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Research Article

On the Rheology of Thixotropic and Rheopexic Suspensions: Accounting of the Trimers Formation

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Semi-empirical equations are derived that describe the dependence of shear stress on shear rate during the flow of a one-component suspension. The suspension is considered as consisting of three fractions: single grains of the solid phase, their dimers, and trimers, between which reversible dimerization and trimerization reactions occur. In this case, dimerization and trimerization are considered as reactions with invariable rate constants, and dissociation of dimers and trimers as reverse reactions with rate constants that increase linearly with shear rate. The derived equations are based on the Krieger-Doherty formula generalized to the case of a multicomponent suspension. The equations describe well pseudoplasticity, dilatancy, thixotropy, and rheopexy, as well as suspensions with variable behaviour (when pseudoplastic behaviour is replaced by dilatant behaviour, and thixotropic behaviour is replaced by rheopexic one, and vice versa).

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Introduction

In a previous work [1], equations were derived that describe the dependence of the shear stress on the shear rate during the flow of concentrated suspensions. The equations were based on the Krieger-Doherty formula [2][3] generalized in our paper [4] to the case of multicomponent suspensions:

$$\eta = \eta_0 \left(1 - \frac{\varphi}{\bar{\varphi}_0}\right)^{-[\bar{\eta}]\bar{\varphi}_0}. \tag{1}$$

Here $[\bar{\eta}]$ and $\bar{\varphi}_0$– parameter values averaged over all solid components:

$$\begin{cases} [\bar{\eta}] = \frac{\sum [\eta_i]\varphi_i}{\varphi_0} \\ \bar{\varphi}_0 = \frac{\varphi_0}{\sum \varphi_i / \varphi_{0,i}} \end{cases}, \tag{2}$$

where φ_0 – is the total volume fraction of the dispersed phase, $[\eta_i]$ is the intrinsic viscosity of the i-th component, φ_i and $\varphi_{0,i}$ – volume fraction and limiting concentration of the i-th component, respectively.

In [1], a one-component suspension was considered as a system consisting of two fractions: single grains ("singlets") of the solid phase and their dimers ("doublets"), where single grains and their dimers correspond to different values of the parameters $[\eta]$ and φ_0, wherein the singlet dimerization was considered as a reaction with an invariable rate constant k_1, and the dissociation of doublets was considered as a reaction with a rate constant k, linearly increasing with the shear rate $\dot{\gamma} : k = k_2 + k_3\dot{\gamma}$. It was shown that the derived equations describe well the flow of both pseudoplastic and dilatant suspensions (if the reaction rate is high and the equilibrium between singlets and doublets is reached almost instantly), as well as thixotropic and rheopexic suspensions (these relaxation effects appear if the time to reach the

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mentioned equilibrium is comparable to the experiment time). It was also shown that pseudoplastic suspensions exhibit thixotropic behaviour when relaxation effects occur, while dilatant suspensions exhibit rheopexic behaviour.

However, it was also shown there that the pseudoplastic suspensions described in the literature, demonstrating rheopexy, as well as suspensions in which they demonstrate alternately rheopexic and thixotropic behaviour (at different shear rates), are not described by the equations derived there. In this regard, it was suggested that taking into account the formation of trimers ("triplets") would also make it possible to describe such behaviour of suspensions.

In [5], it was shown that taking into account the formation of trimers ("triplets") makes it possible to describe suspensions in which the pseudoplastic nature of the flow is replaced by a dilatant one and vice versa (the "equilibrium" case was considered there, i.e., when the equilibrium between singlets, doublets, and triplets is achieved instantly). Therefore, it is natural to make the assumption that taking into account the formation of trimers ("triplets") will also make it possible in the nonequilibrium case to describe suspensions with a variable flow pattern (when thixotropy is replaced by rheopexy and vice versa).

Thus, this work is a generalization, further development, and synthesis of the approaches outlined in [1][5][6] by taking into account both the finite reaction rate and the formation of triplets.

