RHEOLOGICAL EQUATIONS OF STATE FOR WEAK POLYMER SOLUTIONS WITH RIGID ELLIPSOIDAL MACROMOLECULES IN AN ELECTRIC FIELD

P. B. Begoulev and Yu. I. Shmakov

UDC 532.135:541.182.6

On the basis of the structural-continuum concept, rheological equations of state have been derived for weak polymer solutions with rigid ellipsoidal macromolecules in an electric field.

The rheological equations of state for weak polymer solutions in an electric field will be derived on the basis of the structural-continuum concept [1]. In this method of analysis one begins with the rheological equations of state containing a set of phenomenological parameters which characterize the substructure behavior (orientation, deformation, internal interaction) [2-6], and then interprets the rheological functions and the rheological constants in these equations on the basis of experimental flow curves or by the structural theory of internal viscosity in the given kind of medium.

We will consider the flow on an incompressible continuous medium whose particles have at every point a definite orientation. This orientation will be characterized by a vector n_i. An electric field with the intensity E_i is superposed on this flow. We will assume that at every point in the stream the stress tensor t_{ij} is a function of the strain rate d_{ij}, of the orientation vector n_i, and of the electric field intensity E_i at that point:

$$t_{ij} = t_{ij}(n_k,\ E_i,\ d_{km}).$$

Following now Ericksen [2], we consider $\overset{\circ}{n}_i - \omega_{ij} n_j$ a function of the same variables as t_{ij}:

$$\dot{n}_i - \omega_{ij} n_j = h_i(n_k,\ E_i,\ d_{km}).$$

Considering only the case where t_{ij} and h_i are linear functions of d_{ij}, E_j, and $E_i E_j$, we have then

$$t_{ij} = A^0_{ij} + A^1_{ijkm} d_{km} + A^2_{ijk} E_k + A^3_{ijkm} E_k E_m,$$

$$\dot{n}_i - \omega_{ij} n_j = B^0_i + B^1_{ikm} d_{km} + B^2_{ik} E_k + B^3_{ikm} E_k E_m,$$

where A^0_{ij}, A^1_{ijkm}, ..., B^3_{ikm} are tensors transversally isotropic with respect to vector n_i. Using the universal notation for such tensor functions [7], we obtain

$$t_{ij} = -p\delta_{ij} + 2\mu d_{ij} + (\mu_1' + \mu_2 d_{km} n_k n_m) n_i n_j + 2\mu_3 (d_{ik} n_k n_j + d_{jk} n_k n_i) + \mu_4 (d_{ik} n_k n_j - d_{jk} n_k n_i) + \mu_5 E_i E_j + \mu_6 E_k E_k n_i n_j$$
$$+ (\mu_7 + \mu_8 n_k E_k)(n_i E_j - n_j E_i) + (\mu_9 + \mu_{10} n_k E_k)(n_i E_j + n_j E_i) + (\mu_{11} + \mu_{12} n_k E_k) n_m E_m n_i n_j, \tag{1}$$

$$\dot{n}_i - \omega_{ij} n_j = (\nu_0 + \nu_1 E_k E_k + \nu_2 n_k E_k + \nu_3 n_k n_m E_k E_m + \nu_4 d_{km} n_k n_m) n_i + (\nu_5 + \nu_6 n_k E_k) E_i + \nu_7 d_{ik} n_k; \tag{2}$$

The rheological functions in (1) and (2) depend on $n_i n_i$. When the modulus of vector n_i is invariable, there will be no loss of generality in letting $n_i n_i = 1$. Then $n_i \overset{\circ}{n}_i = 0$ and Eq. (2) simplifies to

$$\dot{n}_i - \omega_{ij} n_j = \lambda (d_{ik} n_k - d_{km} n_k n_m n_i) + (\lambda_1 + \lambda_2 n_k E_k)(E_i - n_k E_k n_i). \tag{3}$$

Relations (1) and (2) can be used for deriving the rheological equations of state for fluids with an asymmetric deformable substructure (Eqs. (1), (2)) or a nondeformable substructure (Eqs. (1), (3)) moving in an electric field. Relations approaching (1) and (3) have been obtained by Ericksen [8] under the assumption that the electric field affects the stress tensor only insofar as the orientation varies.

T. G. Shevchenko State University, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 23, No. 1, pp. 88-93, July, 1972. Original article submitted October 5, 1971.

