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ATTI ACCADEMIA NAZIONALE DEI LINCEI  
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI

# RENDICONTI

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## Viscoelastic properties of very dilute solutions of Polymeric Materials

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,  
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 40 (1966), n.4, p. 606–616.*

Accademia Nazionale dei Lincei

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**Chimica** (Principi di Ingegneria Chimica). — *Viscoelastic properties of very dilute solutions of Polymeric Materials*. Nota di GIOVANNI ASTARITA (\*) e A. B. METZNER (\*), presentata (\*\*) dal Corrisp. G. MALQUORI.

RIASSUNTO. — Tre tipi di esperimenti fluidodinamici mettono in evidenza la presenza di considerevoli effetti viscoelastici anche per liquidi di viscosità costante, quali le soluzioni molto diluite di alcuni polimeri: 1° il moto di bolle di gas entro tali liquidi; 2° il flusso turbolento ben sviluppato entro condotti a sezione costante; 3° il flusso con improvvisa riduzione di sezione.

Risultati sperimentali relativi ai casi 1° e 3° sono qui presentati e discussi insieme con una analisi delle equazioni reologiche ipotizzate per fluidi viscoelastici, alcune delle quali includono il modello di un fluido di viscosità costante e con un tempo naturale diverso da zero.

L'esperimento 3°, in particolare, lascia intravedere la possibilità di determinare quantitativamente i parametri elastici laddove risultano insensibili le tecniche convenzionali.

#### INTRODUCTION.

Investigation of viscoelastic flow phenomena requires the consideration of at least one rheological parameter having the dimensions of time [1, 2, 3], herein termed the natural time of the fluid  $T$ . The value of this parameter is difficult to measure directly in dilute solutions of polymeric materials, which, under viscometric flow conditions, in many cases display an approximately constant (Newtonian) viscosity. Similarly the deviatoric normal stresses may be below the threshold of detectability. Nevertheless these solutions do exhibit viscoelastic effects if properly significant flow fields are chosen for study.

A theoretical analysis is given, which shows that elastic effects may indeed be important in constant-viscosity liquids, and may be unrelated to the shear dependency of the viscosity in variable-viscosity liquids. For constant-viscosity liquids no value of  $T$  can be obtained from the  $\mu(\Gamma) = \text{constant}$  curve, while elastic effects still need to be considered on the basis of some value of the natural time. In the experimental portion of this paper a number of critical experiments are described which reveal the presence of elastic effects in such constant-viscosity liquids.

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(\*\*) Nella seduta del 16 aprile 1966.

## THEORETICAL.

a) *Dimensional Analysis.*

When the constitutive equation for a viscoelastic liquid is made explicit in the stress:

$$(1) \quad \mathbf{S} = \mathbf{S}(\mathbf{B}_1, \mathbf{B}_2, \dots)$$

in which  $\mathbf{B}_n$  denotes a properly invariant definition of the  $(n - 1)$  time derivative of the rate of deformation, dimensional invariance requires the existence of as many dimensional rheological parameters as are required to make all the  $\mathbf{B}_n$  tensors dimensionally equivalent to  $\mathbf{S}$ . As shown by Truesdell (1), a viscosity  $\mu_0$  and natural time  $T$  are sufficient: in fact, new kinematic tensors dimensionally equivalent to  $\mathbf{S}$  may be defined as:

$$(2) \quad \mathbf{B}_n^1 = \mu_0 T^{n-1} \mathbf{B}_n$$

For a purely viscous liquid, all the  $\mathbf{B}_n$ 's beyond  $\mathbf{B}_1$  in Equation (1) disappear by definition [4] or, in other words, the natural time  $T$  is zero (1). Still, a purely viscous liquid may display any viscosity function  $\mu(\Gamma)$  whatsoever [4], so that a value of  $T$  could artificially be derived from the shear dependency of viscosity by any one of the suggested procedures [2]. Such a value would of course have no relationship to the non-existent elastic properties of the liquid.