The purpose of this work is to derive equations that take into account both the formation of triplets and the final rate of interconversion of singlets, doublets, and triplets, as well as their experimental verification.

Theory of calculations

So, we will consider a suspension as a system consisting of three fractions: singlets (we denote their volume fraction as φ_1), their dimers, or "doublets" (volume fraction φ_2), and trimers, or "triplets" (volume fraction φ_3).

Let there be n_0 grains of the solid phase per unit volume of the suspension, while the number of singlets per unit volume is n_1, doublets – n_2, triplets – n_3 and let the average volume of grains be equal to v. Then the volume fraction of the solid phase is equal to $\varphi_0 = n_0 v$. At a given shear rate $\dot{\gamma}$ equilibrium is established between singlets, doublets, and triplets with a certain finite rate. In this case, three reversible reactions can occur:

$$\begin{cases} 2n_1 \rightleftarrows n_2 \\ n_1 + n_2 \rightleftarrows n_3, \\ 3n_1 \rightleftarrows n_3 \end{cases}$$

at that $n_1 + 2n_2 + 3n_3 = n_0$. Multiplying the left and right sides of the last equality by v, we obtain

$$\varphi_1 + \varphi_2 + \varphi_3 = \varphi_0. \tag{3}$$

Since the probability of a triple collision is small, we will neglect the contribution to the kinetics of the third reaction.

We will assume that the dimerization rate constant k_1 is invariable, and the reverse reaction rate constant k depends linearly on the shear rate k depends linearly on the shear rate $\dot{\gamma}$, which, in turn, is a certain function of time: $k = k_2 + k_3\dot{\gamma}(t)$. Similarly, for the second reaction: the rate constant of the direct reaction k_4, and the reverse $k_5 + k_6\dot{\gamma}(t)$. Thus, the reaction kinetics is described by the system of differential equations

$$\begin{cases} \frac{d\varphi_1}{dt} = -k_1\varphi_1^2 + \left(k_2 + k_3\dot{\gamma}\right)\varphi_2 - k_4\varphi_1\varphi_2 + \left(k_5 + k_6\dot{\gamma}\right)\varphi_3 \\ \frac{d\varphi_2}{dt} = k_1\varphi_1^2 - \left(k_2 + k_3\dot{\gamma}\right)\varphi_2 - k_4\varphi_1\varphi_2 + \left(k_5 + k_6\dot{\gamma}\right)\varphi_3 \end{cases} \tag{4}$$

Substituting equality (3) into equations (4), we obtain:

$$\begin{cases} \frac{d\varphi_1}{dt} = -k_1\varphi_1^2 + \left(k_2 + k_3\dot{\gamma}\right)\varphi_2 - k_4\varphi_1\varphi_2 \\ \qquad + \left(k_5 + k_6\dot{\gamma}\right)\left(\varphi_0 - \varphi_1 - \varphi_2\right) \\ \frac{d\varphi_2}{dt} = k_1\varphi_1^2 - \left(k_2 + k_3\dot{\gamma}\right)\varphi_2 - k_4\varphi_1\varphi_2 \\ \qquad + \left(k_5 + k_6\dot{\gamma}\right)\left(\varphi_0 - \varphi_1 - \varphi_2\right) \end{cases} \tag{5}$$

As the initial conditions, we choose the concentrations of singlets φ_1^{init}, doublets φ_2^{init} and triplets φ_3^{init} at equilibrium, which is established in the absence of flow, i.e. at $\dot{\gamma} = 0$, $(d\varphi_1)/dt = 0$ and $(d\varphi_2)/dt = 0$. It leads to a system of algebraic equations

$$\begin{cases} -k_1\varphi_1^2 + k_2\varphi_2 - k_4\varphi_1\varphi_2 + k_5\left(\varphi_0 - \varphi_1 - \varphi_2\right) = 0 \\ k_1\varphi_1^2 - k_2\varphi_2 - k_4\varphi_1\varphi_2 + k_5\left(\varphi_0 - \varphi_1 - \varphi_2\right) = 0 \end{cases},$$

whence

$$\begin{cases} k_4\varphi_1\varphi_2 - k_5\left(\varphi_0 - \varphi_1 + \varphi_2\right) = 0 \\ k_1\varphi_1^2 = k_2\varphi_2 \end{cases}$$

