CORRECTION OF DATA MEASURED WITH A ROTATIONAL VISCOMETER IN THE CASE OF NON-NEWTONIAN LIQUIDS

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Received: September 30, 1986
Presented by Prof. Dr. Gy. Varsányi

Abstract

Newtonian and non-Newtonian substances were investigated with a rotational viscometer, featuring cylinder pairs of different radius ratio. Flow-curves calculated from the torque—angular speed data measured with the generally used relationship, valid only for Newtonian liquids, did not coincide for non-Newtonian liquids in the case of different cylinder pairs, and the deviation of the curves was the larger, the more the behaviour of the liquid differed from the Newtonian behaviour. Transforming data with Krieger–Elrod's [7] equation, the points measured with different cylinder pairs were lying along a common flow curve.

Introduction

It often happens that substantially different rheological parameters are obtained when a liquid is studied using different viscometers or methods. This is possible only if but one of the different methods — or none of them — yields the true flow-curve, while the others only some distortion of it.

In the case of Newtonian liquids this distortion is generally small, however, it becomes larger as the deviation from Newtonian behaviour increases.

A parallel-cylinder Searle-type (the inner cylinder rotates) rotational viscometer was used in our work. The possible errors and operational limits of these viscometers were investigated in detail by several authors [1–4]. Of these we investigated the effect of the width of the slot between the two cylinders. For the elimination of this effect a data transformation method, known for a long time but scarcely used, and some of its applications are given.

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Theoretical part

Let the starting conditions be as follows: a cylinder of length L and radius R_i rotates at an angular speed of Ω in a stationary cylinder of radius R_0, and between the two cylinders, at a distance r from the axis of rotation, the angular speed of the liquid layer is $\Theta(r)$.

In steady state (disregarding end-effects) the torque acting on the single liquid layers is:

$$M=\tau 2r^2\pi L=\text{const.} \tag{1}$$

where M is the torque; r the distance of a given point of the liquid from the axis of rotation ($R_i<r<R_0$); τ the shear stress at the given place r.

According to the Newtonian law:

$$\tau=\eta\,\mathrm{d}v/\mathrm{d}r \tag{2}$$

where η is the viscosity and $\mathrm{d}v/\mathrm{d}r$ the velocity gradient or shear rate.

Hence:

$$v=r\Theta \qquad \text{and} \quad \frac{\mathrm{d}v}{\mathrm{d}r}=r\frac{\mathrm{d}\Theta}{\mathrm{d}r}+\Theta \tag{3}$$

Let us define the shear rate for the so-called pure shear (omitting from (3) the term related to rotation):

$$\dot{\gamma}=-r\frac{\mathrm{d}\Theta}{\mathrm{d}r} \tag{4}$$

Using the preceding equations and assuming that $\eta=\text{const.}$, we have for the angular speed [5]:

$$\Theta=\frac{\Omega R_i^2(R_0^2-r^2)}{r^2(R_0^2-R_i^2)} \tag{5}$$

where Ω is the angular speed of the liquid at point R_i.

Substituting its derivative into (4) we get

$$\dot{\gamma}=K\frac{1}{r^2}, \qquad \text{where:} \quad K=\frac{2\Omega}{1/R_i^2-1/R_0^2} \tag{6}$$

For the calculation of the shear rate in rotational viscometers almost exclusively Eq. (6) is used (with the substitution $r=R_0$ or $r=R_i$).

However, it can be seen from the deduction that the formulas obtained are strictly valid only in the case where $\eta=\text{const.}$ If η changes only slightly, and the relative slot width (i.e. $(R_0-R_i)/R_0$) is small, then the error is not great when calculating with Eq. (6). If, however none of the two conditions is satisfied, then this calculation cannot be used. Then the shear rate must be generally defined as [6–8]:

$$\dot{\gamma} = -\frac{\mathrm{d}v}{\mathrm{d}r} = -r\frac{\mathrm{d}\Theta}{\mathrm{d}r} = f(\tau) \tag{7}$$

As Eq. (1) is valid for any liquid, written for the surface of the two cylinders ($r = R_i$ and $r = R_0$) and after rearrangement we get

$$\frac{\tau_i}{\tau_0} = \varepsilon^2, \qquad \text{where} \quad \varepsilon = \frac{R_0}{R_i} \tag{8}$$