b) *Linear Viscoelasticity.*

If a linear theory of viscoelasticity such as discussed, for example, by Fredrickson [8] is accepted as a suitable model for discussing elastic effects in real liquids, the viscosity  $\mu$  turns out to be independent of the shear rate  $\Gamma$ :

$$(3) \quad \mu = \int_0^{\infty} \psi(t) dt$$

in which  $\psi(t)$  denotes the "influence function", or a time-decaying elastic modulus. In contrast with this, a natural time  $T$  may be defined as:

$$(4) \quad T = \frac{P_{11} - P_{22}}{\mu \Gamma^2}$$

(1) Ideally, a purely viscous liquid has no memory although real liquids which are usually regarded as purely viscous may have relaxation times for structural rearrangements of the order of  $10^{-13}$  sec. [5]. This is essentially zero for the velocity fields of interest and will be taken as such. One should note that a number of measurements on conventional gases and liquids, though controversial, have yielded normal stresses equivalent to much larger relaxation times, however [6, 7].

in which  $P_{11}$  and  $P_{22}$  denote the deviatoric normal stresses observed in viscometric flow. The value of  $T$  turns out to be:

$$(5) \quad T = \frac{2 \int_0^{\infty} t \psi(t) dt}{\int_0^{\infty} \psi(t) dt}$$

and may thus be finite in a constant-viscosity liquid. Analogous conclusions can be drawn from other linear theories of viscoelasticity [9, 10], with one exception to be discussed below. Equations of the form of this one may also accommodate the finite normal stresses in ordinary low molecular weight fluids which are known to have constant viscosities, should the controversial results referred to earlier prove to be valid.

c) *Variable Viscosity Theories.*

More general theories of viscoelasticity such as Coleman and Noll's theory of simple fluids [11], Ericksen's theory of anisotropic fluids [12], the Rivlin-Ericksen expansions [13], etc. predict behavior which, under viscometric flow conditions, say under those conditions for which rheological data can be obtained, are not distinguishable from each other: in each case, three totally unrelated material functions are seen to be needed for the characterization of a viscoelastic liquid. One of these functions is the  $\mu(\Gamma)$  curve, and no properties of the other two functions, which typify the elastic character of the liquid, can be inferred from its knowledge.

More restricted theories which do predict a variable viscosity are, among others, the White and Metzner model [14] and Oldroyd's "linear" theory of viscoelasticity [15].

According to White and Metzner's model of a generalized Maxwell fluid, the shear-dependency of  $T$  is the same as that of  $\mu$ , when the single elastic modulus of the liquid is taken as a constant, although the actual values of  $T$  cannot be inferred from the  $\mu(\Gamma)$  curve. In its simplest form (two constant coefficients) this model predicts the Weissenberg pattern of normal stresses which is known not to be correct in detail. If a generalization is made to accommodate finite values of the second normal stress difference even the shear rate dependencies of  $\mu$  and  $T$  may turn out to be mutually independent. Again, this model can accommodate a finite value of  $T$  together with a constant viscosity <sup>(2)</sup>.

(2) If White and Metzner's model is used with a constant value of  $\mu$ , it is equivalent to a linear viscoelastic formulation.

Oldroyd's "linear" theory of viscoelasticity assumes, for a second-order fluid, the following constitutive equation:

$$(7) \quad \left( I + \alpha \frac{D}{Dt} \right) \mathbf{S} = 2 \mu_0 \left( I + [\alpha - T] \frac{D}{Dt} \right) \mathbf{B}_1$$

where  $\mu_0$  is the zero-shear viscosity, and  $D/Dt$  are Jaumann time derivatives. Such a fluid has two time-constants,  $\alpha$  and  $T$ , both of which are relevant to both the elastic properties and the viscosity curve. The  $\mu(\Gamma)$  function is given by:

$$(8) \quad \frac{\mu}{\mu_0} = 1 - \frac{\alpha T \Gamma^2}{I + \alpha^2 \Gamma^2}$$

while the two normal stress differences are given by:

$$(9) \quad P_{11} - P_{22} = 2 (P_{33} - P_{22}) = 2 \mu_0 \Gamma^2 \frac{T}{I + \alpha^2 \Gamma^2}$$

Comparison of Equations 8 and 9 shows that the viscosity may be constant ( $\alpha = 0$ ) and at the same time finite normal stress may exist in viscometric flow ( $T \neq 0$ ). The converse is not true: when deviatoric normal stresses are zero ( $T = 0$ ), the viscosity is necessarily constant.

