Numerical Evaluation of Models Describing Non-Newtonian Behavior

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Many models for describing non-Newtonian behavior have been developed within the past forty years. They are generally one-dimensional, although the extension to two and three dimensions is readily made (*1*). Most are semi-empirical or have been developed from molecular theories. Meter (*2*) lists 21 different models for describing the non Newtonian viscosity. His list was not exhaustive and new models have been developed since then. Within the past five years, major advances have been made in the development of constitutive theories through the application of continuum mechanics. This has led to a unified description of a wide variety of rheological phenomena including, in addition to the non-Newtonian viscosity, the complex viscosity, normal stresses, and elastic recoil.

Despite this trend, simple models for describing the non-Newtonian viscosity find many useful applications. Foremost of these is the description, interpretaton, and correlation of phenomena occurring in viscometric flows. This flow class is industrially important and includes laminar, fully developed axisymmetric flow such as flow between flat plates, in pipes and annuli, and helical flow in annuli. Elastic effects, when they occur, can be ignored in this case because they do not change and do not contribute to the pressure drop. Simple models may also be used to replace the viscous contribution in the equations of the more comprehensive constitutive theories. In this way, the equations become more tractable by elimination of undetermined parameters.

Models are commonly selected on the basis of their theoretical suitability, their utility in solving the hydrodynamic equations, and their ability to fit the data. There are few comparative results to support the latter criteria. This paper reports the results of fitting different models to a wide variety of non-Newtonian data (*3*) and should help fill that void.

MODEL SELECTION

The models selected for study are shown in Table 1. The choice of models was confined to those able to describe the limiting Newtonian viscosities commonly observed in polymer solutions. These viscosities, one at low shear rates, η_0, and the other at high shear rates, η_∞, are separated by a region of changing viscosity.

Referring to Table 1, the Powell-Eyring models are based on absolute reaction rate theory and are amenable to a thermodynamic interpretation. The Oldroyd model is a nonlinear extension of the Jeffreys model from first-order linear viscoelastic theory. It incorporates tensor concepts fundamental to the continuum mechanical approach. The Spriggs-Bird model is an extension of the Oldroyd treatment to the general linear viscoelastic model. Elements of molecular theory are incorporated to eliminate undetermined parameters. The extended Spriggs-Bird model was empirically formulated to correct for experimental deviations from the theoretical model. The Bueche model arises from treating each solute molecule as an independently acting, three-dimensional, vibrating, mechanical system. The Meter and extended Williamson models are empirical extensions of the Peek-McLean and Williamson models, respectively. These latter two models are interpreted in terms of an association-dissociation process involving pairs of spherical solute molecules. In the Peek-McLean model the spheres are embedded in a non-Newtonian fluid (*12*), while in the Williamson model the fluid is Newtonian (*3*). The Seely model is empirical and, at low shear stresses, is equivalent to the Peek-McLean model.

The number of parameters in these models ranges from three to five. However, only one to three parameters are evaluated by data-fitting since the limiting viscosities are known by inspection from the data.

TABLE 1. NON-NEWTONIAN MODELS

Model — Reference

1. three-parameter Powell-Eyring (*4* to *6*)

$$\eta = \eta_\infty + \frac{\alpha_1}{|\dot\gamma|}\sinh^{-1}(\alpha_2|\dot\gamma|)$$

2. five-parameter Powell-Eyring (*4* to *6*)

$$\eta = \eta_\infty + \frac{\alpha_1}{|\dot\gamma|}\sinh^{-1}(\alpha_2|\dot\gamma|) + \frac{\alpha_3}{|\dot\gamma|}\sinh^{-1}(\alpha_4|\dot\gamma|)$$

