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ORIGINAL CONTRIBUTION

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A procedure to determine the viscosity function from experimental data of capillary flow

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Abstract The accurate calculation of the viscosity η as function of the shear rate $\dot{\gamma}$ from capillary viscometry is still a matter of debate in the literature. In fact, this problem involves the inversion of an integral equation, which leads to multiple solutions due to the unavoidable noise present in the experimental data. The purpose of this work is to develop an efficient procedure to determine the viscosity function from experimental data of capillary flow without presenting the difficulties inherent in other methods discussed previously in the literature. The system identification procedure is used here to estimate the parameters of a viscosity model, which is appropriately selected for the fluid under study through preliminary calculations involving the apparent shear rate – shear stress data. Once the model is chosen by satisfying criteria for the fit goodness and its parameters are evaluated, a smooth and continuous function $\eta(\dot{\gamma})$ is obtained in the range of experimental shear rates. The procedure proposed is also applicable to fluids in shear flow that present two Newtonian plateaus, as it is typically found in macromolecular dilute solutions. The mean value theorem of continuous functions is used to reduce significantly the computational time.

Key words Capillary viscometry · Viscosity function · Ill-posed problem

Introduction

Although capillary viscometry is one of the most used techniques to measure the viscosity of several kinds of fluids, the appropriate determination of the rheometric viscosity function $\eta(\dot{\gamma})$ from experimental data is still under analysis and discussion in the literature. Capillary viscometry should allow one to calculate the viscosity η of a given fluid from experimental data involving pressure loss ΔP and flow rate Q in the capillary tube. In this sense, for the case of Newtonian fluids, the viscosity is obtained easily through the Hagen-Poiseuille equation. On the other hand, special considerations must be taken into account for the determination of the viscosity function $\eta(\dot{\gamma})$ when non-Newtonian fluids are considered. In fact, difficulties appear in the calculation of the shear rate $\dot{\gamma}$ because it is non-uniform in the capillary cell. In this framework, to obtain the viscosity function

$$\eta(\dot{\gamma}) = \frac{\sigma}{\dot{\gamma}} \tag{1}$$

both the shear stress σ and the shear rate $\dot{\gamma}$ have to be known at least at one place in the rheometric cell. In the capillary tube, when transient effects are absent, the shear stress σ is evaluated with the following equation (Walters 1975; Bird et al. 1977; Schowalter 1978):

$$\sigma(r) = \frac{\Delta P r}{2L} = \sigma_w \frac{r}{R} \tag{2}$$

where R is the tube radius, L is the tube length, σ_w is the shear stress at the tube wall and the radial coordinate r satisfies $0 \le r \le R$. The shear rate $\dot{\gamma}$, however, is related

to the flow rate Q in the capillary tube through the following expression:

$$Q = \frac{\pi R^3}{\sigma_w^3} \int_0^{\sigma_w} \dot{\gamma}(\sigma)\sigma^2 \mathrm{d}\sigma \tag{3}$$

which involves the no-slip boundary condition of the velocity field. Therefore, the determination of $\dot{\gamma}(\sigma)$ requires the inversion of Eq. (3). This step is the source of difficulties in capillary viscometry, since it constitutes a mathematically ill-posed problem; i.e., a unique solution cannot be found as a consequence of the unavoidable scattering present in the experimental data Q vs σ_w (Honerckamp 1989; Friedrich et al. 1996).

The method most used to evaluate $\dot{\gamma}$ in capillary viscometry is based on the following expression:

$$\dot{\gamma}_w = \frac{1}{4}\dot{\gamma}_a\left(3 + \frac{\mathrm{d}\ln\dot{\gamma}_a}{\mathrm{d}\ln\sigma_w}\right) \tag{4}$$

where $\dot{\gamma}_w$ is the shear rate at the tube wall. Also, for Newtonian fluids, $\dot{\gamma}_w$ is equal to the apparent shear rate $\dot{\gamma}_a = 4Q/\pi R^3$. Equation (4) is obtained by differentiating Eq. (3) with respect to the wall shear stress, and is designated the Weissemberg-Rabinowitsch-Mooney (WRM) equation. Although in the WRM method numerical data of the viscosity function are generated from $\eta = \sigma_w/\dot{\gamma}_w$ as one expects, Eq. (4) is most reliable, and hence useful, only in the cases in which $\left(\mathrm{d}\ln\dot{\gamma}_a/\mathrm{d}\ln\sigma_w\right) \approx 1$ (fluids almost Newtonian) and $\left(\mathrm{d}\ln\dot{\gamma}_a/\mathrm{d}\ln\sigma_w\right) \approx 1/n$ ("power law" fluids with power index n). Apart from these two situations, the numerical results yielded by Eq. (4) are very sensible to $\dot{\gamma}_a$ and to the way the calculation of $\left(\mathrm{d}\ln\dot{\gamma}_a/\mathrm{d}\ln\sigma_w\right)$ is performed because experimental data are always noisy in some degree. Therefore, converting Eq. (3) to a differential expression like Eq. (4) does not eliminate the difficulty associated with the existence of multiple solutions. In this sense, some interesting proposals to solve this problem can be found (Brunn and Vorwerk 1993; Munoz and Yeow 1996).