If  $\mu$  is not constant ( $\alpha \neq 0$ ,  $T \neq 0$ ), and a value of  $T$  is to be inferred from the  $\mu(\Gamma)$  curve, this would be taken as the inverse of the  $\Gamma$  value at which  $\mu$  starts being appreciably different from  $\mu_0$ , say  $\mu/\mu_0 = 1 - \delta$ , with  $\delta$  a suitably defined number:

$$(10) \quad \delta \ll \frac{T}{\alpha} = 1 - \frac{\mu(\Gamma \rightarrow \infty)}{\mu_0}.$$

Thus, a pseudo-natural time  $T_\mu$  would be obtained:

$$(11) \quad T_\mu = \sqrt{\frac{\alpha(T - \delta\alpha)}{\delta}}.$$

Consideration of Equation 10 shows that:

$$(12) \quad T_\mu \cong \sqrt{\frac{\alpha T}{\delta}} \gg \alpha > T$$

say, the value of  $T_\mu$  by far exceeds the value of  $T$ , which, according to Equation (9), is a natural yardstick for elastic effects. Similar conclusions may be drawn from the analysis of higher-order fluids.

The same conclusion can be drawn also directly from Truesdell's suggestion [1] on the evaluation of  $T$  from normal stress data as <sup>(3)</sup>:

$$(13) \quad T = \frac{1}{2 \mu(0)} \lim_{\Gamma \rightarrow 0} \frac{\sqrt{(P_{11} + P_{22} - 2 P_{33})^2 + (P_{11} - P_{22})^2}}{\Gamma^2}$$

(3) Truesdell [1] gives Equation (13) with  $\Gamma$  instead of  $\Gamma^2$  in the denominator, which is an obvious misprint.

while  $T_\mu$  is to be evaluated as:

$$(14) \quad T_\mu = \sqrt{|\mu''(0)| / \mu(0)}$$

Equation (9) shows that the  $T$  value in Equation (7) is indeed the natural time as obtained from Equation (13); while the value of  $T_\mu$  is given, according to Equation (14), by:

$$(15) \quad T_\mu = \sqrt{\alpha T}$$

which, apart from the numerical factor  $\sqrt{1/\delta}$ , coincides with Equation (12) above.

#### EXPERIMENTAL.

Aqueous solutions of certain high molecular weight substances, which are known to be viscoelastic at high concentrations, are characterized by a Newtonian  $\mu(\Gamma)$  curve at low concentrations. Due to experimental difficulties, normal stresses in viscometric flows cannot be measured for the dilute solutions, but neither can their finiteness be excluded. Indirect evidence of elastic properties of these dilute constant-viscosity solutions can be obtained by studying critical effects which may be shown to depend on the elastic properties of the liquid. Three different elastic flow phenomena which have been observed in such fluids are discussed below.

##### a) *Velocity of spherical gas bubbles at high Reynolds numbers.*

The motion of a spherical gas bubble at high Reynolds numbers has been discussed by Levich [16], Chao [17] and Moore [18] for Newtonian liquids; by Astarita and Marrucci [19] for purely viscous power-law fluids; and by Astarita [20] for viscoelastic liquids; the terminal velocity is given, if the liquid has no elastic properties, by:

$$(16) \quad \nu U = \frac{gR^2}{9}$$

where  $\nu$  is the kinematic viscosity,  $g$  is the gravity acceleration and  $R$  the bubble radius. For viscoelastic liquids, the velocity is predicted [20] to be appreciably lower than given by Equation (16).

Terminal velocities of spherical gas bubbles at Reynolds numbers larger than 5 are plotted in fig. 1. The straight line through the origin represents Equation (16). It is clear that, while the data for the presumably purely viscous aqueous solution of sugar are reasonably well correlated by Equation (16) the data relative to the two dilute polymer solutions are appreciably lower. This can be considered a reasonably direct indication of elasticity in the two polymer solutions having constant viscosities.

