DEGREE OF ACCURACY OF TWO-TERMED FORMULAS FOR CALCULATING THE EFFECTIVE VISCOSITY OF STRUCTURED LIQUIDS

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Two-termed formulas used in calculating the rheological curves of effective viscosity as a function of shear stress in coagulative thixotropic systems are compared with each other.

Several two-termed formulas have been proposed in order to describe the effective viscosity as a function of the uniform shear stress P during the stable laminar flow ($Re < Re_k$) of structured thixotropic systems (in this paper only thixotropic structures will be considered).

Thus Philipoff [1] proposes defining the effective viscosity by

$$\eta(P) = \eta_m + \frac{\eta_0 - \eta_m}{1 + \left(\frac{P}{P_0}\right)^2}, \tag{1}$$

on the basis of phenomenological considerations.

The authors of [2] started from molecular kinetic representations, associated with the hole theory of Frenkel' [7], and obtained the following formula for calculating the effective viscosity:

$$\eta(P) = \eta_m + (\eta_0 - \eta_m)\frac{\frac{P}{b}}{\operatorname{sh}\frac{P}{b}}. \tag{2}$$

Yet another two-termed formula was proposed in [3]:

$$\eta(P) = \eta_m + (\eta_0 - \eta_m)\frac{1 - X}{1 + \left(\frac{\eta_0}{\eta_m} - 1\right)X},$$

after allowing for the relationship between the flow velocity gradient, the Brownian motion, and the external shear stress.

In Eq. (2), b is a quantity determined from the structure parameters:

$$b = \frac{2kT}{\delta^3}, \tag{3}$$

while in (3)

$$X = \frac{1 - \exp\left\{-\frac{3}{2}\cdot\frac{P^2 - P_r'^2}{P_{i1}^2}\right\}}{1 - \exp\left\{-\frac{3}{2}\cdot\frac{P_m'^2 - P_r'^2}{P_{i1}^2}\right\}}; \tag{4}$$

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P_{i1} is the shear stress corresponding to the bend on the flow curve, associated with the structure parameters.

Equations (1)-(3) were derived on the assumption that a single inflection existed on the curve relating the effective viscosity to the shear stress. In addition to this, we may consider the problem of describing the effective viscosity curve in terms of the flow velocity gradient rather than the stress. The problem is encountered in this form when considering pseudoplastic systems. Thus the following formula was proposed in [8]:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \alpha\dot{\varepsilon}^{2/3}}. \tag{5}$$

This equation may be used for describing the effective viscosity curves of thixotropic systems if we require that the curve described by Eq. (5) should have at least one point of inflection in a finite range of variation of shear stress, i.e., $d^2\eta/d\dot{\varepsilon}^2 = 0$. If we carry out the corresponding calculations we arrive at the conditions:

$$1.\quad \dot{\varepsilon} = 0,$$
$$2.\quad 1 + 5\alpha\dot{\varepsilon}^{2/3} = 0,$$
$$3.\quad 1 + \alpha\dot{\varepsilon}^{2/3} = 0.$$

Each of these conditions gives no real values of $\dot{\varepsilon}$ for $\alpha \geq 0$ except $\dot{\varepsilon} = 0$. Hence Eq. (5) describes the flow (yield) curve of those pseudoplastic systems for which there are no points of inflection in a finite range of variation of the flow velocity gradient. Equation (5) may therefore not be used to describe the curves of effective viscosity in terms of the flow velocity gradient of thixotropic systems.

The following formula was proposed in [9] for describing the effective viscosity curves in terms of the shear stress of pseudoplastic systems:

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)\exp\{-\sigma P\}. \tag{6}$$

It follows from the structure of this formula that there are no points of inflection on the curves which it describes. Equation (6) may also therefore not be employed in order to describe the effective viscosity of thixotropic structures.

In Rayner's book [10], fairly detailed attention was paid to the Ostwald power formula giving the dependence of the flow φ on the uniform shear stress. The formula was criticized both by Rayner himself and also in [11]. In the latter case, instead of the flow φ two dimensionless quantities φ^* and P^* were introduced; these were also related to each other by a power law and thus had the same disadvantages as the Ostwald formula. In addition to this, the formula proposed in [11]

$$\varphi^* = \exp\{P^*\}$$

only described the $\varphi(P)$ curve for the section lying above the inflection point. There is indeed a more accurate expression for the $\varphi(P)$ relationship, which was obtained in [3].