We will now consider a weak solution of a polymer with rigid macromolecules in a dielectric Newtonian fluid to which an electric field is applied. The macromolecules will be simulated by dielectric ellipsoids of revolution with a constant dipole moment along the symmetry axis. As a consequence of the hydromechanical forces and the electric field, the motion of such a suspended macromolecule will combine translation with compound revolutions. We will characterize the orientation of the macromolecule by a unit vector N_i aligned in the direction of the constant dipole moment. The motion of a dielectric ellipsoid with a constant dipole moment in a simple shear flow

$$v_x = v_z = 0, \quad v_y = Kx, \quad K = \text{const} \tag{4}$$

in the presence of an electric field with the intensity

$$E_x = E, \quad E_y = E_z = 0 \tag{5}$$

has been analyzed by Ikeda [9], showing that the angular velocity components of vector N_i are

$$\omega_\varphi \equiv \dot{\varphi} = \frac{K}{2}(1 + R\cos 2\varphi) - \frac{qE}{f_r}\frac{\sin\varphi}{\sin\theta} - \frac{V(\chi_1 - \chi_2)E^2}{f_r}\sin\varphi\cos\varphi, \tag{6}$$

$$\omega_\theta \equiv \dot{\theta} = \frac{KR}{4}\sin 2\varphi \sin 2\theta + \frac{qE}{f_r}\cos\varphi\cos\theta + \frac{V(\chi_1 - \chi_2)E^2}{f_r}\cos^2\varphi\sin\theta\cos\theta. \tag{7}$$

For an ellipsoid with the equivalent radius $r = \sqrt[3]{ab^2} < 10^{-6}$ m (the solvent is water) the orientation depends also on the rotational Brownian movement and is characterized by the distribution function $F(\varphi, \theta)$ of vector N_i positions, following the equation of steady state in [10]:

$$D_r \Delta F = \operatorname{div}(F\vec{\omega}). \tag{8}$$

In order to obtain the rheological equations of state for our particular kind of medium, we use Eqs. (1), (3). For a simple shear flow (4) in an electric field (5), the orientation equation (3) coincides with Eqs. (6), (7) if $n_i = N_i$ and

$$\lambda = R, \quad \lambda_1 = \frac{q}{f_r}, \quad \lambda_2 = \frac{V(\chi_1 - \chi_2)}{f_r}. \tag{9}$$

Using the results in [11, 12], one can show that the angular velocity of vector N_i in an arbitrary flow and in an arbitrary electric field is described by Eq. (3) when condition (9) is satisfied.

We will let Eq. (1) be the rheological equation of state for our particular kind of medium, averaged through the distribution function of orientation vector positions according to (8) and (3):

$$\begin{aligned} t_{ij} = {} & p\delta_{ij} + 2\mu d_{ij} + \mu_1 \langle n_i n_j \rangle + \mu_2 d_{km} \langle n_k n_m n_i n_j \rangle \\ & + 2\mu_3 (d_{ik} \langle n_k n_j \rangle + d_{jk} \langle n_k n_i \rangle) + \mu_4 (d_{ik} \langle n_k n_j \rangle \\ & - d_{jk} \langle n_k n_i \rangle) + \mu_5 E_i E_j + \mu_6 E_k E_k \langle n_i n_j \rangle \\ & + \mu_7 (\langle n_i \rangle E_j - \langle n_j \rangle E_i) + \mu_8 (E_k E_j \langle n_k n_i \rangle \\ & - E_k E_i \langle n_k n_j \rangle) + \mu_9 (\langle n_i \rangle E_j + \langle n_j \rangle E_i) \\ & + \mu_{10} (E_k E_j \langle n_i n_k \rangle + E_k E_i \langle n_k n_j \rangle) \\ & + \mu_{11} E_k \langle n_k n_i n_j \rangle + \mu_{12} E_k E_m \langle n_k n_m n_i n_j \rangle. \end{aligned} \tag{10}$$

In order to determine the rheological constants in Eq. (10), we will compare the effective viscosity obtained from (1) for a simple shear flow (4) in an electric field $E_x = E\cos\alpha$, $E_y = E\sin\alpha$, $E_z = 0$