Expressing τ similarly from Eq. (1) and differentiating with respect to r:

$$\frac{\mathrm{d}\tau}{\mathrm{d}r} = -\frac{2M}{2r^3\pi L} = -\frac{2\tau}{r} \tag{9}$$

Expressing $r/\mathrm{d}r$ and inserting it into Eq. (7) we get:

$$\mathrm{d}\Theta = f(\tau)\frac{\mathrm{d}\tau}{2\tau} \tag{10}$$

The integral of (10) between the limits $\Theta = 0 \rightarrow \tau = \tau_0$ and $\Theta = \Omega \rightarrow \tau = \tau_i$ is:

$$\Omega = \frac{1}{2}\int_{\tau_0}^{\tau_i} f(\tau)\frac{\mathrm{d}\tau}{\tau} \tag{11}$$

Differentiating this at point τ_i:

$$\left.\frac{\mathrm{d}\Omega}{\mathrm{d}\tau}\right|_{\tau_i} = \frac{1}{2\tau_i}[f(\tau_i) - f(\tau_0)] \tag{12}$$

Using Euler–McLaurin's sum of series, Krieger and Elrod [7] rewrote this equation in a form suitable for calculation:

$$f(\tau_i) = \frac{\Omega}{\ln\varepsilon}\left[1 + \ln\varepsilon\frac{d\ln\Omega}{d\ln\tau_i} + \ln\varepsilon^2\frac{d^2\Omega}{3\Omega d(\ln\tau_i)^2} - \ln\varepsilon^4\frac{d^4\Omega}{45\Omega d(\ln\tau_i)^4} + \dots\right] \tag{13}$$

Let us write

$$\frac{d^n\ln\Omega}{d(\ln\tau_i)^n} = m(n) \tag{14}$$

According to Krieger and Elrod, if

1) $m(1)\ln\varepsilon < 0.2$, then only the first and second term of the expression in parentheses must be reckoned with;

2) if $0.2 < m(1)\ln\varepsilon < 1$, then the term containing the second derivative must also be taken into consideration;

3) if $1 < m(1)\ln\varepsilon$ then the calculation must be continued up to the term containing the fourth derivative.

(The authors above did not meet this latter case [7]).

In the case of a Newtonian liquid:

$$\frac{d^n \ln \Omega}{d(\ln \tau_i)^n} = \begin{matrix} 1, & \text{if} & n=1 \\ 0, & \text{if} & n>1 \end{matrix} \tag{15}$$

Thus:

$$f(\tau_i) = \Omega\left(\frac{1}{\ln \varepsilon} + 1 + \frac{\ln \varepsilon}{3} - \frac{\ln \varepsilon^3}{45} + \ldots\right) \tag{16}$$

If $\varepsilon \simeq 1$, then only the first two of the terms in parentheses are important. According to our calculations Eqs (16) and (6) give for any ε the same shear rate, that is, using the general relationship for Newtonian liquids, the two kinds of deduction give the same result.

It should be mentioned that the equations above are valid only if the whole quantity of substance flows between the cylinders (there is no stationary layer). If the substance investigated is plastic, then it must be taken into consideration that this condition is satisfied only in the case where

$$\tau_0 = \frac{\tau_i}{\varepsilon^2} > \vartheta, \tag{17}$$

where ϑ is the yield stress.

If $\tau_0 < \vartheta < \tau_i$, then there is a stationary layer close to the external cylinder, the internal radius of which is on the basis of Eq. (8):

$$R'_0 = R_i \left[\frac{\tau_i}{\vartheta}\right]^{1/2} \tag{18}$$

Hence, in this case we must calculate in Eq. (13) with a radius ratio of $\varepsilon = R'_0/R_i$.

Experimental part

Measurement

For the measurements a Rheotest Model RV 2 (VEB MLW Prüfgeräte-Werk, Medingen, GDR) rotational viscometer was used.

The Newtonian liquid investigated was a viscosity standard on polymer basis (National Office of Metrology, Hungary).