3. Oldroyd (*7* to *8*)

$$\eta = \eta_0\frac{(1+\alpha_1|\dot\gamma|^2)}{(1+\alpha_2|\dot\gamma|^2)}$$

4. Spriggs-Bird (*9*)

$$\eta = \eta_\infty + \frac{3(\eta_0-\eta_\infty)}{\pi\sqrt{\alpha_1|\dot\gamma|}}\left\{\frac{\sinh\pi\sqrt{\alpha_1|\dot\gamma|}-\sin\pi\sqrt{\alpha_1|\dot\gamma|}}{\cosh\pi\sqrt{\alpha_1|\dot\gamma|}-\cos\pi\sqrt{\alpha_1|\dot\gamma|}}\right\}$$

5. extended Spriggs-Bird (*3*)

$$\eta = \eta_\infty + \frac{3(\eta_0-\eta_\infty)}{\pi\sqrt[\alpha_2]{\alpha_1|\dot\gamma|}}\left\{\frac{\sinh\pi\sqrt[\alpha_2]{\alpha_1|\dot\gamma|}-\sin\pi\sqrt[\alpha_2]{\alpha_1|\dot\gamma|}}{\cosh\pi\sqrt[\alpha_2]{\alpha_1|\dot\gamma|}-\cos\pi\sqrt[\alpha_2]{\alpha_1|\dot\gamma|}}\right\}$$

6. Bueche (*10*)

$$\eta = \eta_\infty + (\eta_0-\eta_\infty)\left(\frac{2+\alpha_1|\dot\gamma|-\sqrt{4\alpha_1|\dot\gamma|+\alpha_1^2|\dot\gamma|^2}}{2}\right)$$

7. Meter (*2*)

$$\eta = \eta_\infty + \frac{(\eta_0-\eta_\infty)}{\left[1+\left(\frac{\tau}{\alpha_1}\right)^{\alpha_2}\right]}$$

8. extended Williamson (*3*)

$$\eta = \eta_\infty + \frac{(\eta_0-\eta_\infty)}{\left[1+\left(\frac{|\dot\gamma|}{\alpha_1}\right)^{\alpha_2}\right]}$$

9. Seely (*11*)

$$\eta = \eta_\infty + (\eta_0-\eta_\infty)\,e^{-(\tau/\alpha_1)}$$

NON-NEWTONIAN DATA

Non-Newtonian data were selected from the literature.

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Only those data were used which could define the entire viscosity curve. This meant that limiting viscosity values must be available as well as data in the region of changing viscosity. η_∞ is generally not well defined in polymer solutions, owing to viscous heating and shear degradation. Often the data available only approached the high shear rate limit. In that case η_∞ was estimated by extrapolation to a reasonable limit. η_∞ is not measured in polymer melts because of shear degradation. Consequently, the theoretical value (*10*) for η_∞, that is, zero, was used for these systems.

Altogether, forty-six sets of non-Newtonian data were selected for this study. Eight of these were from polymer melts. The remainder were largely from solutions of macromolecules. They represent a wide variety of chemical and physical properties. Their general characteristics are described in Table 2.

TABLE 2. GENERAL CHARACTERISTICS OF DATA

Solute or Characteristic Molecule	Solvent	Mol. Wt. of Characteristic Molecule	Degree of Non-Newtonian Behavior	Shear Rate Range of Data, Decades	Reference
		Non-Newtonian Solutions			
polyisobutylene	decalin	6.3×10^5	high	5-7	(*13*)
polystyrene	tetralin	2.8×10^6	moderate	3	(*14*)
cis-polybutadiene	benzene	$1.5\text{-}8.7 \times 10^5$	moderate	2.5	(*11, 15*)
cis-polyisoprene	hexane-isopentane	1.3×10^6	moderate	2	(*11, 15*)
butadiene-styrene copolymer	water	—	slight	2	(*16*)
nitrocellulose	*n*-butyl acetate	2.1×10^6	high	10	(*17*)
hydroxyethyl cellulose	water	High	moderate	4.5	(*2*)
milling yellow dye	water	—	slight	2	(*18*)
polyacrylic acid	water	1.8×10^5	moderate	5	(*19*)
DNA	water	5.6×10^6	slight	3	(*20*)
poly-γ-benzyl-L glutamate	m-cresol	2.7×10^5	high	4-7	(*21*)
		Non-Newtonian Melts			
polyethylene	—	—	mod. high	6	(*22*)
polyisoprene	—	6.4×10^5	slight	3	(*23*)
polyvinyl butyral	—	—	high	4-5	(*22*)

DATA FITTING

The data were graphically smoothed on logarithmic coordinates, then sampled using a logarithmic sampling interval of one-third decade in shear rate. This sampling procedure results in an economic sampling rate, yet provides for uniform preservation of the viscosity information over all shear rates (*24*).