By defining $\eta_a = \sigma_w/\dot{\gamma}_a$, Eq. (4) may be rewritten as

$$\eta = \eta_a\left(1 - \frac{1}{4}\frac{\mathrm{d}\ln\eta_a}{\mathrm{d}\ln\sigma_w}\right)^{-1} \tag{5}$$

From this equation, Brunn and Vorwerk (1993) observed that when η is a purely monotonic function, η_a always lie to the right of η. In this context of analysis, a shift factor $\beta \leq 1$ was introduced to yield $\eta_a(\sigma_w) = \eta(\beta\sigma_w)$. These authors concluded that the method provides approximate values of $\eta(\sigma_w)$ and for some typical viscosity models the shift factors can be analytically found. Nevertheless, this method cannot be applied to fluids that show two Newtonian plateaus.

On the other hand, without considering directly a viscosity model, Munoz and Yeow (1996) suggested the numerical determination of the function $\eta(\sigma)$ by applying the maximum entropy (ME) method to capillary data. With this purpose, the authors used the following integral equation

$$Q = \frac{\pi R^3}{\sigma_w^3} \int_0^{\sigma_w} \frac{\sigma^3}{\eta(\sigma)}\mathrm{d}\sigma \tag{6}$$

which was the result of introducing $\dot{\gamma}(\sigma) = \sigma/\eta(\sigma)$ in Eq. (3). These authors indicated that the prediction of this method is strongly dependent on the "prior" knowledge of the viscosity function. In addition, the results generated by the ME method did not excel those obtained with the classical WRM method. To show this aspect of the problem, the authors carried out a deep and well-described comparison between the WRM and the ME methods. It should be emphasized here that the ME method uses a viscosity model for guessing algorithmic functions only, and that the target is to get numerical values of the viscosity function directly from experimental data. This general framework has also been discussed in the recent literature (Friedrich et al. 1996) by including the analysis of regularization methods, which introduce further information into the basic ill-posed problem with the purpose of defining a unique solution from many that are attainable.

To deal with the ill-posed problem in capillary viscometry, in this work we propose to extend the analysis carried out by Brunn and Vorwerk (1993) by using the system identification procedure (Dahlquist et al. 1974) to determine the parameters of an appropriate viscosity model which is chosen by satisfying criteria for the fit goodness. The starting point is to rewrite the basic equations of capillary viscometry in terms of a viscosity model as described below. The approach to solve this problem should overcome the difficulties presented by the methods described above. Therefore, two requirements are imposed here: (a) the procedure must be also applied to fluids that show two Newtonian plateaus; (b) the procedure should excel those results obtained with the classical WRM method and other methods not directly using a viscosity model. In this sense, instead of determining $\eta(\sigma)$ numerically, we suggest to identify the set of parameters corresponding to a viscosity model, which can be readily selected for the fluid under study through preliminary calculations involving the apparent shear rate – shear stress data; i.e., from $\eta_a = \sigma_w/\dot{\gamma}_a$ having taken into account that either σ_w and $\dot{\gamma}_a$ can be evaluated with simple algebraic expressions and the capillary experimental data. For this reason, throughout this work we will designate this proposal the System Identification (SI) procedure. Also, once the model parameters are known, the rheometric viscosity function $\eta(\dot{\gamma})$ is easily calculated in the range of shear rates of the experimental data. Nevertheless, the success of the strategy involved in the SI procedure relies on the adequate consideration of two aspects. One is to

compute the integral equation of first kind with the viscosity model of unknown parameters selected, and the other is to use properly the mean value theorem of continuous functions to reduce significantly the computational time as it is explained below.