From the second equation $\varphi_2 = (k_1\varphi_1^2)/k_2$; substituting this equality into the first equation, we obtain a cubic equation for φ_1:

$$\frac{k_1k_4}{k_2}\varphi_1^3 + \frac{k_1k_5}{k_2}\varphi_1^2 + k_5\varphi_1 - k_5\varphi_0 = 0 \tag{6}$$

To find the roots of the cubic equation, we used the Vieta trigonometric formula [7].

The system of equations (5) is the Riccati equations, which, in the general case, cannot be integrated in quadratures [8]. Therefore, it was solved numerically by the classical fourth-order Runge-Kutta method [9]. The result of the numerical solution will be denoted as $\varphi_1(t)$.

The Krieger–Doherty formula for a three-component suspension according to (1) and (2) has the form

$$\tau = \tau_0 + \eta_0 \dot{\gamma} \left(1 - \frac{\varphi_1}{\varphi_{10}} - \frac{\varphi_2}{\varphi_{20}} - \frac{\varphi_3}{\varphi_{30}}\right)^{-\frac{[\eta_1]\varphi_1 + [\eta_2]\varphi_2 + [\eta_3]\varphi_3}{\varphi_1/\varphi_{10} + \varphi_2/\varphi_{20} + \varphi_3/\varphi_{30}}} \tag{7}$$

with τ as the shear stress, τ_0 as the yield stress, η_0 as the viscosity of the dispersion medium, $\dot{\gamma}$ as the shear rate, φ_1 and φ_2 as the volume fractions of singlets and doublets (the result of the numerical solution of the system of equations (5)), φ_3 as the volume fraction of triplets (in accordance with (3) $\varphi_3 = \varphi_0 - \varphi_1 - \varphi_2$), φ_{10} and φ_{20} as the corresponding limiting concentrations, $[\eta_1]$ and $[\eta_2]$ as the corresponding intrinsic viscosities.

Having a numerical solution $\varphi_1(t)$ and $\varphi_2(t)$ of the system of differential equations (5), it is possible to calculate the shear stress using formula (7).

Results and discussion

For the experimental verification of the derived equations, the data published in the literature [10] [11] were used.

Although the parameters included in the equations have a clear physical meaning, they are not calculated theoretically and cannot be determined in independent experiments. Therefore, they were considered as "tuning" parameters. This means that they are chosen in such a way as to minimize the discrepancy (the standard deviation of the theoretical curve from the experimental points). For this purpose, a computer program was developed that minimized the discrepancy by varying the parameters.

The results of comparing theory with experiment are shown in the following figures.

