii} = \frac{w(t^{*-}) - w(t^{*+})}{\pi R^2}$$

iii) Triple Jet (7)

$$\dot{\gamma}_e = \frac{v - u}{L}$$

$$\tau_{ii} = \frac{\Delta T}{\pi R^2}\left(\frac{v - u}{u \ln\left(\frac{v}{u}\right)}\right)$$

Complications Due To Viscoelasticity

Many liquid solutions consist of long polymer chains which are incorporated to give a proper "texture" to a fluid. These chains act somewhat like tiny springs which can be stretched by a straining force and will recoil when that force is removed. These molecules are responsible for the viscoelastic properties of the fluid.

Viscoelasticity is commonly modelled by the two types of linear equations described earlier. These linear equations assume that the elastic and viscous components can be treated separately. They are suitable for modelling relaxation phenomena but they cannot predict normal stresses which occur during shearing flows. In this situation, a non-linear equation (such as the Spriggs model) must be employed.

Viscoelastic models require the determination not only of the viscosity coefficient for flow but also the elasticity coefficient for elastic stretch and recoil. Considering the Maxwell model (commonly used for low to medium viscosity liquids), for an abrupt change in strain rate the stress relaxes according to:

$$\tau_{ij} = \tau_0 \exp(-Gt/\eta)$$

Therefore, a plot of $\ln \tau_{ij}$ vs t would yield G/η and with η determined from a simple shear experiment, G could be calculated. Another technique is to apply a sinusoidal strain rate. A dynamic viscosity coefficient is then defined by:

$$\eta^* = \eta' - i\eta'' = \tau_0 \sin\delta/(w\gamma_0) - i\,\tau_0 \cos\delta/(w\gamma_0)$$

... where δ is the phase angle between stress and strain. The dynamic, elastic coefficient is then given:

$$G^* = iw\,\eta^*$$

For the non-linear viscoelastic models, one needs to measure normal stresses which occur due to shear flow. This defines a "cross-viscosity" phenomenon. Fortunately, there are instruments which are capable of doing this, such as the famous Weissenberg cone and plate rheogoniometer.

F, W = forces (F)

G   = Young's elastic modulus (F/L^2)

L   = length (L)

m   = slope of log Ω vs log τ

ΔP = pressure drop (F/L^2)

Q   = volumetric flow rate ($L^3 t^{-1}$)

R, r = radius (L)

t   = time (t)

T   = torque (FL)

u, v = velocities (L/t)

w   = frequency (t^{-1})

x   = distance (L)

ψ = angle

δ = phase angle

η_o = coefficient of shear viscosity (Ft/L^2)

η_e = coefficient of extensional viscosity (Ft/L^2)

γ = shear strain

$\dot{\gamma}$ = shear strain rate (t^{-1})

Ω = rotational speed (t^{-1})

τ = shear stress (F/L^2)

τ_{ii} = normal stress (F/L^2)

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        The density, vapor pressure, surface tension and viscosity
of thickened Dowanol, DPM, were measured experimentally according to
standard techniques. Each of the techniques is explained in detail and
a brief summary of the theory is also presented.

        A new parameter called the "dissolved density" was defined
which promises to allow differentiation between thickening polymers.
The addition of an acrylate polymer had no effect on the surface tension
or vapor pressure of the solvent. The effect of thickener concentration
on viscosity was determined over a range of shear rates where the thic-
kened solutions were found to follow the power-law fluid model.

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