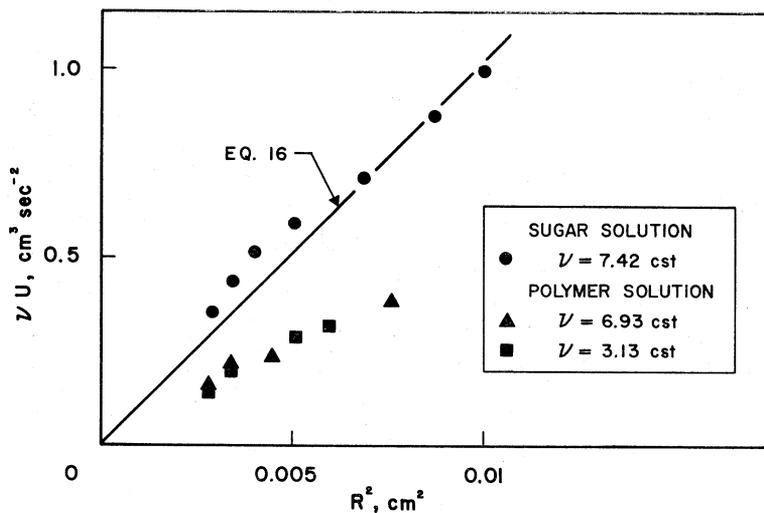


Fig. 1. — Velocities of spherical gas bubbles in inelastic and in elastic liquids. Reynolds numbers larger than 5.

b) *Drag reduction.*

The phenomenon of drag reduction during turbulent flow of some polymer solutions has been observed by a number of workers [21–30], and has rather firmly been established as being due to viscoelastic effects [21, 23, 24, 25, 26]. This phenomenon has been observed also in very dilute solutions which display a constant viscosity [27–31].

c) *Entrance pressure drop in laminar flow through pipes.*

The problem is that of flow into a small tube from a large upstream reservoir, as indicated in fig. 2. Let us assume that:

(i) The upstream reservoir is so large in extent that the fluid velocities and deformation rates at Section 1 are negligibly small. This implies that both the kinetic energy and any elastic energy developed in the fluid as a result of its deformation are negligibly small at this section.

(ii) Section 2 is sufficiently far downstream from the entry for the flow field (velocity profile and all stresses) to have become well-developed prior to this position.

An energy balance written over the system defined by Sections 1 and 2 and the intermediate walls of the vessel gives, for the case of no energy exchange with the surroundings:

$$\begin{array}{l} \text{Mech. energy} \\ \text{flux at} \\ \text{Section 1.} \end{array} = \begin{array}{l} \text{Mech. energy} \\ \text{flux at} \\ \text{Section 2.} \end{array} + \begin{array}{l} \text{Rate of energy dissipation} \\ \text{in region bounded by Sections} \\ \text{1 and 2 and walls of ducts.} \end{array}$$

or:

$$(17) \quad \dot{p}_1 w / \rho = \int_0^R \left( \frac{\rho u^2}{2} \right) u \cdot 2 \pi r dr + \int_0^R (-\tau_{11}) u \cdot 2 \pi r dr + \\ + \int_0^R E \cdot u \cdot 2 \pi r dr + \int_V (D_V) dV.$$

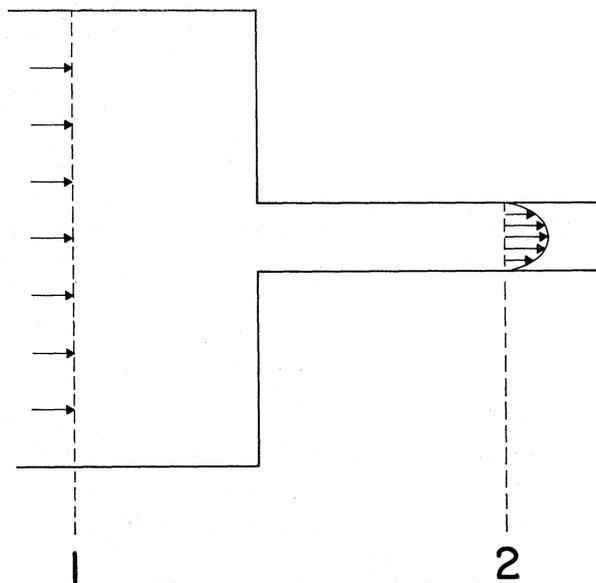


Fig. 2. - Control surfaces for energy balance in tube inlet problems.