Fundamentals

Equation (3) can be used to evaluate the relationship between Q and σ_w for a given fluid, by inserting the function $\dot{\gamma}(\sigma)$ and performing the integration. Clearly, the function $\dot{\gamma}(\sigma)$ is chosen from the menu of viscosity models available in the literature for different fluids and the SI procedure shall be applied with the rules (criteria for fit goodness) established for the best choice, as it is described in the Appendix. Since Eq. (3) can be evaluated analytically for simple models only, like the well known "power law" model, for a more general viscosity model we suggest to use the following pair of equations of capillary viscometry:

$$\sigma_w \frac{r}{R} = \eta(\dot{\gamma}(r), p_1, \ldots, p_{\mathrm{M}})\, \dot{\gamma}(r) \tag{7}$$

$$Q = \frac{\pi \sigma_w}{R} \int_0^R \eta(\dot{\gamma}, p_1, \ldots, p_{\mathrm{M}})^{-1}\, r^3 \mathrm{d}r \tag{8}$$

Equation (7) is the result of combining Eqs. (1) and (2), where $\eta(\dot{\gamma}, p_1, \ldots, p_{\mathrm{M}})$ represents a viscosity model with a fixed number of parameters p_i (usually $\mathrm{M} \leq 4$). Equation (8) is obtained from Eq. (3) by substituting the new variable of integration r for σ. Therefore, when the experimental technique satisfies the requirements to assure that the flow is viscometric (steady state, no-slip at the wall, end effects negligible, isothermal flow), one may estimate the set of parameters $\{p_1, \ldots, p_{\mathrm{M}}\}$ by fitting the experimental data Q^{ex} vs σ_w^{ex} with Eqs. (7) and (8). In these expressions, the superscript ex refers to experimental values. One should observe that this problem cannot be solved by standard fitting methods available in the literature. With the purpose of describing the SI procedure, we define the following sum, which is the objective function to be minimized in the evaluation of unknown parameters:

$$S = \sum_{i=1}^{\mathrm{N}} \left(\frac{Q_i - Q_i^{ex}}{Q_i^{ex}} \right)^2 \tag{9}$$

where N is the number of experimental data Q_i^{ex}. In Eq. (9), Q_{i} represents the flow rate value resulting from Eqs. (7) and (8) for each value of $\sigma_{w,i}^{ex}$ and a trial set of parameters. Thus, Q_i must be determined with Eq. (8) once $\dot{\gamma}(r)$ is found from the inversion of Eq. (7). This inversion is readily carried out with the Newton-Raphson algorithm (Carnahan et al. 1969) where a conservative initialization is $\dot{\gamma} = 0$ for each value of r. Then, we determine a new set of parameters $\{p_1, \ldots, p_{\mathrm{M}}\}$ that makes S as small as possible. In this iterative mathematical framework, it is required to minimize simultaneously the following functions:

$$F_j = \frac{\mathrm{d}S}{\mathrm{d}p_j} = \sum_{i=1}^{\mathrm{N}} \frac{2}{Q_i^{ex}} \left(\frac{Q_i - Q_i^{ex}}{Q_i^{ex}} \right) \frac{\mathrm{d}Q_i}{\mathrm{d}p_j}, \quad j = 1 \text{ to } \mathrm{M} \tag{10}$$

Numerical procedure

Defining $F = [F_1, \ldots, F_M]^{\mathrm{T}}$ and $p = [p_1, \ldots, p_{\mathrm{M}}]^{\mathrm{T}}$, the problem to be solved is expressed as

$$\underline{F}(\underline{p}) = 0 \tag{11}$$

The best estimate of $\underline{p}$ is obtained with the Newton-Raphson algorithm for systems of non-linear algebraic equations. This method involves an iterative process in which p is modified through the following recurrence law

$$\underline{p}^{(n+1)} = \underline{p}^{(n)} - \underline{\underline{F'}}(\underline{p}^{(n)})^{-1} \cdot \underline{F}(\underline{p}^{(n)}) \tag{12}$$

from an initial vector $\underline{p}^{(0)}$ up to get that the normalized difference $\left| \left(\underline{p}^{(n+1)} - \underline{p}^{(n)} \right) / \underline{p}^{(n)} \right|$ becomes sufficiently small and less than $\xi \leq 10^{-3}$. In Eq. (12), $\underline{\underline{F'}} = \mathrm{d}\underline{F} / \mathrm{d}\underline{p}$ is a matrix of dimensions $\mathrm{M} \times \mathrm{M}$ that is inverted through the Gaussian elimination subroutine.