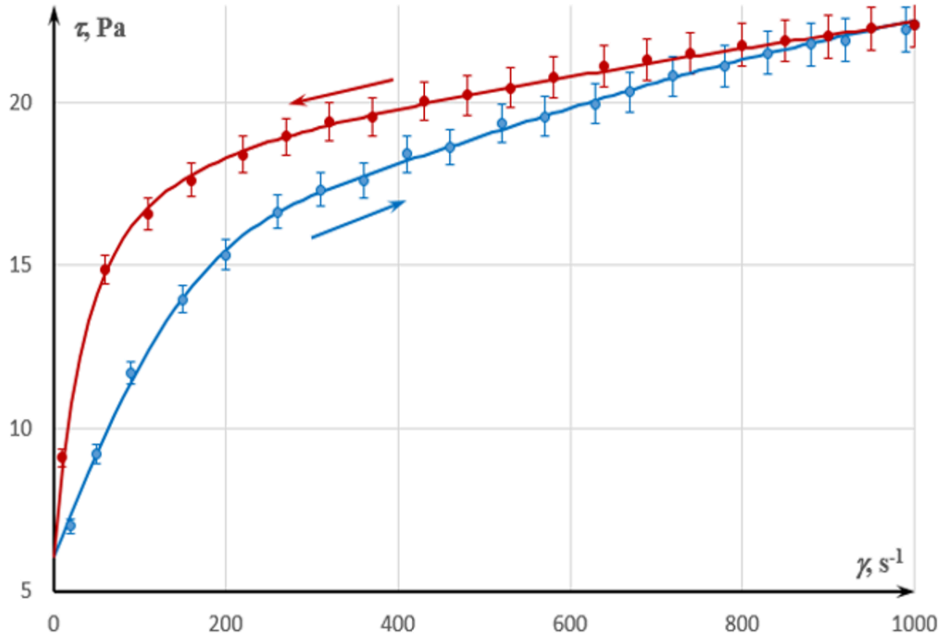

Fig. 1. Aqueous suspension of palygorskite. Dependence of shear stress on shear rate according to [10].
Parameter values:
$k_1 \approx 1,96s^{-1}$; $k_2 \approx 2,41s^{-1}$;$k_3 \approx 0,0219$; $k_4 \approx 6,98s^{-1}$; $k_5 \approx 0,0629s^{-1}$; $k_6 \approx 0,000222$;
$\varphi_0 \approx 0,456$; $\varphi_1 0 \approx 0,740$; $\varphi_2 0 \approx 0,110$; $\varphi_3 0 \approx 0,462$;$\tau_0 \approx 5,73Pa$; $\eta_0 \approx 0,0009Pa\ s$;
$[\eta_1] \approx 2,59$: $[\eta_2] \approx 38,6$; $[\eta_3] \approx 2,50$.
The standard deviation of the curves from the points is 0.11 Pa (0.62% of the mean shear stress). The error indicator shows a spread of 3% (experimental error).

The points in Fig. 1 represent the experiment according to the data of [10], and the solid curves are the calculations according to the derived equations. It is easy to see that the derived equations are in exceptionally good agreement with the experiment, and the rheological parameters of the equations (φ_{10}, φ_{20}, φ_{30}, $[\eta_1]$, $[\eta_2]$ и $[\eta_3]$) take realistic values.

The calculated dependences of the viscosity of the suspension, as well as the volume fractions of singlets, doublets, and triplets on the shear rate, corresponding to the results presented in Figs. 1, are shown in Figs. 2 and 3, respectively.