The symbols used in Equation (17) are defined as follows:

- $w$  : mass rate of flow,
- $\dot{p}_1$  : hydrostatic (isotropic) pressure at Section 1,
- $\rho$  : fluid density,
- $u$  : fluid velocity at radius  $r$ , at Section 2,
- $R$  : radius of tube (Section 2),
- $\tau_{11}$  : axial component of total stress tensor, consisting of a hydrostatic pressure term and a deviatoric term arising from the fluid elasticity at Section 2:

$$\tau_{11} = -p + P_{11}$$

- $E$  : stored elastic energy per unit volume of fluid,
- $D_V$  : dissipation rate per unit volume of fluid

Equation (17) may be rearranged:

$$(18) \quad p_1 - 2 \int_0^1 p_2 \left( \frac{u}{v} \right) x dx = 2 \int_0^1 \frac{\rho u^2}{2} \left( \frac{u}{v} \right) x dx + \\ + 2 \int_0^1 (E - P_{11}) \left( \frac{u}{v} \right) x dx + \left( \frac{\rho}{w} \right) \int_V D_V dV$$

in which  $x$  denotes the dimensionless radial position  $r/R$ .

The term  $(E - P_{11})$  may be shown to be positive for real fluids [32]. Thus the energy balance differs from that for purely-viscous materials (such as Newtonian fluids) by the inclusion of this additional contribution, implying that the measured pressure drop over the entry,  $p_1 - p_2$ , will be greater for

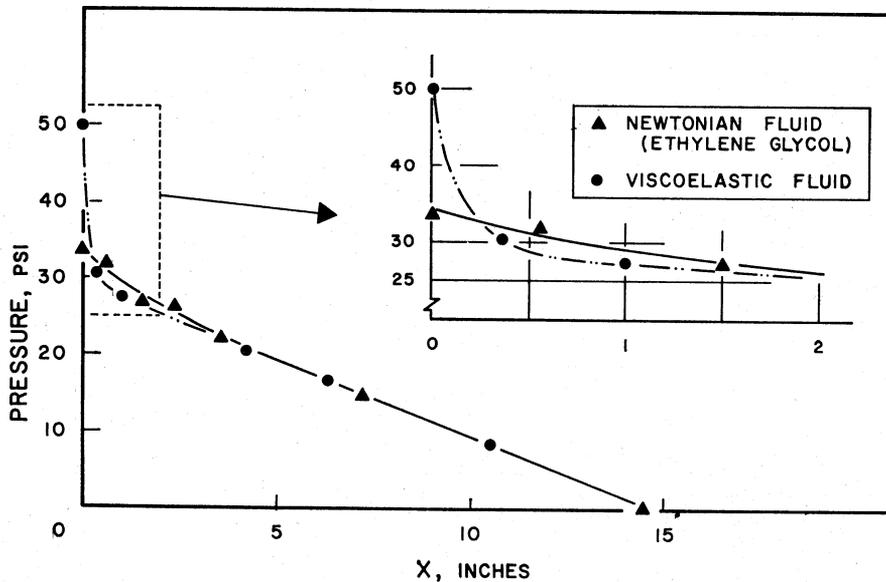


Fig. 3. - Comparison of pressure-axial distance profiles for Newtonian and viscoelastic fluids. Data of Feig [32].

The greater entrance pressure drop and shorter tube length required for development of a constant pressure gradient, as observed here for the viscoelastic fluid, are effects which appear to be common for viscoelastic fluids rather generally.

viscoelastic fluids. This difference between the values of  $(p_1 - p_2)$  for purely viscous and viscoelastic fluids will be denoted as  $\Delta P_{xs}$  and may be obtained from experimental measurements of the total pressure profile;  $\Delta P_{xs}$  will contain any additional dissipation terms in the viscoelastic case as well as the contribution due to  $(E - P_{11})$ .

The data depicted in Figure 3 show that  $\Delta P_{xs}$  is large and well-defined. These results are for fairly viscous systems [32] for which the physical properties may readily be measured rheogoniometrically by means of any of several

available techniques [33]. The same effects have, however, been noted in very dilute solutions having essentially constant viscosity coefficients and in which any stresses arising out of the fluid elasticity and manifested as normal stresses under steady laminar shearing flow conditions appear to be too small to be measured rheogoniometrically [34]: i.e. in solution which would be described as Newtonian if standard Viscometric and rheogoniometric techniques were employed to determine their physical properties.

TABLE I.

*Excess pressure drop (end effect) for flow of viscoelastic fluids into a tube.*

Data of Pruitt and Crawford [31].