In addition, each of the jk-components of matrix $\underline{\underline{F'}}$ are obtained by differentiating Eq. (10) to find

$$F'_{jk} = \sum_{i=1}^{\mathrm{N}} \frac{2}{Q_i^{ex}} \left[\frac{1}{Q_i^{ex}} \frac{\mathrm{d}Q_i}{\mathrm{d}p_k} \frac{\mathrm{d}Q_i}{\mathrm{d}p_j} + \left(\frac{Q_i - Q_i^{ex}}{Q_i^{ex}} \right) \frac{\mathrm{d}^2 Q_i}{\mathrm{d}p_k \mathrm{d}p_j} \right] \tag{13}$$

It is also clear that $\underline{\underline{F'}}$ is a symmetrical matrix, i.e., $F'_{jk} = F'_{kj}$, since $\mathrm{d}^2(\eta^{-1})/(\mathrm{d}p_k \mathrm{d}p_j) = \mathrm{d}^2(\eta^{-1})/(\mathrm{d}p_j \mathrm{d}p_k)$.

In Eqs. (10) and (13) the expressions for $\mathrm{d}Q_i/\mathrm{d}p_j$ and $\mathrm{d}^2 Q_i/(\mathrm{d}p_k \mathrm{d}p_j)$, which carry information about the viscosity model selected, must be included. Therefore, these differential expressions are obtained from Eq. (8):

$$\frac{\mathrm{d}Q}{\mathrm{d}p_j} = \frac{\pi \sigma_w}{R} \int_0^R \frac{\mathrm{d}(\eta^{-1})}{\mathrm{d}p_j} r^3 \mathrm{d}r = \frac{\pi \sigma_w R^3}{4} \left\langle \frac{\mathrm{d}(\eta^{-1})}{\mathrm{d}p_j} \right\rangle_{\dot{\gamma}_m} \tag{14}$$

$$\frac{\mathrm{d}^2 Q}{\mathrm{d}p_j\, \mathrm{d}p_k} = \frac{\pi \sigma_w}{R} \int_0^R \frac{\mathrm{d}^2(\eta^{-1})}{\mathrm{d}p_j\, \mathrm{d}p_k} r^3 \mathrm{d}r = \frac{\pi \sigma_w R^3}{4} \left\langle \frac{\mathrm{d}^2(\eta^{-1})}{\mathrm{d}p_j\, \mathrm{d}p_k} \right\rangle_{\dot{\gamma}_m} \tag{15}$$

where the first and second derivatives of η^{-1} are evaluated analytically from the viscosity model selected. For the purposes of the SI procedure, these derivatives could also be calculated numerically. Nevertheless, analytical expressions shall be preferred for higher precision. The second equalities in Eqs. (14) and (15) result from the application of the mean value theorem of continuous functions (Korn and Korn 1968). Thus, the expressions placed within the angular brackets $\langle \cdot \rangle$ are

evaluated at $\dot{\gamma}_m = \dot{\gamma}(r_m)$, where $r_m = \vartheta r$ and $0 \le \vartheta \le 1$ in the integration domain. The use of the mean value theorem is useful to reduce the computational time in the SI procedure during the calculations of dQ_i/dp_j and $d^2Q_i/(dp_k dp_j)$, as it is discussed below.

Before ending this section, a brief description of a criterion for the initialization of the Newton-Raphson algorithm applied to Eq. (12) is required. In fact, since the iterative process described by Eq. (12) in the calculation of $\underline{F}(\underline{p}) = 0$ always converges when $\underline{p}^{(0)}$ is chosen sufficiently close to the root $\underline{p}$ (Dahlquist et al. 1974), the appropriate selection of the initial values is a crucial step in the SI procedure. In this sense, the set $\{p_1^{(0)}, \ldots, p_M^{(0)}\}$ introduced in our calculations is obtained by carrying out a preliminary fitting of the data η_a vs $\dot{\gamma}_a$ with the viscosity model $\eta(\dot{\gamma}, p_1, \ldots, p_M)$ and substituting $\dot{\gamma}_a$ for $\dot{\gamma}$. This task can be readily carried out by using standard subroutines for fitting explicit nolinear algebraic equations included in classical mathematical software.

To summarize the numerical algorithm used in the SI procedure, a calculation scheme is presented in the Appendix. There one finds that the input data are N experimental values Q^{ex} vs σ_w^{ex}, while the output is the appropriate set of parameters $\{p_1, \ldots, p_M\}$ that belongs to the viscosity model considered in the calculations. In this sense the fit goodness of the calculations is measured through both the determination coefficient $\hat{r}^2$ and the standard deviation $\hat{s}$, as they are defined in the Appendix.