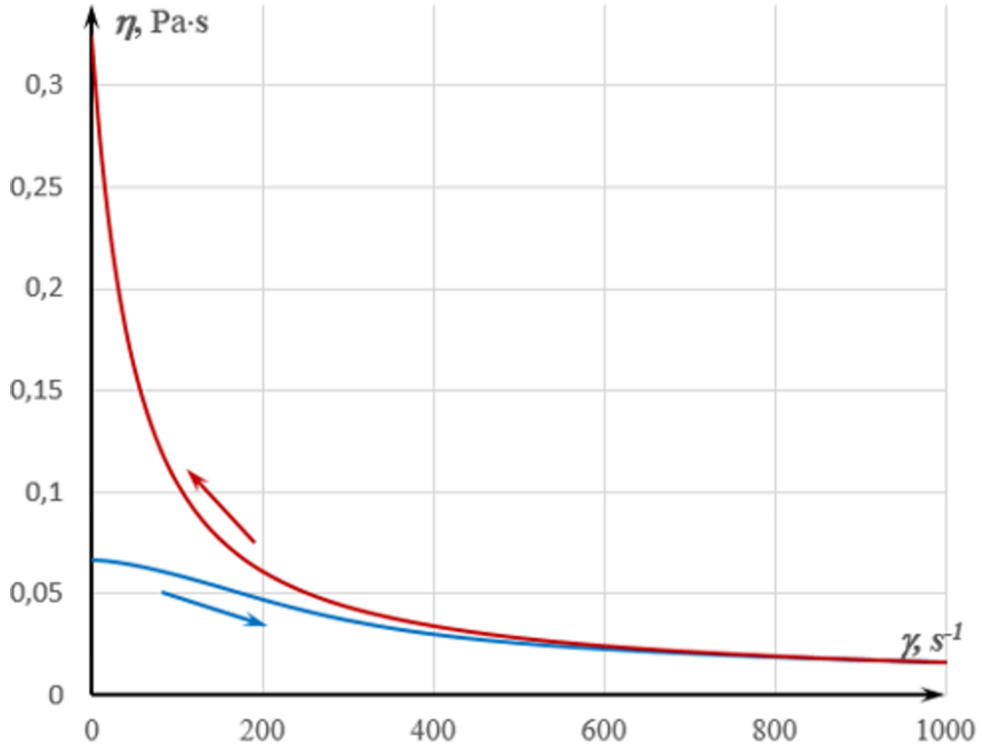

Fig. 2. Aqueous suspension of palygorskite. The calculated dependence of viscosity on shear rate, corresponding to the results in Fig. 1.

It can be seen from Fig. 2 that as the shear rate increases, the viscosity of the suspension decreases, i.e., the suspension is pseudoplastic. However, with a decrease in the shear rate, the viscosity is restored not with a delay, as one would expect, but with an advance. Without taking into account the formation of triplets, this behaviour would be impossible to explain, and taking that into account – the reason for this behaviour becomes clear if we watch the kinetics of changes in the concentrations of the components (Fig. 3).

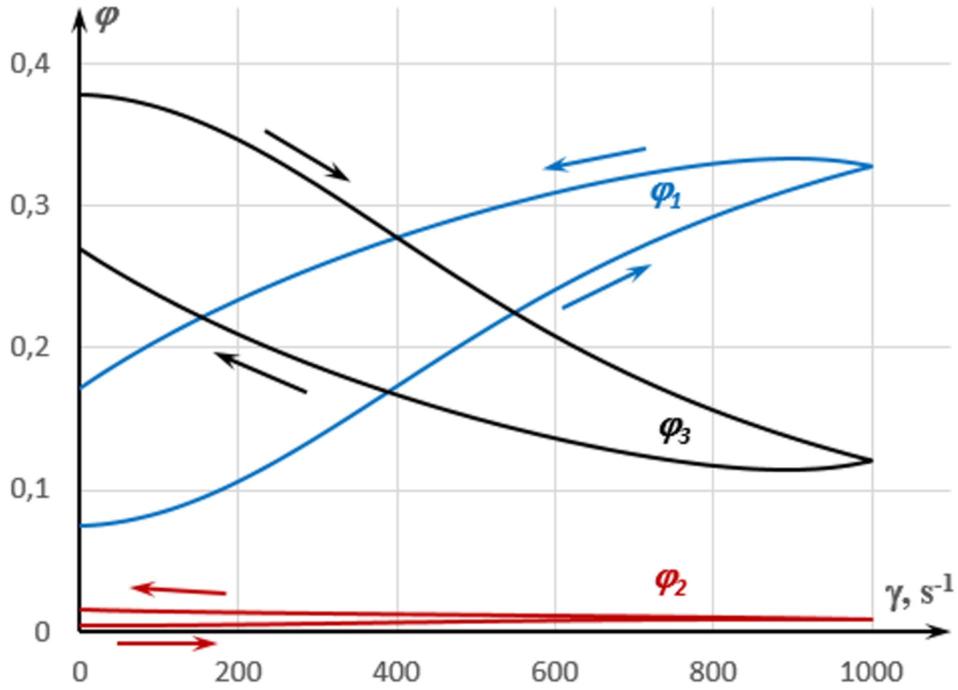

Fig. 3. Aqueous suspension of palygorskite. The calculated dependences of the concentrations of the components on the shear rate, corresponding to the results in Figs. 1.