The models were fitted to the data by using the least squares procedure. The error term was defined as

$$\epsilon_i = \frac{f_i - y_i}{f_i} \qquad (1)$$

and treats only relative deviations from the data. The data fitting ability of a model was described by the RMS Error

$$\text{RMS Error} = \sqrt{\frac{\sum_{i=1}^{N} \epsilon_i^2}{N}} \qquad (2)$$

The summation included only those points in the region of changing viscosity since the models fit the data exactly in the Newtonian terminal regions of the viscosity curve.

The models were fitted to the entire viscosity curve rather than a select portion of the curve. The fitting of the power law model is a common example of the latter procedure and the parameters are not constants but depend upon the portion of the curve that is fitted. Fitting to the entire curve, as was done here, insures that the parameters are functions only of the intrinsic physical and chemical properties of the system.

RESULTS

The extended Williamson and five-parameter Powell-Eyring models fit the data significantly better than the remaining models. Mean errors, calculated as the average of the RMS Errors, were determined for each of the models. The mean errors for the extended Williamson and five-parameter Powell-Eyring models were about 5%, while those for the Meter and extended Spriggs-Bird models were about 9%. Mean errors for the other models, based on all the data, are as follows: Bueche, 13%; three-parameter Powell-Eyring, 14%; Spriggs-Bird, 19%; Seely, 20%; Oldroyd, 38%. The mean error results, broken down in terms of the solution data, melt data, and then all data combined, are given in Figure 1.

The five-parameter Powell-Eyring model should be used to fit experimental data when a thermodynamic interpretation is desired. Otherwise, the extended Williamson model is recommended. It has one less undetermined parameter than the Powell-Eyring model. Reasonable estimates of the extended Williamson model parameters can readily be made upon inspection of the experimental data while this is not true of the Powell-Eyring model. Finally, numerical constraints on values of the extended Williamson model parameters are better than for the Powell-Eyring model, since the difference between non-Newtonian terms in the latter model is conceptual rather than numerical. Because the shear rate is an implicit function of other quantities in the models, neither yields analytic solutions to simple hydrodynamic problems. Except for the power law and the two-parameter Powell-Eyring models (*4*), this is also true of most other models for the non-Newtonian viscosity.

Powell-Eyring Models

The five-parameter model was, on the average, a distinct improvement over the three-parameter model. However, both of these models, fit with the same precision data for solutions of low molecular weight polybutadiene, polystyrene, and polyacrylic acid at low concentrations, milling yellow dye, DNA, and butadiene-styrene copoly-