Applications of the SI procedure

Viscosity model

The viscosity function $\eta(\dot{\gamma})$ for most fluids of practical interest, such as polymeric solutions, melts, colloidal suspensions, and emulsions, presents typically three zones: a low shear rate plateau followed by a near power-law decrease that ends finally at a high shear rate plateau. This behavior is satisfactorily described by several viscosity models proposed in the literature (see, for example, Bird et al. 1977; Barnes et al. 1991). To present calculations with the SI procedure here, we pick out, for instance, the following viscosity function:

$$\eta(\dot{\gamma}) = \frac{\eta_o - \eta_\infty}{1 + (\lambda\dot{\gamma})^\alpha} + \eta_\infty \tag{16}$$

where η_o and η_∞ are the limiting viscosity values, corresponding to the asymptotic shear rates $\dot{\gamma} \to 0$ and $\dot{\gamma} \to \infty$, respectively (Cross 1965). In addition, λ is a characteristic relaxation time for the fluid and $\alpha > 0$ is the exponent that measures the severity of shear thinning. Although we adopt Eq. (16) for the purposes of this work, any other model can be also used to apply the SI procedure in practical situations. Therefore, to get the viscosity function from viscometric capillary data in the theoretical framework described above, Eq. (16) is used in the algorithm (Eqs. 7, 8, 14, and 15) by defining $p_1 = \eta_o$, $p_2 = \lambda$, $p_3 = \alpha$, and $p_4 = \eta_\infty$. In this application, Eq. (16) is also used to obtain the set of initial values $\{p_1^{(0)}, p_2^{(0)}, p_3^{(0)}, p_4^{(0)}\}$ by fitting the data η_a vs $\dot{\gamma}_a$ as was explained in the previous section.

Synthetic data

To test the SI procedure, we generate samples of synthetic data $4Q_t^{ex}/\pi R^3$ vs σ_w^{ex}. The subscript T means true data or equivalently error-free data. Here the expression $4Q^{ex}/\pi R^3$, which involves experimental errors from Q^{ex} and R, is preferred instead of using Q^{ex} directly. Therefore, discrete values of $4Q_t^{ex}/\pi R^3$ in a given range of σ_w^{ex} were obtained from Eqs. (7), (8), and (16) with a prefixed set of parameters η_o, λ, α, and η_∞. Then, different levels of the pseudo experimental error δ were introduced in the flow rate data as follows (Munoz and Yeow 1996):

$$\frac{4Q_\delta^{ex}}{\pi R^3} = \frac{4Q_T^{ex}}{\pi R^3}(1 + \delta G) \tag{17}$$

In Eq. (17) G is a Gaussian random number with zero mean and unit variance, which is included to simulate the experimental noise. Therefore, experimental data of capillary viscometry with different levels of error ($\delta = 0.02$, 0.05, 0.1) were produced to be analyzed with the SI procedure.

Calculations with the WRM method

The results obtained by applying the SI procedure to data $4Q_\delta^{ex}/\pi R^3$ vs σ_w^{ex} are compared with those evaluated with the WRM method, which is the one most frequently used in capillary viscometry. Therefore, the derivative $(d\ln\dot{\gamma}_a/d\ln\sigma_w)$ in Eq. (4) is calculated numerically by averaging the slopes of two adjacent data points as follows (Kincaid and Cheney 1991):

$$\frac{dy}{dx} \equiv \frac{1}{2}\left(\frac{y_{i+1} - y_i}{x_{i+1} - x_i} + \frac{y_i - y_{i-1}}{x_i - x_{i-1}}\right) \tag{18}$$

where $y_i = \ln(4Q_\delta^{ex}/\pi R^3)_i$, and $x_i = \ln(\sigma_w^{ex})_i$.

Results and discussion

We first analyzed a set of synthetic data labeled Sample I, which represents the shear flow response of a hypothetical fluid with $\eta_o = 1$ Pas, $\lambda = 20$ ms, $\alpha = 0.6$, and $\eta_\infty = 0.1$ Pas. The SI procedure is applied to these

data by following the calculation scheme described above and in the Appendix. Results are shown in Fig. 1, where the viscosity function $\eta(\dot{\gamma})$ obtained for different levels of δ is plotted. In the same figure, the prediction of the WRM method is also included for comparison. It is observed that, while the WRM method generates viscosity values highly scattered as δ increases, the numerical predictions obtained with the SI procedure are not affected significantly by the experimental noise.