The fact is that it is not the viscosity that is restored with a delay, but the concentrations of singlets, doublets, and triplets. How the viscosity changes depends on the ratio of the rheological characteristics of the fractions – $\varphi_{10}, \varphi_{20}, \varphi_{30}, [\eta_1], [\eta_2]$ и $[\eta_3]$.

From Fig. 3, it can be seen that before the start of the experiment, the established equilibrium between the components in the suspension has triplets (the intrinsic viscosity of which is relatively low) predominating, which leads to a low viscosity of the suspension.

As the shear rate increases, triplets are destroyed, and singlets begin to predominate in the suspension, the characteristic viscosity of which is slightly higher than that of triplets, and the limiting concentration is higher, i.e., singlets make a smaller contribution to the viscosity of the suspension, so its viscosity decreases slightly. With a thereafter decrease in the shear rate, the concentrations of singlets and triplets approach each other, and the concentration of doublets increases from 0.46% to 1.63%, i.e., 3.6 times. And although the concentration of doublets remains relatively small, due to the fact that they have a very high intrinsic viscosity and low limiting concentration, their contribution to the viscosity of the suspension becomes dominant, which leads to a rapid increase in viscosity.

Of interest are also the suspensions described in the literature [8] with a "variable" flow pattern: at low shear rates, rheopexy is observed, and at high shear rates, thixotropy. The equations derived in the previous work [1] without taking into account the formation of triplets did not allow for the description of such behaviour. Taking them into account makes it possible to do this, as can be seen from the following figures.