The non-Newtonian samples were aqueous polymer solutions:

- — 2% hydroxypropyl methylcellulose (Methocell F4M, Dow Chemical Co. Ltd.)
- — 3% non-neutralized polymethylmetacrylic acid (Carbopol 940, B. F. Goodrich Co.)

— 1% pharmaceutical hydrogel containing Carbopol 940, neutralized with triethanolamine.

The polymer solutions were prepared as described in the literature [9, 10].

Measurements were carried out at 25.0 ± 0.1 °C, at three different radius ratios, with the internal cylinders of the apparatus marked S1, S2, S3. Geometrical data of the cylinders are contained in Table I.

Table I

Geometrical data of inner cylinders

Mark of cylinder	S1	S2	S3
$\varepsilon = \frac{R_0}{R_i}$	1.020	1.064	1.235
L (cm)	7.2	7.2	7.2

Calculation

From the torque measured with the viscometer the shear stress was calculated on the basis of (1). $\Omega - \tau$ points obtained in this way were transformed on a computer to points $f(\tau_i) - \tau_i$ according to Eq. (13). To increase the accuracy of calculation, Eq. (13) was written in a form containing only the derivatives of the function $\ln \Omega - \ln \tau_i$.

$$f(\tau_i) = \frac{\Omega}{\ln \varepsilon} \left\{ 1 + \ln \varepsilon m(1) + \frac{\ln \varepsilon^2 m(1)^2}{3} + \frac{\ln \varepsilon^2 m(2)^2}{3} - \right.$$
$$\left. - \frac{\ln \varepsilon^4}{45} [m(1)^4 + 6m(1)^2 m(2) + 4m(1)m(3) + 3m(2)^2 + m(4)] \right\} \quad (19)$$

where

$$m(n) = \frac{dm(n-1)}{d \ln \tau_i} = \frac{d^n \ln \Omega}{d(\ln \tau_i)^n} \qquad (n > 1) \qquad (20)$$

(the third-fourth terms in parenthesis are identical with the third term in Eq. (13), while the last five terms with the fourth term of Eq. (13).)

The tables contain partial results of calculation:

$\dot{\gamma}(6)$ — shear rate calculated according to formula (6);

$\dot{\gamma}(1)$ — shear rate, if in Eq. (19) only the first two of the terms in parentheses;

$\dot{\gamma}(2)$ — shear rate if also the following two terms;

$\dot{\gamma}(4)$ — shear rate if all the terms were taken into consideration.

Numerical derivation was made by polynomial fitting.

Evaluation

Newtonian liquid

Figure 1 shows the flow curve of the Newtonian liquid, measured with all the three cylinders, and calculating shear rate according to Eq. (6). It can be seen that the points actually lie along a straight line, and within the accuracy of the instrument (4%) are independent of slot width, the maximum deviation being 2.5%. Transformation according to (19) did not change the flow curve. The value of *m*(1) differed by not more than 5% from unity, so that higher derivates had not to be taken into consideration (see also Eq. (15)).

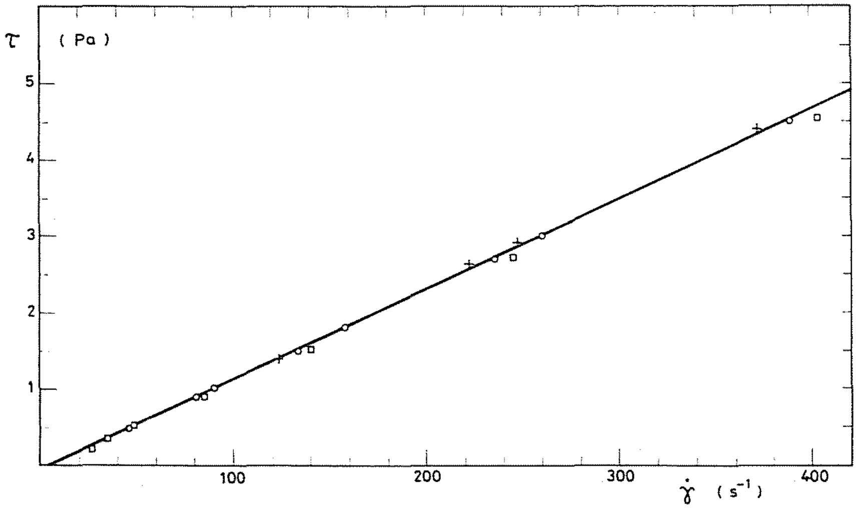

Fig. 1. Flow curve of viscosity standard at 25 °C, measured with cylinder + S1; o S2; □ S3