In view of these circumstances, only Eqs. (1)-(3) were selected for comparison.

A comparative estimation of the accuracy of Eqs. (1)-(3) at the points $P = P'_r$, $P = P'_m$ was given in [4]; at these points Eq. (3) gave a result coinciding, by hypothesis, with experiment. The errors were only indicated at the points $P = P'_r$ and $P = P'_m$, and no comparison was made with experiment at any other points. Furthermore, Eq. (1) may only be used for calculating the effective viscosity of structured liquids for which $\eta_0/\eta_m < 2$, and (2) for $\eta_0/\eta_m < 10$. No limitations are imposed upon η_0/η_m in the case of (3).

Since none of the equations (1)-(3) is strictly accurate, any theoretical comparison between them outside the points $P = P'_r$ and $P = P'_m$ presents serious difficulties.

In the present investigation we set ourselves the task of comparing the results of calculations based on Eqs. (1)-(3) at internal points of the segment $[P'_r, P'_m]$ with experimental data embracing a wide range of variation of viscosity, from one to several orders of magnitude.

All the calculations were carried out on the Ural-2 computer. In Eqs. (1)-(3) the variable is the stress P; the remaining quantities are known and constant for each curve. In the calculations we assumed $k = P_0 = P'_r$ in (1) and $k = b = P'_r$ in (2).

TABLE 1. Comparison of the Effective Viscosities Calculated by Eqs. (1), (2), and (3)

Material	Input data for the calculation	Stress, $P \cdot 10^3$ dyne/cm²	Experimental viscosity, P	Calculated viscosity according to		
				(1)	(2)	(3)
Printing dye № 53	$P_0 = P'_r = 10^3$ dyne/cm²	1	$3{,}1 \cdot 10^8$	$1{,}55 \cdot 10^8$	$2{,}6 \cdot 10^8$	$3{,}1 \cdot 10^8$
	$b = P'_r = 10^3$ dyne/cm²	34	1308	266743	144	2106
	$P'_r = 10^3$ dyne/cm²	53	1062	108643	144	919
	$\eta_0 = 3{,}1 \cdot 10^8$ P	70	466	62143	144	549
	$\eta_m = 144$ P	101	246	30423	144	307
	$P'_m = 240 \cdot 10^3$ dyne/cm²	135	198	16883	144	211
	$P_{i1} = 158 \cdot 10^3$ dyne/cm²	158	186	12543	144	180
		177	171	9753	144	164
	$\frac{\eta_0}{\eta_m} = 2{,}1 \cdot 10^6$	207	159	7273	144	151
		240	144	5529	144	144
		299	144	3553	144	144
		353	144	2623	144	144
BN-IV	$P_0 = 4 \cdot 10^3$ dyne/cm²	1	1000	948	990	1000
bitumen at	$b = 4 \cdot 10^3$ dyne/cm²	2	1000	823	975	1000
$t = 120°$ C	$P'_r = 4 \cdot 10^3$ dyne/cm²	4	1000	558	868	1000
	$\eta_0 = 1000$ P	5	625	460	805	769
	$\eta_m = 115$ P	6,5	650	358	704	526
	$P'_m = 20{,}5 \cdot 10^3$ dyne/cm²	7,1	592	328	662	455
	$P_{i1} = 20 \cdot 10^3$ dyne/cm²	8,1	579	289	596	370
		9	450	261	539	323
	$\frac{\eta_0}{\eta_m} = 8{,}7$	9,5	365	248	490	294
		10	294	237	478	278
		12	240	203	380	208
		14	219	181	302	172
		16	160	167	244	147
		18,6	127	154	193	125
		19,3	111	151	183	120
		20	—	—	—	117
		20,5	115	147	168	115
		23	116	131	147	115
Asphalt at	$P_0 = 1{,}5 \cdot 10^3$ dyne/cm²	0,5	50	48	49,5	50
$t = 80°$ C	$b = 1{,}5 \cdot 10^3$ dyne/cm²	0,7	50	46	49	50
	$P'_r = 1{,}5 \cdot 10^3$ dyne/cm²	1,5	50	39	46,7	50
	$\eta_0 = 50$ P	2	40	36	44,6	39
	$\eta_m = 28$ P	2,4	35,3	34	43	34
	$P'_m = 3{,}1 \cdot 10^3$ dyne/cm²	2,8	31	33	41	30
	$P_{i1} = 3 \cdot 10^3$ dyne/cm²	3	28	32,4	40	28,6
		3,1	28	32	39	28
	$\frac{\eta_0}{\eta_m} = 1{,}8$	3,7	28	31	37	28
		5	27, (7)	30	33	28
		5,8	28	29	31	28