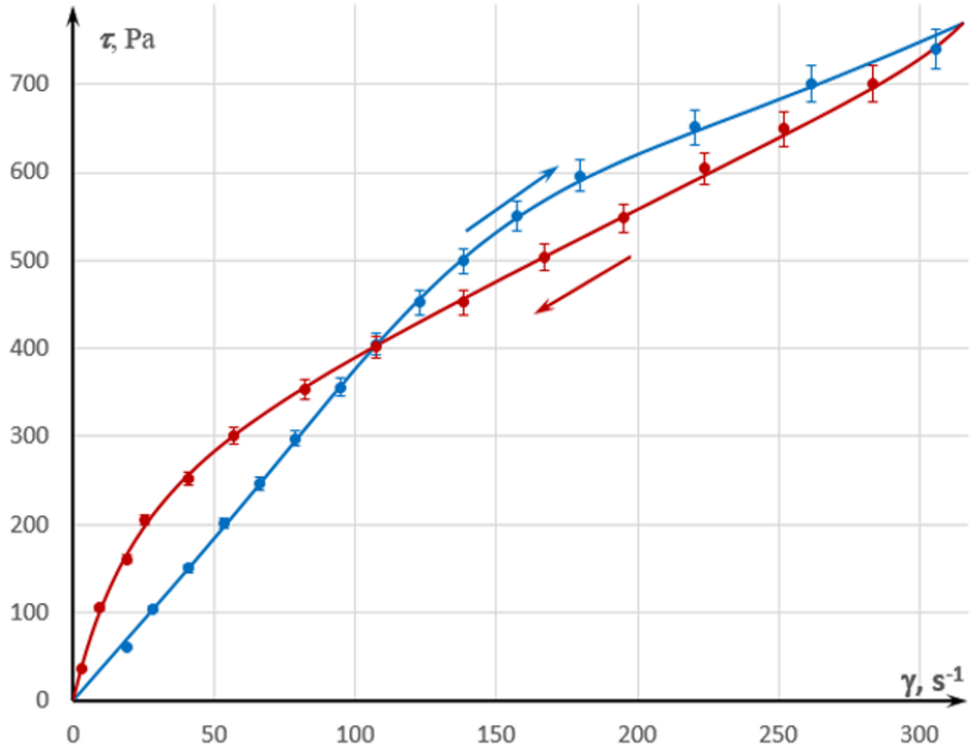

Fig. 4. Polymer suspension filled with ceramic nanoparticles. Dependence of shear stress on shear rate according to [11].
Parameter values:
$k_1 \approx 0,335 s^{-1}$; $k_2 \approx 0,0997 s^{-1}$; $k_3 \approx 0,00625$; $k_4 \approx 0,000174 s^{-1}$; $k_5 \approx 0,0000359 s^{-1}$; $k_6 \approx 0,00243$; $\varphi_0 \approx 0,630$; $\varphi_1 0 \approx 0,758$; $\varphi_2 0 \approx 0,510$; $\varphi_3 0 \approx 0,880$; $\eta_0 \approx 0,00163 Pa\ s$; $[\eta_1] \approx 5,13$; $[\eta_2] \approx 3,56$; $[\eta_3] \approx 4,96$.The standard deviation of the curves from the points is 5.1 Pa (1.3% of the mean shear stress). The error indicator shows a spread of 3% (experimental error).

Fig. 4 shows the dependence of shear stress on shear rate for a polymer suspension filled with ceramic nanoparticles according to [11].

It is easy to see that the equations derived taking into account the formation of triplets describe this behaviour of the suspension well, and the rheological parameters φ_{10}, φ_{20}, φ_{30}, $[\eta_1]$, $[\eta_2]$ and $[\eta_3]$ take realistic values.

The calculated dependences of the viscosity of the suspension, as well as the concentrations of singlets, doublets, and triplets, on the shear rate are shown in Figs. 5 and 6, respectively.

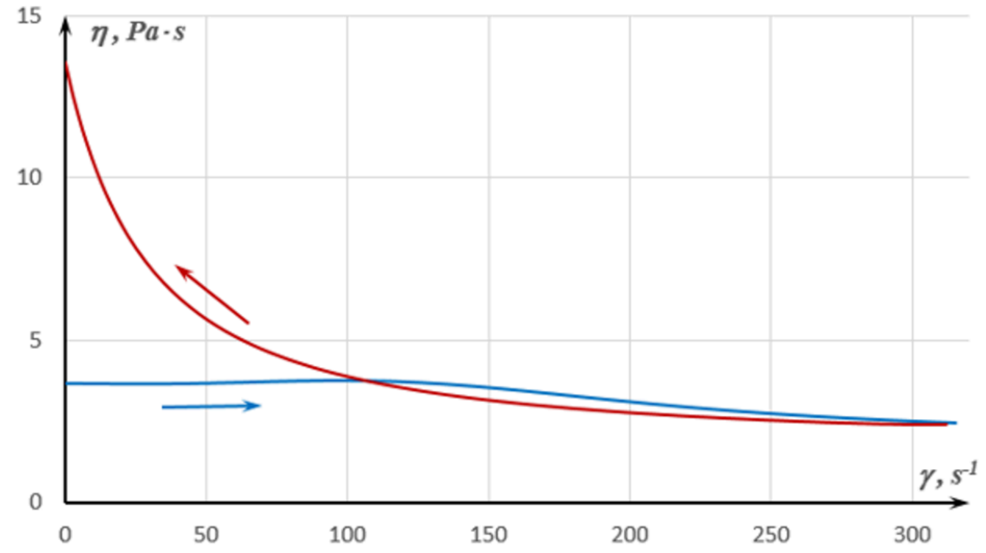

Fig. 5. Polymer suspension filled with ceramic nanoparticles. The calculated dependence of viscosity on shear rate, corresponding to the results in Fig. 4.

As in the previous example, the outstripping increase in viscosity with a decrease in shear rate below 100 s^{-1} is surprising. And, as in the previous case, consideration of kinetics helps to explain this behaviour.