Pseudoplastic liquid

Figure 2 shows the flow curves of 2% HPMC gel, measured with all the three cylinders. The shear rate was calculated with formula (6), and transformed according to (19). It can be seen that decreasing shear rate is obtained for given shear stress with increasing slot width when calculating with the equation deduced for Newtonian liquids (maximal deviation between transformed and non-transformed data being about 15% in our case).

Results of transformation calculations for cylinder S3 are contained in Table II. Shear rate ratios calculated with (6) ($\dot{\gamma}(6)$), obtained in the partial calculations ($\dot{\gamma}(1)$, $\dot{\gamma}(2)$), and under consideration of all the terms of (19) ($\dot{\gamma}(4)$) are given. It can be seen that in the case of cylinder S3, the terms containing the

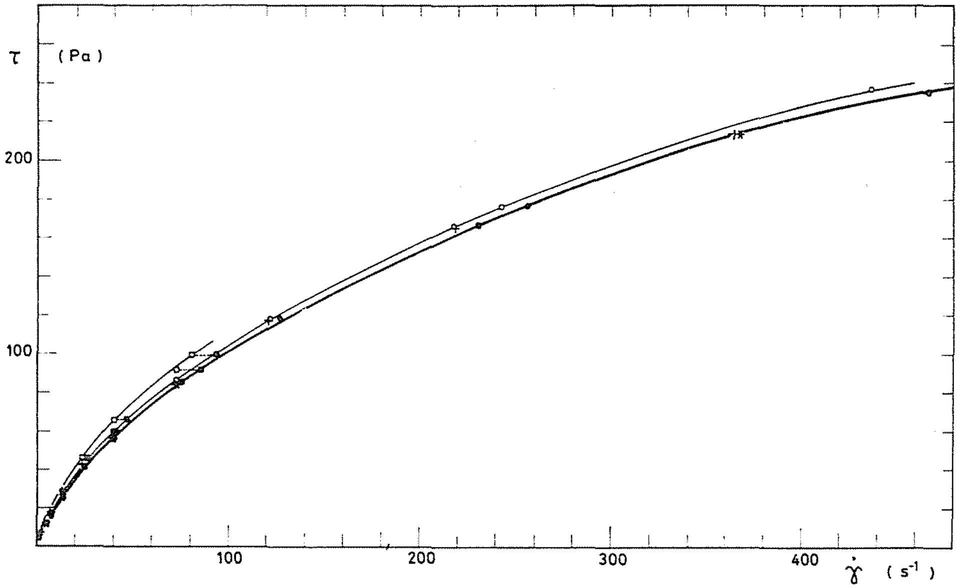

Fig. 2. Flow curve of 2% hydroxypropyl methylcellulose at 25 °C, measured with cylinder + S1; o S2; ☐ S3; measured with cylinder ∗ S1; ● S2; ■ S3 and transformed

Table II

Results calculated for 2% hydroxypropyl methylcellulose, measured with cylinder S3

	τ_i Pa	$m(1) \ln \varepsilon$ —	$\dot{\gamma}(6)$ 1/s	$\frac{\dot{\gamma}(6)}{\dot{\gamma}(4)}$ —	$\frac{\dot{\gamma}(1)}{\dot{\gamma}(4)}$ —	$\frac{\dot{\gamma}(2)}{\dot{\gamma}(4)}$ —	$\dot{\gamma}(4)$ 1/s
1.	4.3	0.22	1.5	0.98	0.99	1.00	1.53
2.	7.4	0.24	2.7	0.96	0.98	1.00	2.81
3.	11.7	0.25	4.5	0.95	0.98	1.00	4.74
4.	18.4	0.26	8.1	0.94	0.98	1.00	8.62
5.	28.1	0.24	13.5	0.95	0.98	1.00	14.1
6.	45.6	0.27	24.3	0.93	0.97	1.00	26.2
7.	66.5	0.35	40.5	0.86	0.96	1.00	47.0
8.	91.5	0.38	72.9	0.85	0.97	1.00	85.9
9.	99.6	0.37	81.0	0.86	0.97	1.00	94.5

second derivative must also be taken into consideration, for the calculation error not to exceed 3–4% (the greatest deviation of $\dot{\gamma}(1)/\dot{\gamma}(4)$ from unity). This is not necessary with narrower slots.