In order to compare the accuracy of Eqs. (1)-(3) with experimental data, we used the graphs of the flow curves given in [5, 6]. The velocity gradient $\dot{\varepsilon}$ is determined from the flow curves, and the effective viscosity from the equation

$$\eta = P/\dot{\varepsilon}\,. \tag{7}$$

The resultant values of $\dot{\varepsilon}$ and η were taken as the experimental data. The results of the calculations are presented in Table 1. Table 2 gives the relative errors obtained by comparing the experimental data with the values calculated from Eqs. (1) and (2) at the characteristic points $k = P'_r,\ 2P'_r,\ P'_m$ of the segment $[P'_r,\ P'_m]$ for printing dye No. 53, where z_1, z_2 are the relative errors in comparing Eqs. (1) and (2) with (3) [4].

We see from Tables 1 and 2 that Eqs. (1) and (2) give an unsatisfactory result for a ratio of $\eta_0/\eta_m = 2.1 \cdot 10^6$. Equation (3) gives a result close to the experimental value, and so may be recommended for calculating the effective viscosity with a η_0/η_m ratio of the order of 10^6.

TABLE 2. Relative Errors Obtained by Comparing the Experimental Data with the Values Calculated from Eqs. (1) and (2) at the Characteristic Points P'_r, $2P'_r$, P'_m of the Segment $[P'_r, P'_m]$

$k=P_0$ $k=b$	z_1 $k=P'_r$	z_1 $k=P_m$	z_2 $k=P'_r$	z_2 $k=P'_m$
a) for printing dye No. 53				
$k=P'_r$	0,5	—0,000017	0,15	0
$k=2P'_r$	0,2	—0,000069	0,04009	0
$k=P'_m$	0	—0,5	0	—0,15
b) for BN-IV bitumen at t = 120°C				
$k=P'_r$	0,5	—0,0366	0,15	—0,0615
$k=2P'_r$	0,2	—0,132	0,04009	—0,384
$k=P'_m$	0,032	—0,5	0,0063	—0,15
c) for asphalt at t = 80°C				
$k=P'_r$	0,5	—0,189	0,15	—0,532
$k=2P'_r$	0,2	—0,483	0,04	—0,842
$k=P'_m$	0,198	—0,5	0,037	—0,15

In order to determine the degree of accuracy of (1)-(3) when calculating an effective viscosity varying within one order of magnitude ($\eta_0/\eta_m < 10$), we use the experimental data obtained in [6] for BN-IV bitumen at t = 120°C, $\eta_0/\eta_m = 8.7$. In this case we see from Tables 1 and 2 that Eq. (1) has an average deviation of 29.5% from the experimental data on the S-shaped part of the curve, while the deviation of Eq. (2) is 36.1% and that of Eq. (3) only 17%.

In the third example of Table 1 we used experimental data relating to the flow of asphalt at t = 80°C [6] for which $\eta_0/\eta_m = 1.8$. This example was considered in view of the fact that Philipoff's [1] experimental verification of Eq. (1) was carried out for an η_0/η_m ratio very close to this value. We see from Tables 1 and 2 that Eq. (1) gives an average deviation of 9% from the experimental data on the S-shaped part $[2 \cdot 10^3;\ 3 \cdot 10^3]$, while Eq. (2) gives one of 27% and Eq. (3) 3%.

NOTATION

$\eta(P)$ is the effective viscosity;
η_0 is the viscosity of the almost unbroken structure;
η_m is the viscosity of the completely disintegrated structure;
P is the uniform shear stress;
P_0 is a parameter chosen from experimental data;
P'_r is the stress corresponding to the onset of the S-shaped part of the flow curve;
P'_m is the stress corresponding to the end of the S-shaped part of the flow curve;
k is Boltzmann's constant;
T is the absolute temperature;
δ is the distance between the solid-phase particles;
η_∞ is the viscosity corresponding to an infinite flow velocity gradient;
α is a structure parameter greater than zero;
σ is the pressure-drop parameter;
$\dot{\varepsilon}$ is the flow velocity gradient;
P_{i1} is the shear stress corresponding to the point of inflection on the flow curve.

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