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On the rheology of thixotropic and rheopexic suspensions: accounting for the formation of trimers

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Abstract

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 di- and trimerization reactions occur. Wherein, dimerization and trimerization are considered as reactions with invariable rate constants, and the dissociation of dimers and trimers – as reverse reactions with rate constants that increase linearly with the 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 one, and thixotropic behaviour is replaced by rheopexic one, and vice versa).

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 $\bar{\varphi}_0$ – значения параметров, усредненных по всем твердым компонентам:

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

where φ is the total volume fraction of the dispersed phase, $[\eta_i]$ is the intrinsic viscosity of 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 [η] 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 rheopex suspensions (these relaxation effects appear if the time to reach the mentioned equilibrium is comparable to 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.

This work is a continuation and further development of the approach described in [1] by taking into account the formation of triplets.

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), doublets (volume fraction φ_2) and 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:

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

and $n_1 + 2n_2 + 3n_3 = n_0$. 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 $\dot{\gamma}$, 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

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

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

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

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. $\dot{\gamma} = 0$, $\frac{d\varphi_1}{dt} = 0$ and $\frac{d\varphi_2}{dt} = 0$. It leads to a system of algebraic equations

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

whence

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

From the second equation $\varphi_2 = \frac{k_1\varphi_1^2}{k_2}$; 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 a cubic equation, there is the Cardano formula, but it requires operations with complex numbers, which is not very convenient for practical computer calculations, so equation (6) was solved numerically by the Newton method.

The system of equations (5) is the Riccati equations, which, in the general case, unfortunately cannot be integrated in quadratures [5]. Therefore, it was solved numerically by the classical fourth-order Runge-Kutta method [6]. 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 is the shear stress, τ_0 is the yield stress, η_0 is the viscosity of the dispersion medium, $\dot{\gamma}$ is the shear rate, φ_1 and φ_2 are the volume fractions of singlets and doublets (the result of the numerical solution of the system of equations (5)), φ_3 is the volume fraction of triplets (in according to (3) $\varphi_3 = \varphi_0 - \varphi_1 - \varphi_2$), φ_{10} and φ_{20} are the corresponding limiting concentrations, $[\eta_1]$ и $[\eta_2]$ are 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 [7][8] were used. The results of comparing theory with experiment are shown in the following figures.

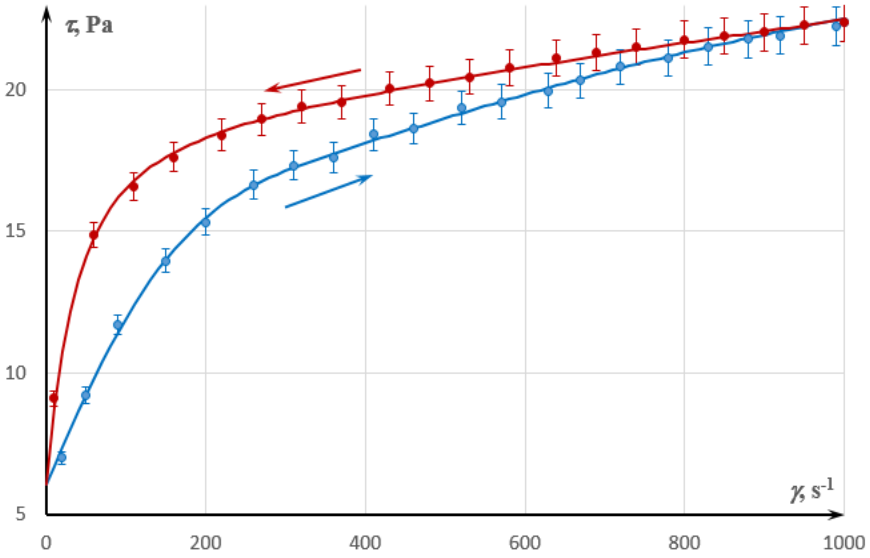

Fig. 1. Aqueous Suspensions of Palygorskite.
Shear stress vs. shear rate according to data [7]

Fig. 1. Aqueous suspension of palygorskite. Dependence of shear stress on shear rate according to [7].

Parameter values:
$k_1 \approx 1{,}719$; $k_2 \approx 0{,}9625$;
$k_3 \approx 0{,}01310$; $k_4 \approx 3{,}446$;
$k_5 \approx 0{,}003725$; $k_6 \approx 0{,}0002261$
$\varphi_0 \approx 0{,}4808$; $\varphi_{10} \approx 0{,}8816$;
$\varphi_{20} \approx 0{,}1804$; $\varphi_{30} \approx 0{,}4959$;
$\tau_0 \approx 6{,}046$; $\eta_0 \approx 0{,}07798\ Pa \cdot s$;
$[\eta_1] \approx 2{,}859$; $[\eta_2] \approx 27{,}32$;
$[\eta_3] \approx 2{,}726$. The standard deviation of the curves from the points is 0.14 Pa (0.73% of the mean shear stress). The error indicator shows a spread of 3%.