Sample I represents suspensions and dilute solutions which show two Newtonian plateaus in the range of $\dot{\gamma}$ considered. Nevertheless, in the case of polymeric fluids such as concentrated solutions and melts, $\eta_o \gg \eta_\infty$, and hence, the second Newtonian plateau is not reached experimentally (Bird et al. 1977). To illustrate these situations, we next use Eq. (16) with three parameters, i.e., $\eta_\infty \approx 0$ is imposed. Thus, data labeled Sample II were generated for a polymeric fluid with $\eta_o = 1$ Pas, $\lambda = 5$ ms, and $\alpha = 0.6$. Results obtained by applying the SI procedure to these data are presented in Fig 2, where the resulting function $\eta(\dot{\gamma})$ is compared with the prediction of the WRM method. This figure thus shows the same features as those already discussed in relation to Fig. 1. In fact, the SI procedure predicts almost the same viscosity curve for the different levels of pseudo experimental error considered.

In order to reduce the computation time in the SI procedure, an alternative way to calculate dQ_i/dp_j and $d^2Q_i/(dp_k dp_j)$ was tested by using the second equalities of

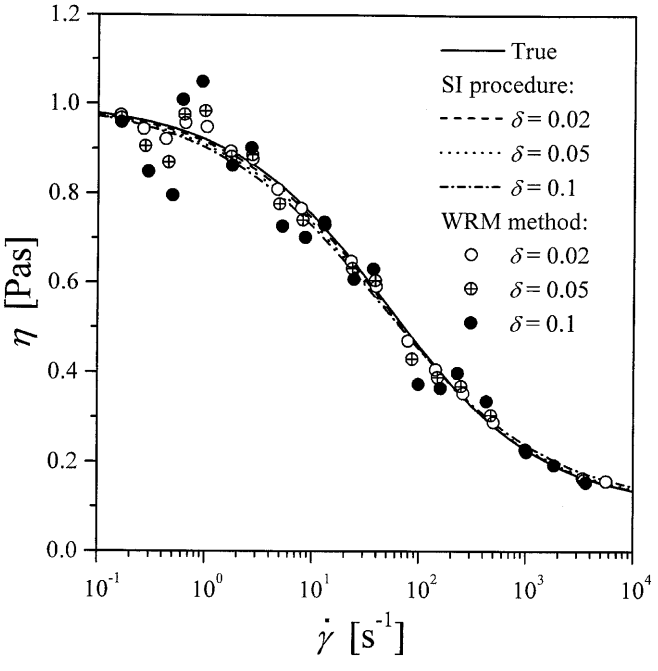

Fig. 1 Viscosity η as function of shear rate $\dot{\gamma}$ obtained from the capillary data of Sample I (Eq. 16 with four parameters) for different values of the experimental error δ. *Lines* represent the predictions of the SI procedure and *symbols* refer to the classical WRM method

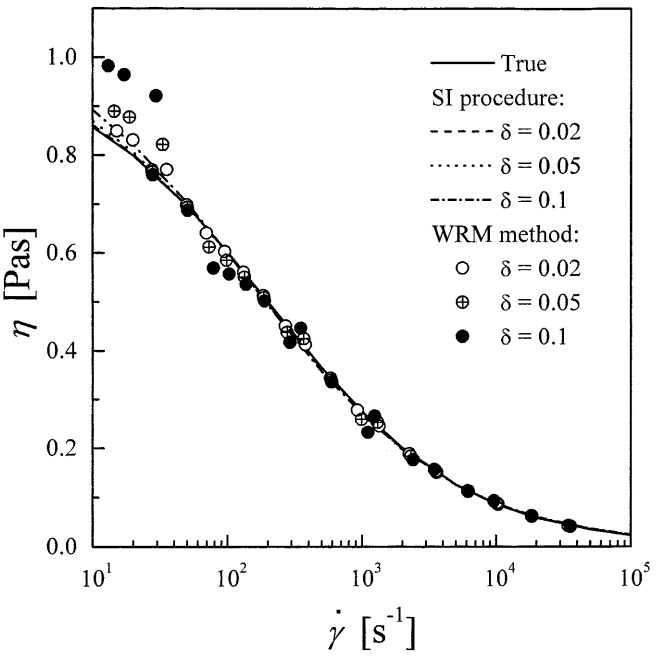

Fig. 2 Viscosity η as function of shear rate $\dot{\gamma}$ obtained from capillary data of Sample II (Eq. 16 with three parameters) for different values of the experimental error δ. *Lines* represent the predictions of the SI procedure and *symbols* refer to the classical WRM method

Eqs. (14) and (15). Since $\dot{\gamma}_m$ is unknown and different for each derivative of η^{-1}, one may perform approximate calculations by assuming either $\dot{\gamma}_m = \dot{\gamma}_w$ or $\dot{\gamma}_m = \dot{\gamma}_a$. In comparing the results obtained by using these approximations with those coming from the exact calculations, it was observed that the parameter values, as well as $\hat{r}^2$ and $\hat{s}$, presented minor variations for different levels of error. Nevertheless, the computational time was significantly diminished in relation to that required when the exact calculations of dQ_i/dp_j and $d^2Q_i/(dp_k dp_j)$ are included in the algorithm.