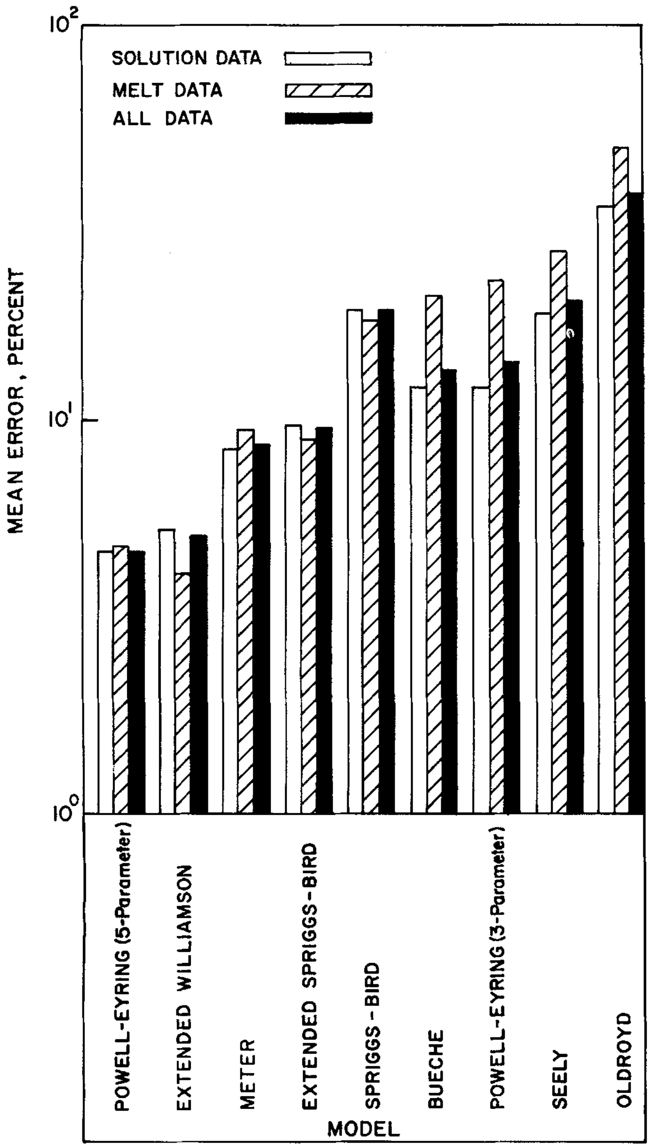

Fig. 1. Error data summary.

mer, indicating that the second non-Newtonian flow unit was not necessary in these instances. This was confirmed by the ratio α_4/α_2, which ranged from 0.2 to 5, meaning that there was little difference in the behavior of the two inverse hyperbolic functions.

For several of the data sets the curve produced by the five-parameter model crossed the data curve a number of times in the region of changing viscosity. This occurred whenever α_1/α_3 was greater than 10 and the time constants α_2 and α_4 differed by a factor greater than 50. The reason for this behavior is that the two non-Newtonian flow units responded to shear rates of widely different magnitude and the response of one has subsided before the next begins. Under these conditions a third flow unit appears desirable to fill the gap in response between the other two.

The most frequent deviations of the five-parameter Powell-Eyring model from the data occurred near the ends of the region of changing viscosity. The fitted curve tended to vary a little more rapidly with shear rate than the data did near the low shear rate end. The converse was true at the high shear rate end. These deviations were usually small.

Extended Williamson Model

The most frequent deviations of the extended Williamson model also occurred near the ends of the region of changing viscosity. In this case, however, the fitted curve tended to vary a little less rapidly with shear rate than did the data. This was true at both ends of the region and again the deviations were usually small.

An essentially linear relationship was maintained by α_1 with concentration when plotted on logarithmic coordinates. This relationship is defined by the proportionality

$$\alpha_1 \propto C^{-b} \tag{3}$$

and was good for concentrations varying by as much as an order in magnitude. Based on a limited number of data, unbranched polymers or ones where the pendant branches are small compared to the repeating unit in the chair backbone are characterized by $b \sim 3$. Polymers possessing large side branches are characterized by $b < 3$.

Values of α_2 ranged largely between 0.6 and 1. α_2 for the melt data varied from 0.53 to 0.86, bracketing the value of 0.75 proposed by Bueche and Harding (*25*). The absolute slope of 0.5, predicted by the molecular theories of Bueche (*10*) and Rouse (*26*), probably represents the lower limit of α_2 for systems of macromolecules. In some instances α_2 decreased slightly with concentration, while in others, it increased. Interpolation is readily accomplished since, over two to four-fold ranges in concentration, α_2 is proportional to the logarithm of the concentration.

While few data were available to confirm the temperature dependence of α_1, the theory (*3*) predicts that

$$\alpha_1 \propto Te^{-E/RT} \tag{4}$$

Thus, α_1 increases exponentially at low temperatures but changes to a linear dependence at higher temperatures.