$$\begin{aligned} \mu_a = {} & \mu + \frac{\mu_1}{2K} \langle \sin 2\varphi \sin^2\theta \rangle + \frac{\mu_2}{4} \langle \sin^2 2\varphi \sin^4\theta \rangle \\ & + \mu_3 \langle \sin^2\theta \rangle + \mu_4 \langle \cos 2\varphi \sin^2\theta \rangle + \frac{E}{K}\Big[\mu_7 \langle \sin(\varphi - \alpha)\sin\theta \rangle \\ & + \mu_9 \langle \sin(\varphi + \alpha)\sin\theta \rangle + \frac{\mu_{11}}{2} \langle \cos(\varphi - \alpha)\sin 2\varphi \sin^3\theta \rangle \Big] \\ & + \frac{E^2}{K}\Big[\mu_5 \sin\alpha\cos\alpha + \mu_6 \langle \sin\varphi\cos\varphi\sin^2\theta \rangle + \mu_{10} \langle \sin(\varphi + \alpha) \\ & \times \cos(\varphi - \alpha)\sin^2\theta \rangle + \mu_8 \langle \cos(\varphi - \alpha)\sin(\varphi - \alpha)\sin^2\theta \rangle + \frac{\mu_{12}}{2} \langle \cos^2(\varphi - \alpha)\sin 2\varphi \sin^4\theta \rangle \Big], \end{aligned} \tag{11}$$

with the effective viscosity obtained for our particular case on the basis of the structural concept:

$$\mu_a = \mu_0\left(1 + \frac{\Phi}{ab^4\alpha_0'}\right) + 6\mu_0\frac{\Phi}{ab^2}\cdot\frac{a^2 - b^2}{a^2\alpha_0 + b^2\beta_0}\cdot\frac{D_r}{K} < \sin 2\varphi \sin^2\theta >$$
$$+ \mu_0\frac{\Phi}{ab^2}\left[\frac{\alpha_0'' + \beta_0''}{2b^2\alpha_0'\beta_0''} - \frac{2}{\beta_0'(a^2 + b^2)}\right] < \sin^2 2\varphi \sin^4\theta >$$
$$+ \mu_0\frac{\Phi}{ab^2}\left(\frac{2}{\beta_0'(a^2 + b^2)} - \frac{1}{b^2\alpha_0'}\right) < \sin^2\theta > + \frac{3\Phi E}{8\pi ab^2K} < [q$$
$$+ EV(\chi_1 - \chi_2)\cos(\varphi - \alpha)\sin\theta]\,[R\sin 2\varphi\cos(\varphi - \alpha)\sin^3\theta$$
$$- R\sin(\varphi + \alpha)\sin\theta + \sin(\varphi - \alpha)\sin\theta] >. \tag{12}$$

Relation (12) represents a generalization of results obtained by Mason [14] for the special case without Brownian movement (q = 0), the Brownian movement has been accounted for in (12) according to Saito [15], and α_0, α_0', α_0'', β_0, β_0', β_0'' have been determined in [13]. From (11) and (12) we obtain the following expression for the rheological constants:

$$\mu = \mu_0\left(1 + \frac{\Phi}{ab^4\alpha_0'}\right), \tag{13}$$

$$\mu_1 = 12\mu_0 D_r\frac{\Phi}{ab^2}\cdot\frac{a^2 - b^2}{a^2\alpha_0 + b^2\beta_0}, \tag{14}$$

$$\mu_2 = 2\mu_0\frac{\Phi}{ab^2}\left(\frac{\alpha_0'' + \beta_0''}{b^2\alpha_0'\beta_0''} - \frac{4}{\beta_0'(a^2 + b^2)}\right), \tag{15}$$

$$\mu_3 = \mu_0\frac{\Phi}{ab^2}\left(\frac{2}{\beta_0'(a^2 + b^2)} - \frac{1}{b^2\alpha_0'}\right), \tag{16}$$

$$\mu_4 = 0, \tag{17}$$

$$\mu_5 = \mu_6 = 0, \tag{18}$$

$$2R\mu_7 = -2\mu_9 = \mu_{11} = \frac{3\Phi R}{4\pi ab^2}q, \tag{19}$$

$$2R\mu_8 = -2\mu_{10} = \mu_{12} = \Phi R(\chi_1 - \chi_2). \tag{20}$$

Expressions (13)-(17) have been derived in [1] and they define the stress tensor at $|\mathbf{E}| = 0$. We note that in the general case, at $|\mathbf{E}| \neq 0$ this tensor is asymmetric.