We then test the SI procedure with experimental capillary data corresponding to real fluids. With this purpose, three sets of experimental data are taken from the literature and presented in Fig. 3. In fact, Sample III is a 3.5% carboximetil-cellulose solution reported by Fredrickson (1964) (p 309), Sample IV is a polyisobutylene solution reported by Schowalter (1978) (p 114), and Sample V is a 24.8% cellulose acetate solution reported by Skelland (1967) (p 158). These experimental data cover the low shear rate plateau and mainly the power law region. Thus, the viscosity model selected for these three samples was Eq. (16) with $\eta_\infty \approx 0$. The SI procedure was applied to each sample and the resulting parameters are presented in Table 1.

Figure 4 shows the relative viscosity η/η_o as function of shear rate $\dot{\gamma}$ for Samples III, IV, and V. Once more, it is observed that the WRM methods generate viscosity values with a high degree of scattering, with the

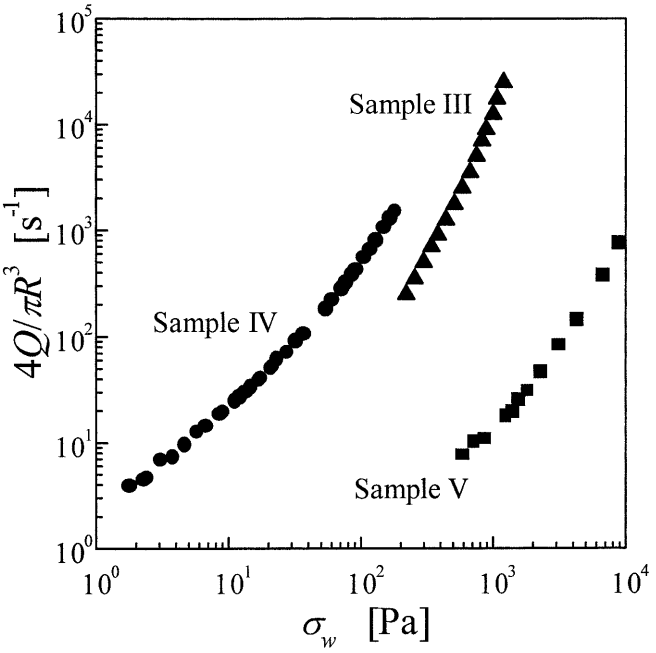

Fig. 3 Experimental data of capillary rheometry for different fluids. The samples are: III, 3.5% carboximetil-cellulose solution (Fredrickson 1964) (p 309); IV, polyisobutylene solution (Schowalter 1978) (p 114); V, 24.8% cellulose acetate solution (Skelland 1967) (p 158)

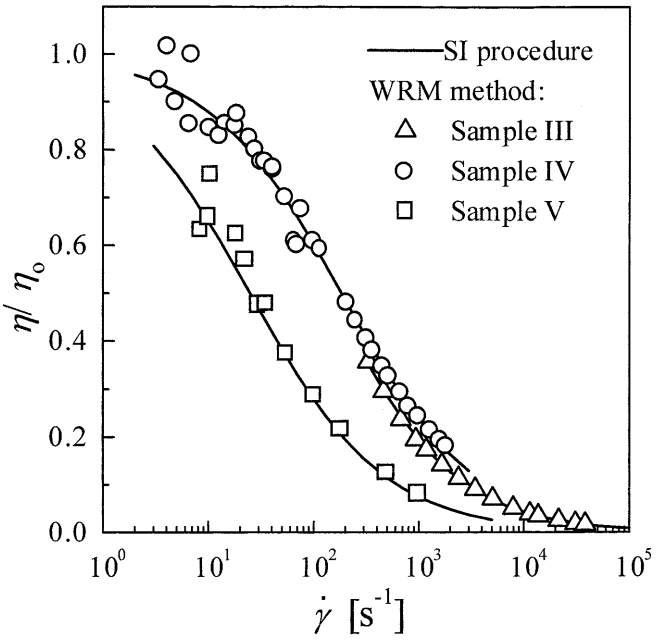

Fig. 4 Relative viscosity η/η_o as function of shear rate $\dot{\gamma}$ obtained from the experimental capillary data presented in Fig. 3. *Lines* represent the predictions of the SI procedure by using Eq. (16) with three parameters, and *symbols* refer to the classical WRM method

Table 1 Parameters of Eq. (16) obtained through the SI procedure, for the different sets of experimental capillary data presented in Fig. 3

Samples	η_o [Pas]	λ [ms]	α	$\hat{r}^2$	$\hat{s}$ [s^{-1}]
III	1.864	6.97	0.731	0.99818	380
IV	0.553	5.45	0.683	0.99938	11
V	111.8	40.3	0.680	0.99967	6.7

exception of those corresponding to Sample III which has a near "power law" response (see also Fig. 3). The full lines in Fig. 4 are the functions $\eta(\dot{\gamma})/\eta_0$ obtained from the SI procedure.