NOTATION

C = concentration
E = activation energy
f_i = experimental value of dependent variable
N = number of data points in a set
R = gas constant
T = absolute temperature
y_i = fitted value of dependent variable
α_n = model parameters
$|\dot{\gamma}|$ = shear rate
ϵ_i = error term in fitting procedure
η = viscosity, η_0, limiting viscosity at zero shear rate; η_∞, limiting viscosity at infinite shear rate

LITERATURE CITED

1. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, Transport Phenomena," John Wiley, New York (1960).
2. Meter, D. M., Ph.D. thesis, Univ. Wisconsin, Madison (1964).
3. Cramer, S. D., Ph.D. thesis, Univ. Maryland, College Park (1968).
4. Eyring, H., *J. Chem. Phys.*, **4**, 283 (1936).
5. Ree, F. H., T. Ree, and H. Eyring, *Ind. Eng. Chem.*, **50**, 1036 (1958).
6. Ree, T., and H. Eyring, *J. Appl. Phys.*, **26**, 793 (1955).
7. Oldroyd, J. G., *Proc. Roy. Soc.* (*London*), **A200**, 523 (1950).
8. *Ibid.*, **A245**, 278 (1958).
9. Spriggs, T. W., and R. B. Bird, *Ind. Eng. Chem. Fundamentals*, **4**, 182 (1965).
10. Bueche, F., *J. Chem. Phys.*, **22**, 1570 (1954).
11. Seely, G. R., *AIChE J.*, **10**, 56 (1964).
12. Kreiger, I. M., and T. J. Dougherty, *Trans. Soc. Rheol.*, **3**, 137 (1959).
13. Brodnyan, J. G., F. H. Gaskins, and W. Philippoff, *ibid.*, **1**, 109 (1957).
14. Passaglia, E., J. T. Yang, and N. J. Wegemer, *J. Poly. Sci.*, **47**, 333 (1960).

15. Seely, G. R., personal communication (November 1, 1965).
16. Maron, S. H., and A. W. Sisko, *J. Colloid Sci.*, **12**, 99 (1957).
17. Philippoff, W., F. H. Gaskins, and J. G. Brodnyan, *J. Appl. Phys.*, **28**, 1118 (1957).
18. Peebles, F. N., J. W. Prados, and E. H. Honeycutt, Jr., *J. Polymer Sci.*, **51**, Part C, No. 5, 37 (1963).
19. Brodnyan, J. G., and E. L. Kelly, *Trans. Soc. Rheol.*, **5**, 210 (1961).
20. Eisenberg, H., *J. Polymer Sci.*, **25**, 257 (1957).
21. Hermans, Jan, Jr., *J. Colloid Sci.*, **17**, 638 (1962).
22. Philippoff, W., and F. H. Gaskins, *J. Polymer Sci.*, **21**, 205 (1956).
23. Holden, G., *J. Appl. Polymer Sci.*, **9**, 2911 (1965).
24. Cramer, S. D., and J. M. Marchello, *AIChE J.*, **14**, 814 (1968).
25. Bueche, F., and S. W. Harding, *J. Polymer Sci.*, **32**, 177 (1958).
26. Ferry, J. D., "Viscoelastic Properties of Polymers," p. 176, John Wiley, New York (1961).

Comments on Turbulence Measurement in Water using an Electrokinetic Probe

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Recently, Chuang and Cermak presented a paper (*1*) on turbulence measurements in a pipe flow of distilled water using an electrokinetic probe. They are to be commended for their pioneering study of the probe technique. However, the shortcomings of their analyses also must be pointed out.

In the section on theory, they presented the following equation for charge transport in an incompressible fluid:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underset{\rightarrow}{U}) + \frac{\rho}{\tau} = 0 \qquad (1)$$

To obtain Equation (1), one must assume that the conductivity of the fluid is a constant, and that the charge transport due to diffusion is negligible. Without these assumptions, the corresponding equation, as derived by Gavis and Koszman (*2* to *5*), becomes

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underset{\rightarrow}{U}) + \frac{\rho}{\tau} = \frac{\lambda^2}{\tau} \nabla^2 \rho + \nabla \psi \cdot \nabla \sigma \qquad (2)$$

where the two terms on the right-hand side of Equation (2) represent the effects of diffusion and variation in conductivity.