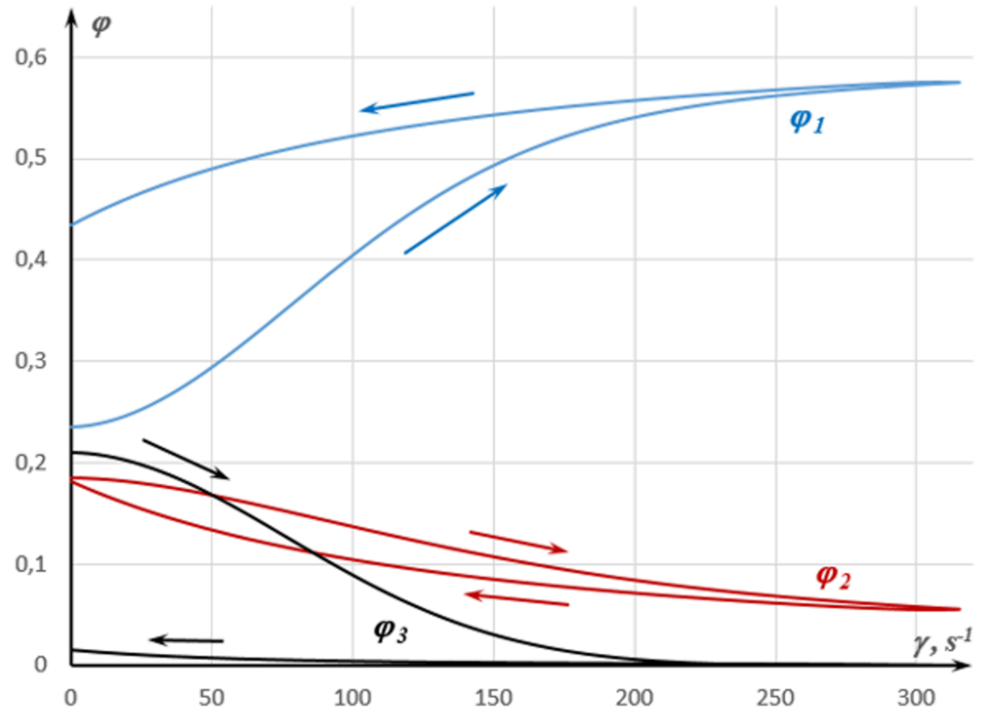

Fig. 6. Polymer suspension filled with ceramic nanoparticles. The calculated dependence of the concentrations of the components on the shear rate, corresponding to the results in Fig. 4.

Fig. 6 shows that the concentrations of doublets at the beginning and at the end of the experiment practically coincide, while at the beginning, the concentrations of singlets and triplets differ little, and at the end, singlets predominate. At the same time, singlets have a higher intrinsic viscosity and a lower limiting concentration than triplets; therefore, they make a greater contribution to the viscosity of the suspension. Therefore, their predominance leads to the observed increase in viscosity.

Conclusions

1. Accounting for the formation of triplets makes it possible to describe in a uniform and natural way all types of rheological behaviour of suspensions: pseudoplasticity, dilatancy, thixotropy, and rheopexy.
2. The proposed model describes well suspensions that demonstrate "variable" behaviour, i.e., cases when, with a change in shear rate, pseudoplasticity is replaced by dilatancy and vice versa, and also when thixotropy is replaced by rheopexy and vice versa.
3. The type of rheological behaviour of the suspension depends on the ratio of six parameters: limiting concentrations of components φ_{10}, φ_{20} and φ_{30}, their intrinsic viscosities $[\eta_1]$, $[\eta_2]$ and $[\eta_3]$, as well as on the kinetics of interconversions of singlets, doublets, and triplets.
4. Pseudoplastic suspensions, under certain conditions, can demonstrate rheopexy behaviour, as, probably, dilatant suspensions can be thixotropic.

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Declarations

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