The points in fig. 1 represent the experiment according to the data of [7], the solid curves are the calculation according to the derived equations. It is easy to see that the derived equations are in exceptionally good agreement with the experiment, and the parameters of the equations take realistic values.

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

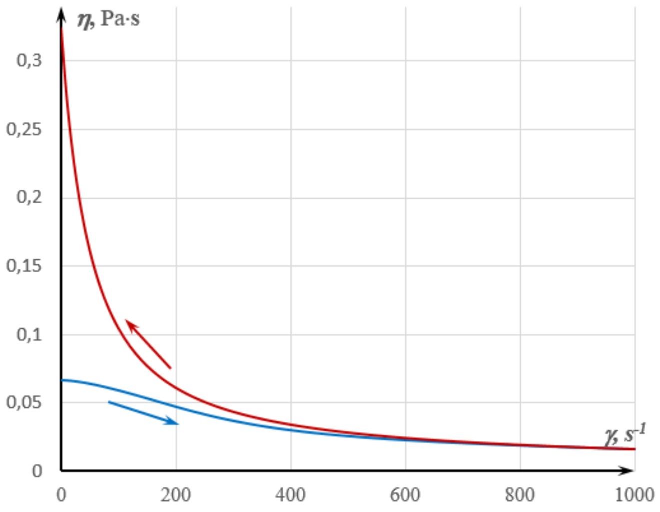

Fig. 2. Aqueous Suspensions of Palygorskite. Viskosity vs. shear rate (calkulated)

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. 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)

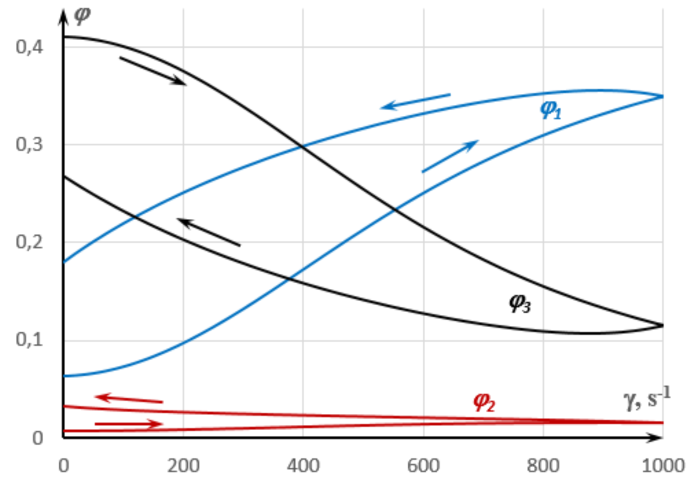

Fig. 3. Aqueous Suspensions of Palygorskite. Volume fractions vs. shear rate (calkulated)

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.

It can be seen that before the start of the experiment, in the established equilibrium between the components in the suspension, triplets (the intrinsic viscosity of which is relatively low) predominate, which leads to a low viscosity of the suspension.

As the shear rate increases, the triplets are destroyed, and singlets begin to predominate in the suspension, the rheological characteristics of which differ little from those of triplets, and the viscosity decreases insignificantly. With a thereafter decrease in the shear rate, the concentrations of singlets and triplets approach each other, and the concentration of doublets increases from 0.7% to 3.3%, i.e. almost 5 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 to describe such behaviour. Taking them into account makes it possible to do this, as can be seen from the following figures.

Fig. 4 shows the dependence of the shear stress on the shear rate for a polymer suspension filled with ceramic nanoparticles according to [8].
It is easy to see that the equations derived taking into account the formation of triplets describe well this behaviour of the suspension as well, and the parameters take realistic values.