As shown by Gavis and Koszman, the assumption of a constant conductivity is valid only for fluids of low dielectric constant and low conductivity, such as electrokinetic effects in hydrocarbons or charge transport phenomena in gases. For water and solutions thereof, the conductivity varies essentially over the diffuse layer and the term $\nabla \psi \cdot \nabla \sigma$ can not be omitted from Equation (2). It seems doubtful that any result derived from Equation (1) can be considered even as a good approximation for water and its solutions. The omission of the diffusion term is also subject to question, especially in regard to the diffusion perpendicular to wall.

Another assumption used by the authors, following the derivation of Equation (5) of their paper, was that $\sigma \nabla \phi = \bar{\rho} \underset{\rightarrow}{u}$. Mathematically and physically, this means the fluctuating current densities due to turbulence convection at any point in the fluid were considered to be counterbalanced in each direction by the corresponding fluctuating conduction-current densities at the same point. If this assumption were true, it would then be impossible to record any electrokinetic-potential fluctuation between any two electrodes located on a pipe wall, since the convective current density at the wall must then be zero in order to satisfy the no-slip condition. However, experimental findings indicated the contrary to be true. Bocquet (*6*), Binder (*7*), Duckstein (*8*), and Liu (*9, 10*) all measured electrokinetic-potential fluctuations by wall electrodes.

In the section called *Discussion of Experimental Results,* Chuang and Cermak made one more assumption regarding the electrokinetic-potential fluctuations. They assumed that the potential fluctuation of electrokinetic-potential difference between two closely spaced electrodes aligned in any direction is considered to be linearly proportional to the fluctuating turbulent velocity (of the neighboring fluid?) in that direction.

It should be pointed out that to date (1968) no data taken by any other investigator except those reported by Chuang (*1, 11*) have yet confirmed this hypothesis. I have conducted a series of tests but all of them indicated no directional sensitivity (*9*). In view of this, I had to use a quite different rationale to explain my experimental data (*9, 10*). It is hoped that other researchers in this field will conduct more experiments to testify the hypotheses of directional sensitivity and linear proportionality.

NOTATION

t = time
$\underset{\rightarrow}{u}$ = fluctuating component of velocity vector
$\underset{\rightarrow}{U}$ = instantaneous velocity vector

Greek Letters

λ = diffuse-layer thickness
ρ = instantaneous true charge density
$\bar{\rho}$ = time-mean charge density
σ = conductivity
τ = relaxation time of the fluid
ϕ = fluctuating electric potential
ψ = instantaneous electric potential

LITERATURE CITED

1. Chuang, H., and J. E. Cermak, *AIChE J.*, **13**, 266 (1967).
2. Gavis, J., and I. Koszman, *J. Colloid. Sci.*, **16**, 375 (1961).
3. Koszman, I., and J. Gavis, *Chem. Eng. Sci.*, **17**, 1013 (1962).
4. *Ibid.*, 1023 (1962).
5. Gavis, J., *Chem. Eng. Sci.*, **19**, 237 (1964).
6. Bocquet, P. E., C. M. Sliepeevich, and D. F. Bohr, *Ind. Eng. Chem.*, **48**, 197 (1956).
7. Binder, G. J., Ph.D. dissertation, Colorado State Univ., Fort Collins (1960).
8. Duckstein, L., Ph.D. dissertation, Colorado State Univ., Fort Collins (1962).
9. Liu, H., Ph.D. dissertation, Colorado State Univ., Fort Collins (1966).
10. ———, *AIChE J.*, **13**, 644 (1967).
11. Chuang, H., Ph.D. dissertation, Colorado State Univ., Fort Collins (1962).