If the macromolecule is sufficiently large, $r = \sqrt[3]{ab^2} > 10^{-4}$ m, then the Brownian movement may be disregarded [10] and, according to [1],

$$\mu_1 = 0, \tag{21}$$

with the orientation determined only by Eq. (3), which has steady-state solutions when d_{ij} and E_i are in some definite relations with one another [16]. In this case Eq. (10), with the aid of (21) and the stationary condition $\dot{n}_i = 0$, will be turned into

$$t_{ij} = -p\delta_{ij} + 2\mu d_{ij} + \mu_2 d_{km}n_k n_m n_i n_j + 2\mu_3(d_{jk}n_k n_i + d_{ik}n_k n_j)$$
$$+ 2\mu_0\frac{\Phi}{ab^2}\cdot\frac{a^2 + b^2}{a^2\alpha_0 + b^2\beta_0}\,[\omega_{ik}n_k n_j - \omega_{jk}n_k n_i + R(d_{ik}n_k n_j - d_{jk}n_k n_i)$$
$$+ R(\omega_{ik}n_k n_j + \omega_{jk}n_k n_i) + R^2(d_{ik}n_k n_j + d_{jk}n_k n_i) - 2R^2 d_{km}n_k n_m n_i n_j]. \tag{22}$$

The effective viscosity based on Eq. (22) for a simple shear flow (4) in an electric field (5) coincides with that obtained by Chaffey and Mason [17].

NOTATION

t_{ij} is the stress tensor;
δ_{ij} is the Kronecker delta;
p is the isotropic pressure;
d_{ij} is the strain rate tensor;
ω_{ij} is the velocity vortex tensor;

n_i	is the orientation vector;
$\mu, \mu_1, \ldots, \mu_{12}, \nu, \nu_1, \ldots, \nu_7$	are the rheological functions;
$\lambda, \lambda_1, \lambda_2$	are the rheological constants;
r	is the equivalent radius oi a rigid ellipsoidal macromolecule;
a, b	are the major and minor semiaxis respectively of an ellipsoid of resolution;
v_x, v_y, v_z	are the velocity components in the Cartesian system of coordinates x, y, z;
$\omega_\varphi, \omega_\theta$	are the components of the angular velocity of the ellipsoid axis in the spherical system of coordinates r, φ, θ;
D_r	is the coefficient of rotational diffusivity;
f_r	is the coefficient of rotational friction;
$\vec{\omega}$	is the vector of angular velocity;
$\langle\ \rangle$	is the symbol of averaging with distribution function;
μ_0	is the dynamic viscosity of solvent;
Φ	is the volume concentration of suspended particles;
$\alpha_0, \alpha_0', \alpha_0'', \beta_0, \beta_0', \beta_0''$	are the functions governed by a and b, according to Jeffery's theory;
V	is the macromolecule volume;
$V\chi_1$, $V\chi_2$	are the functional values of the dielectric susceptibility in the direction of the axis of rotation and in the direction normal to it respectively;
q	is the magnitude of constant dipole moment along the symmetry axis;
$\dot{n}_i$	is the total time derivative of n_i;
φ	is the angle between X axis and the projection of n_i on plane XY;
θ	is the angle between Z and n_i;
E_i	is the electric field intensity.

LITERATURE CITED

1. Yu. I. Shmakov and E. Yu. Taran, Inzh. Fiz. Zh., 18, 1019 (1970).
2. J. L. Ericksen, Koll. Zeitschr. [German], 173, 117 (1960).
3. J. L. Ericksen, Arch. Ration. Mech. Anal., 4, 231 (1960).
4. S. J. Allen and C. N. DeSilva, J. Fluid Mech., 24, 801 (1966).
5. S. J. Allen, C. N. DeSilva, and K. A. Kline, Phys. Fluids, 10, 2551 (1967).
6. K. A. Kline and S. J. Allen, Zeitschr. Angew. Mech. Phys. [German], 19, 898 (1968).
7. V. V. Lokhin, Dokl. Akad. Nauk SSSR, 149, 1282 (1963).
8. J. L. Ericksen, Arch. Ration. Mech. Anal., 23, 266 (1966).
9. S. Ikeda, Chem. Phys., 38, 2839 (1963).
10. A. Peterlin, Zeitschr. Phys. [German], 111, 232 (1938).
11. V. N. Pokrovskii, Koll. Zh., 29, 676 (1967).
12. C. E. Chaffey and S. G. Mason, J. Coll. Sci., 19, 525 (1964).
13. J. B. Jeffery, Proc. Roy. Soc., A102, 161 (1922).
14. C. E. Chaffey and S. G. Mason, J. Coll. Sci., 27, 115 (1968).
15. N. Saito, J. Phys. Soc. Japan, 6, 297 (1951).
16. R. A. Allan and S. G. Mason, Proc. Roy. Soc., A267, 62 (1962).
17. C. E. Chaffey and S. G. Mason, J. Coll. Sci., 20, 330 (1965).