VISCOSITY CHARACTERISTIC OF A CONCENTRATED IONOMER SOLUTION NEAR THE ION CLUSTER FORMATION

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This study deals with the viscosity of a concentrated ionomer solution near the phase transformation which is of the clustering kind. The analysis is based on the dissipation function for viscous flow. It is shown that, under certain conditions, there may occur a viscosity jump during transition through the critical point.

A matter of considerable interest in practical applications is the synthesis of polymers with new thermophysical and strength characteristics. Many possibilities in this area have been created by the appearance of ionomers (ion copolymers). Despite the intensive research activity, it is difficult to ascertain the trend of various kinetic characteristics of concentrated ionomer solutions (as well as of other characteristics of nonequilibrium transfer processes in non-Newtonian fluids [1]. The one property of ionomers which offers interesting possibilities in practical applications is the ability of ions to cluster under certain conditions [2]. The exact conditions of ion clustering are, however, difficult to pinpoint experimentally. The authors analyze here the viscosity characteristics of a concentrated ionomer solution near the phase transformation which is of the clustering kind.

Properties of the Dissipative Flow Function. We consider the viscous flow of a concentrated ionomer solution. As a result of dissipation processes during flow, the mechanical energy is converted to heat. The dissipation of mechanical energy in a moving fluid will be characterized by the dissipation function Ψ, per unit volume, which depends on the components of the velocity gradient and also on certain coefficients determined by the microstructure of the substance. These coefficients, in turn, depend also on the local temperature T' in the particular moving volume element singled out for analysis. We will consider the case where the conditions in some flow zone are close to critical with respect to clustering. An ion cluster will be characterized by the parameter μ which becomes equal to zero below the transition point and has a value other than zero above that point. Parameter μ may be made to correspond to the mean distance between ions forming a cluster. This parameter is a monotonic function of the temperature of the substance, also of the velocity gradient in the zone under study.

An experiment for determining the viscosity characteristic near the transition point must be performed under conditions where the energy brought into the medium through dissipation would not cause the temperature field and the velocity-gradient field to become very nonuniform. Such nonuniformities would introduce complexities and ambiguities into a determination of the viscosity of the substance on the basis of test data. Existing methods of viscosity measurements allow the necessary conditions to be established under which the velocity gradient will remain constant with time and constant along a streamline while heat is removed through the outer surfaces at a constant rate. Under such conditions the viscosity remains constant along a streamline, while analytically derived relations involving the viscosity and used for evaluating the test data will more accurately describe the processes which have occurred during the test. These necessary conditions can, apparently, always be realized at sufficiently small velocity gradients.

In order to stringently maintain the temperature constant along a streamline, as required, the dissipation function must have one special property. Let us dwell on this. We single out a small moving volume of the substance. A change in its temperature T', with heat leaving this volume at a constant rate,

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is determined by the change in the energy dissipated here. For simplicity, the substance will be considered incompressible. A change in the dissipation function is then determined by the change in parameter μ only. Consequently, we may write for the temperature T' of the singled out volume element

$$\delta T' = \left(\frac{\partial T'}{\partial \Psi}\right)\left(\frac{\partial \Psi}{\partial \mu}\right)\delta\mu = 0.$$

Since $\partial T'/\partial \Psi$ is never equal to zero, for any arbitrary $\delta\mu$ we have

$$\frac{\partial \Psi}{\partial \mu} = 0. \tag{1}$$

Condition (1) signifies the existence of an extremum of Ψ as a function of μ, with the realizable value of μ to be determined from relation (1) at given values of the system parameters. We note that this method based on using the dissipation function is analogous to the earlier methods based on using the increase of entropy in nonequilibrium systems. Several extremum theorems have been thoroughly established for such systems [3-5], similar in meaning to the said extremality property of the dissipative flow function. Therefore, we will use this property for determining the sought relations. It should be added here that, on the basis of physical considerations, the extremum of the dissipation function must be a minimum (this corresponds to the least disturbance of thermal equilibrium by random variations of the flow parameters).