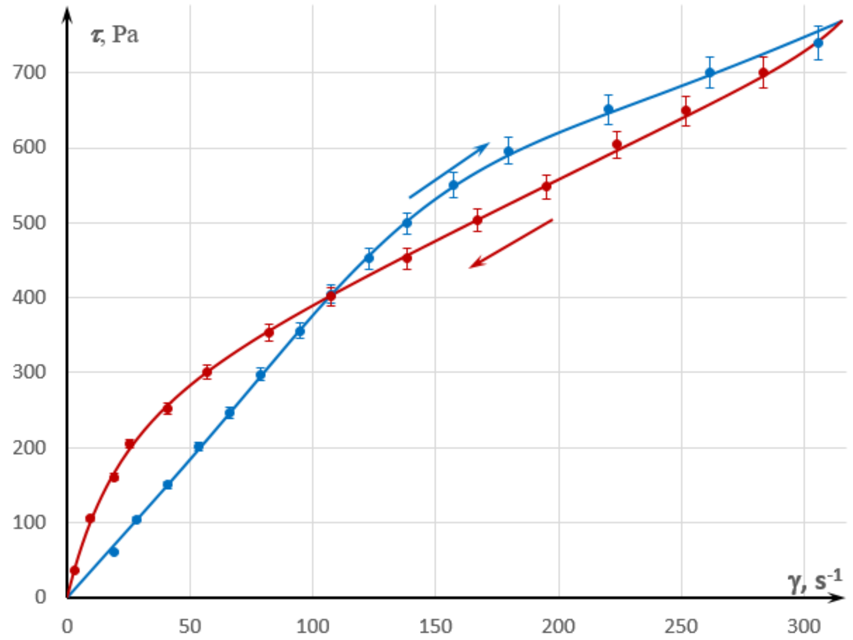

Fig. 4. Polymer Suspensions Filled with Ceramic Nanoparticles according to data [8]

Fig. 4. Polymer suspension filled with ceramic nanoparticles. Dependence of shear stress on shear rate according to [8].
Parameter values:
$k_1 \approx 0{,}3354$; $k_2 \approx 0{,}09968$;
$k_3 \approx 0{,}006248$; $k_4 \approx 0{,}0001742$;
$k_5 \approx 0{,}00003591$; $k_6 \approx 0{,}002430$;
$\varphi_0 \approx 0{,}6298$; $\varphi_{10} \approx 0{,}7582$;
$\varphi_{20} \approx 0{,}5096$; $\varphi_{30} \approx 0{,}8801$;
$\eta_0 \approx 0{,}001625\ Pa \cdot s$;
$[\eta_1] \approx 5{,}134$; $[\eta_2] \approx 3{,}557$
$[\eta_3] \approx 4{,}961$.
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%

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.

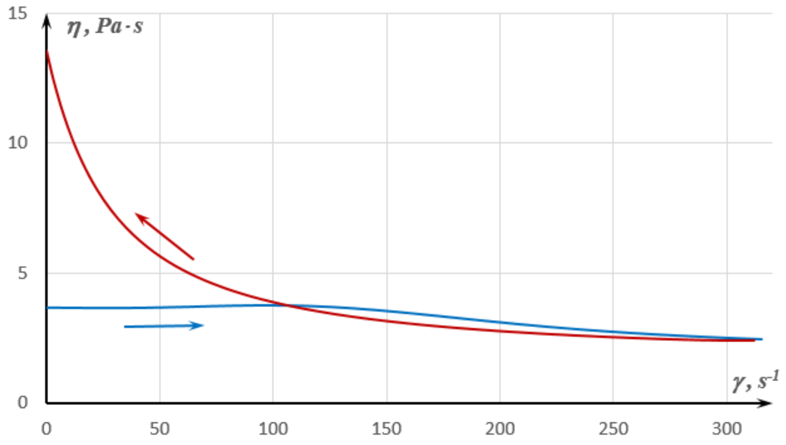

Fig. 5. Polymer Suspensions Filled with Ceramic Nanoparticles. Viskosity vs. shear rate (calkulated)

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 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.

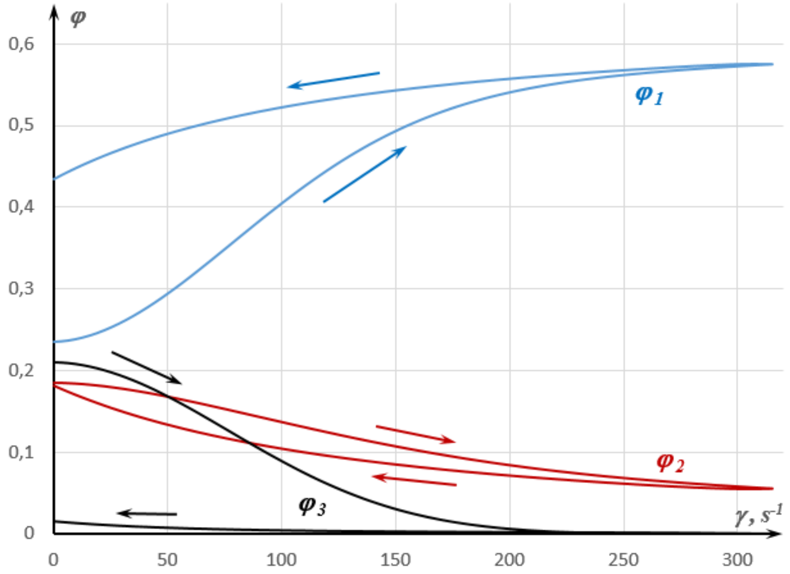

Fig. 6. Polymer suspensions filled with ceramic nanoparticles
Volume fraction vs. shear rate (calkulated)

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

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 as well good 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 from the kinetics of interconversions of singlets, doublets and triplets.
4. Pseudoplastic suspensions under certain conditions can demonstrate rheopex behaviour, as, probably, dilatant suspensions – thixotropic.

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