In a wider context of analysis, it is also possible to use better rheometric viscosity models by increasing the number of rheological parameters, this depending, of course, on the physical view and considerations of the analysis being carried out for the fluid sample. Under any circumstances, it will always be of great interest to obtain a smooth curve of the viscosity function rather than having numerical values of this function with some degree of scattering, which increases significantly with the value of δ.

Conclusions

The SI procedure to determine the viscosity function $\eta(\dot{\gamma})$ in capillary viscometry is presented with the following advantages on other methods published previously in the literature:

1. A smooth and continuous function $\eta(\dot{\gamma})$ is obtained in the range of shear rates of the experimental data, which is generated by satisfying criteria of fit goodness.
2. The procedure can be applied to fluids in shear flow that present two Newtonian plateaus.
3. This procedure uses the mean value theorem of continuous functions to simplify the basic problem, facilitate the calculations, and reduce significantly the computational time. The initialization of parameters in the iterative process is established and the success of the results produced depends critically on this aspect.

To the present time, the SI procedure seems to give results with higher precision than those obtained with methods avoiding the direct use of a viscosity model. Nevertheless, one should always prefer to be able to infer not only parameters but also functions from experimental data to better characterize the system under investigation.

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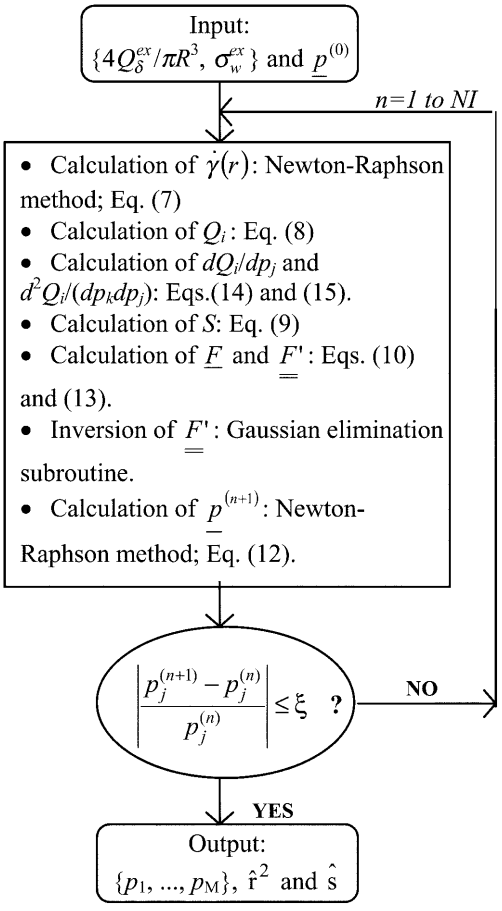
Appendix

Calculation scheme for the SI procedure in capillary rheometry



Evaluation of the standard deviation s and the determination coefficient $\hat{r}^2$

The determination coefficient $\hat{r}^2$ is calculated as follows (Carnahan et al. 1969):

$$\hat{r}^2 = \frac{\hat{s}_{xy}^2}{\hat{s}_{xx}\,\hat{s}_{yy}}$$

where

$$\hat{s}_{xx} = \sum_{i=1}^{N} \left(Q_i^{ex} - Q^{ex,m}\right)^2$$

$$\hat{s}_{yy} = \sum_{i=1}^{N} \left(Q_i - Q^{m}\right)^2$$

$$\hat{s}_{xy} = \sum_{i=1}^{N} \left(Q_i^{ex} - Q^{ex,m}\right)\left(Q_i - Q^{m}\right)$$

In these expressions, the superscript *av* indicates average values.

The standard deviation $\hat{s}$ is

$$\hat{s} = \sqrt{\frac{1}{(N-M)} \sum_{i=1}^{N} \left(\frac{4Q_i^{ex}}{\pi R^3} - \frac{4Q_i}{\pi R^3}\right)^2}$$

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