It may be seen from Fig. 2 that transformed points lie along the same curve. Since the shear rate changes most strongly in the case of the greatest slot width (S3) and practically does not change in the case of the narrowest slot after transformation, this new common curve must be the true flow curve.

Plastic liquids

Figures 3 and 4 show the flow curves of Carbopol 940 gels, calculating the shear rate on the basis of (6) and (19), respectively. Calculation results for unneutralized gel are contained in Table III in the case of all three cylinders, for the sample containing neutralized gel in Table IV in the case of cylinder S3.

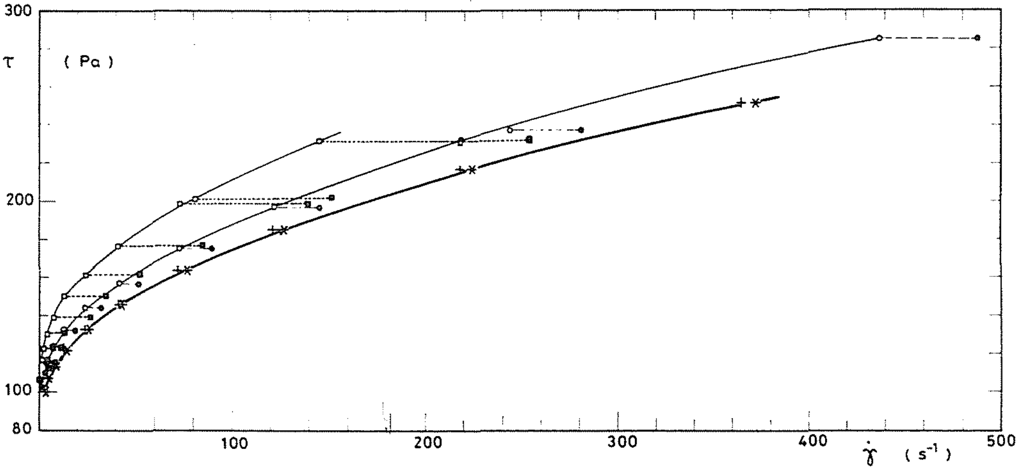

Fig. 3. Flow curve of 3% unneutralized Carbopol 940 at 25 °C, measured with cylinder + S1; o S2; ☐ S3 measured with cylinder ✳ S1; ● S2; ■ S3 and transformed

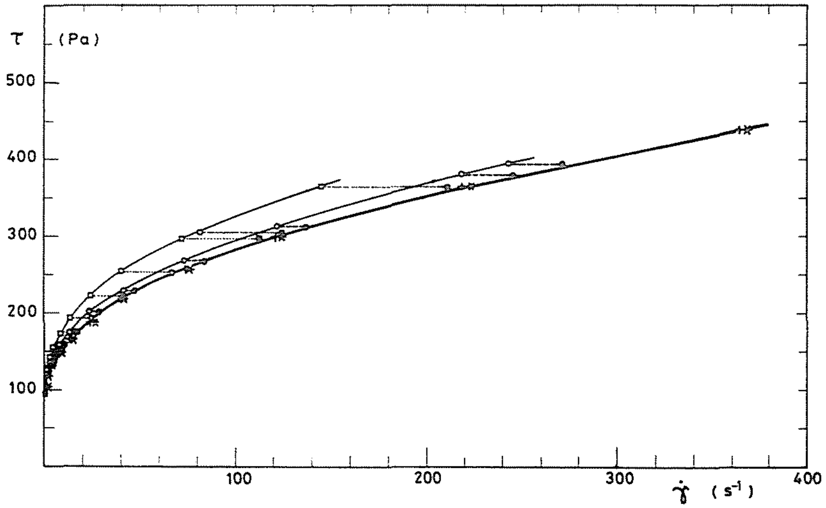

Fig. 4. Flow curve of 1% neutralized pharmaceutical hydrogel containing Carbopol 940 at 25 °C, measured with cylinder + S1; o S2; ☐ S3 measured with cylinder ✳ S1; ● S2; ■ S3 and transformed