Viscosity Jump. Without deviating much from realizable test conditions, we regard the flow within the transition zone to be uniform along the x-axis at a velocity v which is a function of the z-coordinate. At small departures from the critical conditions corresponding to this kind of phase transformation, the characteristic parameter μ remains still sufficiently small for the dissipation function within the transition range to be expandable into powers of μ accurately down to a few first terms:

$$\Psi = \Psi_0 + A\mu^2 + B\mu^3 + C\mu^4. \tag{2}$$

The coefficient of the linear term in (2) becomes identically equal to zero, by virtue of condition (1) applied to the region where clusters exist ($\mu = 0$) as well as based on considerations of symmetry at the transition point. Function Ψ_0 depends on the velocity gradient. At sufficiently small velocity gradients there occur no other significant phase transformations in the fluid and function Ψ_0 for the region where $\mu = 0$ can be expressed as for a normal fluid [1]:

$$\Psi_0 = \eta_0\left(\frac{\partial v}{\partial z}\right)^2,$$

with η_0 denoting the viscosity below the transition point. With $u = \partial v/\partial z$, we have below the transition point

$$\eta = \eta_0 = \frac{1}{2}\frac{\partial^2 \Psi_0}{\partial u^2}.$$

By virtue of the sufficiently small velocity gradient and the absence of any other significant phase transformation, as compared to the intensive one occurring at the transition point, for the viscosity above that point we may use the analogous relation

$$\eta = \frac{1}{2}\frac{\partial^2 \Psi}{\partial u^2}.$$

The subsequent analysis follows closely the earlier developed phenomenological description of phase transformations of the second kind [6]. Coefficients A, B, C are functions of u and depend on the temperature conditions at the boundary. It follows from the minimality of function Ψ that $A > 0$ below the transition point (because here $\mu = 0$) and $A < 0$ above the transition point (here $\mu > 0$). This means that at the transition point

$$A_{tr} = A(u_{tr}, T_{tr}) = 0. \tag{3}$$

Expression (3) relates the velocity gradient at the transition point to the temperature conditions at the boundary. It follows from the condition that Ψ is minimum at the transition point as well as from symmetry considerations, that $B_{tr} \equiv 0$ and $C_{tr} > 0$. Obviously, the condition that $C_{tr} > 0$ is satisfied also within a certain vicinity of the transition point.

Finally, we obtain for $\Psi(\mu, u)$:

$$\Psi = \eta_0 u^2 + A\mu^2 + C\mu^4.$$

The condition that Ψ is minimum yields

$$\mu(A + 2C\mu^2) = 0.$$

Below the transition point

$$\mu = 0, \quad \Psi = \eta_0 u^2, \quad \eta = \eta_0.$$

Above the transition point

$$\mu^2 = -\frac{A}{2C}, \quad \Psi = \Psi_0 - \frac{A^2}{4C},$$

$$\eta = \eta_0 - \frac{1}{4C}\left(\frac{\partial A}{\partial u}\right)^2 - \frac{A}{4C}\left(\frac{\partial^2 A}{\partial u^2}\right) + \frac{A}{2C^2}\left(\frac{\partial A}{\partial u}\right)\left(\frac{\partial C}{\partial u}\right) + \frac{A^2}{8C^2}\left(\frac{\partial^2 C}{\partial u^2}\right) - \frac{A^2}{4C^3}\left(\frac{\partial C}{\partial u}\right)^2.$$

Near the transition point

$$A = \alpha(u - u_{\mathrm{tr}}), \quad \alpha = \left(\frac{\partial A}{\partial u}\right)\Big|_{u=u_{\mathrm{tr}}}, \quad C = C_{\mathrm{tr}}.$$

For the viscosity in the immediate vicinity of the transition point we have just above that point

$$\eta = \eta_0 - \frac{\alpha^2}{4C_{\mathrm{tr}}}, \tag{4}$$

and just below that point

$$\eta = \eta_0. \tag{5}$$

Relations (4) and (5) indicate that, under the conditions stipulated here, at the transition point where clusters disappear there must occur a viscosity jump. Experiments could possibly confirm the existence of such a transition and a viscosity jump, they would also provide additional useful information about clustering processes in ionomers.

NOTATION

Ψ_0, Ψ, $\Psi(\mu, u)$	is the dissipation function;
T'	is the local temperature;
μ	is the parameter which characterizes the mean distance between ions in a cluster;
v	is the flow velocity;
x, z	are the space coordinates;
η, η_0	is the viscosity coefficient;
A, B, C	are the coefficients in the series expansion;
A_{tr}, B_{tr}, C_{tr}	are the values of coefficients A, B, C at the transition point;
u_{tr}	is the velocity gradient at the transition point;
T_{tr}	is the temperature at the transition boundary.

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