FLUID DESCRIPTION	Viscosity cp.	Shear rate sec <sup>-1</sup>	$\Delta P_{xs}$ , Dynes/cm <sup>2</sup>	p.s.i.	$\Delta P$ ratio *
WSR-301 (**) 250 ppm conc. ....	1.3 (5)	$3 \times 10^4$	0	0	1.00
	1.3 (4)	$4 \times 10^4$	$2.5 \times 10^5$	3.6	3.1
	1.3 (0)	$1 \times 10^5$	$7.5 \times 10^5$	10.8	2.0
	1.4 (3)	$0.3 \times 10^4$	0	0	1.00
K-PAM (***) 250 ppm conc. ....	1.4 (0)	$1. \times 10^4$	$2.5 \times 10^4$	0.36	4.2
	1.3 (7)	$3. \times 10^4$	$9.1 \times 10^4$	1.31	2.3
	1.3 (4)	$1. \times 10^5$	$3.3 \times 10^5$	4.75	1.4

(\*)  $\Delta P$  ratio denotes the ratio:  $\frac{\Delta P_{xs}, \text{ viscoelastic fluid}}{\Delta P_{xs}, \text{ Newtonian fluid}}$

(\*\*) Polyethyleneoxide having a molecular weight of approx. 4 million.

(\*\*\*) Polyacrylamide having a molecular weight of approx. 8.3 million.

Table I summarizes the results of measurements using two polymeric solutions at a concentration level of only 250 p.p.m. (0.025%). These solutions were so nearly Newtonian that viscosity measurements over a hundred-fold range of shear rates revealed only a 15% change in one case and 10% in the second, and a part of even these small changes is quite possibly due to viscous heating effects at the high shear rate levels employed [35]. However, in spite of this near-constancy of the viscosity one notes very large values of the term  $\Delta P_{xs}$  to as much as over four times the value for comparable Newtonian fluids.

The significance of these results in the interpretation of viscometric measurements is of interest, as the "end effect" pressure loss is sufficiently greater than that of Newtonian fluids to render conventional end effect corrections for the latter useless. This can be illustrated by calculating the equivalent length of a straight tube required to incur the same pressure loss,  $L_e$ .

TABLE II.

*Equivalent length of tubes required to produce a pressure loss equivalent to  $\Delta P_{ss}$ .*

FLUID	Shear Rate sec <sup>-1</sup>	$L_e$ Diameters
WSR-301 . . . . .	$3 \times 10^4$	0
	$4 \times 10^4$	105
	$1 \times 10^5$	125
K-PAM . . . . .	$0.3 \times 10^4$	0
	$1 \times 10^4$	40
	$3 \times 10^4$	50
	$1 \times 10^5$	55

As shown in Table II for fluid K-PAM the "equivalent length" of the entry is 50 diameters at a shear rate of  $3 \times 10^4$  sec<sup>-1</sup>. This means that if a tube having a length of 50 diameters were used in a viscosity determination (and this length/diameter ratio is in excess of that frequently used), and if the conventional Newtonian correction [36, 37] of  $2.12 (\rho U^2/2)$  had been made to the measured pressure drop, the interpretation of the remaining pressure drop over the system in terms of viscous (Poiseuille) effects would lead to a value for the viscosity of just twice the true one. Similarly, at a shear rate of  $10^5$  sec<sup>-1</sup> for fluid WSR-301 the calculated viscosity would be in error by a factor of  $(125 + 50)/50$ , or 3.5. Obviously the determination of the viscosity of these highly elastic dilute solutions requires either the use of *very* long tubes ( $L > 1,250 D$ , for 10% error or less, for fluid WSR-301) or, more practically, the use of several tube lengths to enable the experimental determination of the actual end effect, unless strain gages are used to monitor the pressure gradient directly, thereby eliminating an overall pressure drop measurement. In view of the widespread use of dilute solution viscosity measurements to evaluate molecular properties of polymers these comments are seen to be of broad significance unless care is exercised to restrict the measurements to moderate or low shear rates, under which conditions these elastic effects appear to be too small to be significant.

*Acknowledgement.*—This analysis is part of a study of the structure and properties of dilute polymeric solutions, having application in water conservation and treatment, and has been supported by the Water Resources Center of the University of Delaware.

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