Curves calculated with (6) shifted in the same direction with increasing slot width, but to a much larger extent than the curves of the pseudoplastic liquid. This can be attributed to the fact that the behaviour of a plastic liquid differs in general more from the Newtonian, than that of a pseudoplastic.

The shift is larger in the case of the 3% unneutralized gel. This can be easily understood, as indeed, the behaviour of a liquid is the "more non-Newtonian", the more its viscosity changes with shear rate. The slope of the tangent drawn to the flow curve of plastic substances is usually defined as plastic viscosity. This is in close connection with $m(1)$. It will be noted from Figs

Table III

Results calculated for 3% unneutralized Carbopol 940
Measured with cylinder S1

	τ_i	$m(1) \ln \varepsilon$	$\dot{\gamma}(6)$	$\frac{\dot{\gamma}(6)}{\dot{\gamma}(4)}$	$\frac{\dot{\gamma}(1)}{\dot{\gamma}(4)}$	$\frac{\dot{\gamma}(2)}{\dot{\gamma}(4)}$	$\dot{\gamma}(4)$
	Pa	—	1/s	—	—	—	1/s
1.	84.8	−0.05	1.05	1.08	0.99	1.00	1.38
2.	100.4	0.16	2.7	0.89	0.99	1.00	3.03
3.	107.1	0.18	4.5	0.87	0.99	1.00	5.15
4.	113.8	0.18	8.1	0.88	0.99	1.00	9.22
5.	121.6	0.14	13.5	0.91	1.00	1.00	14.8
6.	133.9	0.12	24.3	0.93	1.00	1.00	26.2
7.	146.2	0.11	40.5	0.94	1.00	1.00	43.2
8.	164.1	0.09	72.9	0.95	1.00	1.00	76.8
9.	185.3	0.08	121.5	0.96	1.00	1.00	126.0
10.	217.6	0.07	218.7	0.97	1.00	1.00	225.0
11.	252.2	0.06	364.5	0.98	1.00	1.00	373.0

Measured with cylinder S2

	τ_i	$m(1) \ln \varepsilon$	$\dot{\gamma}(6)$	$\frac{\dot{\gamma}(6)}{\dot{\gamma}(4)}$	$\frac{\dot{\gamma}(1)}{\dot{\gamma}(4)}$	$\frac{\dot{\gamma}(2)}{\dot{\gamma}(4)}$	$\dot{\gamma}(4)$
	Pa	—	1/s	—	—	—	1/s
1.	74.6	0.29	0.5	0.86	1.04	1.00	0.58
2.	110.1	0.58	2.7	0.62	0.92	1.00	4.36
3.	116.0	0.57	4.5	0.64	0.94	1.00	7.05
4.	124.3	0.51	8.1	0.67	0.96	1.00	12.0
5.	132.6	0.46	13.5	0.70	0.97	1.00	19.2
6.	144.4	0.39	24.3	0.74	0.97	1.00	32.7
7.	157.5	0.35	40.5	0.77	0.98	1.00	52.7
8.	176.4	0.30	72.9	0.81	0.98	1.00	90.4
9.	197.7	0.25	121.5	0.84	0.99	1.00	145.1
10.	232.1	0.22	218.7	0.86	0.99	1.00	254.3
11.	237.0	0.22	243.0	0.86	0.99	1.00	281.3
12.	285.3	0.18	437.4	0.89	1.00	1.00	488.7

Table III (continued)

Measured with cylinder S3

	τ_i Pa	$m(1) \ln \varepsilon$ —	$\dot\gamma(6)$ 1/s	$\frac{\dot\gamma(6)}{\dot\gamma(4)}$ —	$\frac{\dot\gamma(1)}{\dot\gamma(4)}$ —	$\frac{\dot\gamma(2)}{\dot\gamma(4)}$ —	$\dot\gamma(4)$ 1/s
1.	104.4	3.19	0.17	0.31	1.07	2.5	0.54
2.	107.6	3.84	0.3	0.13	0.52	1.13	2.32
3.	118.8	2.68	1.5	0.29	0.89	1.18	5.14
4.	123.7	2.23	2.7	0.38	1.01	1.34	7.15
5.	131.7	1.92	4.5	0.32	0.77	1.07	14.0
6.	139.7	1.87	8.1	0.29	0.70	0.93	27.6
7.	149.4	1.57	13.5	0.38	0.81	0.98	35.4
8.	162.2	1.31	24.3	0.47	0.90	1.04	51.8
9.	177.5	1.18	40.5	0.48	0.86	1.00	85.2
10.	197.5	1.03	72.9	0.52	0.87	0.98	139.8
11.	202.4	0.99	81.0	0.54	0.88	0.98	151.1
12.	272.9	0.78	145.8	0.67	0.99	1.04	218.4

Table IV

Results calculated for 1% neutralized pharmaceutical hydrogel on Carbopol 940 basis, measured with cylinder S3

	τ_i Pa	$m(1) \ln \varepsilon$ —	$\dot\gamma(6)$ 1/s	$\frac{\dot\gamma(6)}{\dot\gamma(4)}$ —	$\frac{\dot\gamma(1)}{\dot\gamma(4)}$ —	$\frac{\dot\gamma(2)}{\dot\gamma(4)}$ —	$\dot\gamma(4)$ 1/s
1.	94.8	1.13	0.17	0.45	0.78	1.07	0.38
2.	128.5	1.49	1.5	0.39	0.80	0.98	3.85
3.	141.3	1.17	2.7	0.50	0.90	1.02	5.38
4.	155.8	1.04	4.5	0.53	0.90	1.02	8.46
5.	175.1	1.06	8.1	0.50	0.86	1.00	16.2
6.	192.7	0.99	13.5	0.53	0.88	1.00	25.5
7.	221.6	0.87	24.3	0.58	0.91	1.00	41.7
8.	252.1	0.80	40.5	0.61	0.91	1.00	66.3
9.	297.1	0.73	72.9	0.64	0.92	1.00	114.1
10.	305.1	0.72	81.0	0.64	0.92	1.00	125.7
11.	366.2	0.65	145.8	0.69	0.94	1.00	211.6

3 and 4 that the flow curve of the unneutralized gel is flatter, thus, its plastic viscosity is lower at the same shear rate. On the other hand, it can be seen from Tables III and IV that $m(1)$ is considerably higher for the 3% unneutralized gel.

It can be seen from the tables that in the case of $m(1) \ln \varepsilon > 1$ terms containing fourth derivatives had to be actually taken into account. (It should be mentioned, however, that with increasing order of the derivatives the error of differentiation rapidly increases, particularly at the extreme points, which must be taken into consideration in the evaluation of the results.)

After transformation, the points of the neutralized gel on Carbopol 940 basis are located along the same curve. For the unneutralized gel this agreement is less complete. In our opinion this may be due to the end effects (additional torque arising at the ends of the rotating cylinder), which was not corrected for. Similarly to the effect of slot width, it is also true for the end effects that they are the larger, the more the behaviour of the liquid differs from the Newtonian.

Summary

It was shown that with the data transformation method described by Krieger and Elrod exact rheological parameters can be calculated also for non-Newtonian substances. This calculation could be applied also in the case of such strongly non-Newtonian liquids, that were not investigated by the authors cited above. The advantage of the transformation is that it yields an exact flow curve even if we cannot choose a very small slot width because of the limitations set by the rotational viscometer or the sample.

Moreover, it was shown that shear rates calculated with the formula deduced for Newtonian liquids can considerably differ from the true value in the case of non-Newtonian substances even in the case of the cylinder pair with the narrowest slot, while in the case of a larger slot they are unusable.

The application of the transformation method is the more justified, the greater is the deviation from Newtonian behaviour, which means for plastic substances, the lower is the plastic viscosity.

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