Interactions between falling spheres in the wormlike micellar solutions

MONIKA KOSTRZEWA[,2], LUBOMIRA BRONIARZ-PRESS[1], ANDREAS WIERSCHEM[2], ANTONIO DELGADO[2]
[1]Department of Chemical Engineering and Equipment
Poznan University of Technology
Pl. M. Sklodowskiej-Curie 2, PL 60-965 Poznan
POLAND
[2]Department of Fluids Mechanic
Friedrich-Alexander University Nuremberg-Erlangen
Cauerstrasse 4, D 91058 Erlangen
GERMANY
mirka@box43.pl

Abstract: Due to increasing use of the wormlike micellar solutions in many branches of industry, it may suggest that the study of sedimentation and interactions between falling particles in the gel-like liquids is necessary. In this paper the flow instabilities during the sedimentation of side-by-side falling rigid spheres, have been presented. The cetyltrimethylammonium bromide with addition of sodium salicylate (CTAB/NaSal) aqueous solutions of concentrations of 40/40 mM and 10/40 mM, have been used. The interactions between the falling particles in micellar solutions more strongly depend on the initial separate distance than in the polymer solutions. It has been shown that before and even after the collision still the oscillations appear. The fluctuations in wormlike micellar solutions are with the time damped.

Key-Words: wormlike micellar solution, flow instability, particles interactions

1 Introduction

Concerning particle interactions in the non-Newtonian mediums it was estimated besides drafting and kissing also chaining as the principal interactions between suspending particles [1, 2]. The interactions depend on the rheological properties of a liquid as well as on the initial separation distance between two suspending particles and configuration [3]. The case of falling spheres fall in polymer solutions has been widely studied. Due to "corridor of reduced viscosity" the particles form the chain if the initial distance between them is small enough. Because the side-by-side configuration the falling spheres tend to attract and align vertically as well as exist the side-by-side critical separation distance [4]. Independently of the initial configuration (centreline or side-by-side), the particles reach after collision the long body arrangement.

In this paper the results of particle interactions in viscoelastic non-Newtonian wormlike micellar solutions, have been presented. The rheological properties of the solutions used are similar to these ones of polymer solutions, but in contrary to them, the structure of micelles may break up and recombine [5]. The most interesting rheological behaviours possess the wormlike solutions composed from cationic surfactant CTAB and anionic salt NaSal, responsible for the micelle structure forming. It should be underlined that the shear-thickening effect under shearing in cationic dilute solution and that in semi-dilute solutions stress plateau and flow instabilities such as shear-banding exhibit [5-7]. In the region of the shear stress plateau is often observed the chaotic stress fluctuations at constant applied shear stress conditions [5-8].

The dynamical viscoelastic properties at low frequencies are often described with the single Maxwell model. Except the first relaxation time λ there are observed a continuous spectrum of relaxation processes; storage modules plateau or as well as the presence of the second relaxation time at high applied frequencies existed [7].

The up to now results published were concerned only on the single particle fall in wormlike micellar solutions [9, 10]. Contrary to the polymer solutions, the sedimentation of single rigid sphere in surfactant solutions is characterized with the strong flow instabilities. The reason for the flow fluctuation is not well-defined and may be due to competition between the gel-like character of a liquid (a very high elasticity under small amplitude deformations)

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and very strong shear-thinning during the larger strains [11]. As well the unsteady motion could be caused by the formation and breaking of flow-induced structures [9] or as suggested by [10] as the results of the large extensional stresses developed within micelles.

2 Problem Formulation

The growing importance of surfactants in a solution as rheology modifiers and thickeners in many products, suggests that the study on sedimentation and interactions between falling particles in the gel-like liquids is necessary. In this paper are presented the results of experiments directed on the flow instabilities during the sedimentation and as well as on the divergences between particle falling in surfactant and polymer solutions.

3 Problem Solution

Experiments were carried out for two wormlike micellar solutions CTAB/NaSal 40/40 mM (A) and CTAB/NaSal 10/ 40 mM (B). At these concentrations the solution are known as semi-dilute wormlike micellar solutions [6]. Rheological properties were measured using the controlled-stress rheometer Physica MCR 301 from Anton Paar equipped with a cone-and-plate system of a diameter of 50 mm and an aperture angle of 1º at temperature T = 295 K. Using the single Maxwell model from the frequency sweep test were determined the relaxation time values λ_A = 4.5 s and λ_B=1.3 s the calculated.

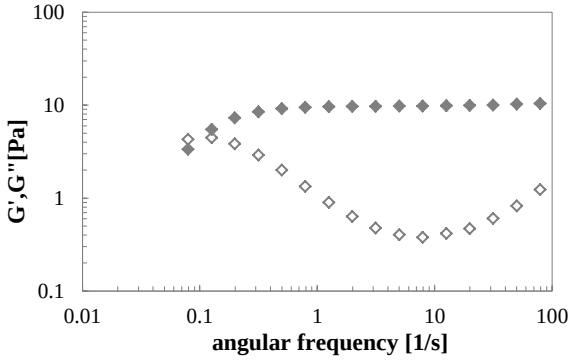

Fig.1 Frequency sweep test for the CTAB/NaSal 40/40 mM micellar solution at strain amplitude 5% and temperature T = 295 K:
♦ – storage modulus, ◊ – loss modulus

Further the transient nature of wormlike structure causes the departure from the single Maxwell model and invokes the plateau of the storage modules and the loss modules go to minimum (Fig.1). The plateau of storage modulus is the effect of the formation of entanglements in the micellar network, whereas the first single relaxation time describes their dynamics [5,7].

At high frequencies it should be expected the continuum of relaxation processes due to movement of individual single micelles.

Both solutions possess shear-thinning properties; similar to the polymer solutions. Contrary to the flow curve of the CTAB/NaSal 40/40 mM solution shows additionally the shear stress plateau with the onset at the shear rate $\dot{\gamma}$ = 0.31 s^{-1} (Fig.2).

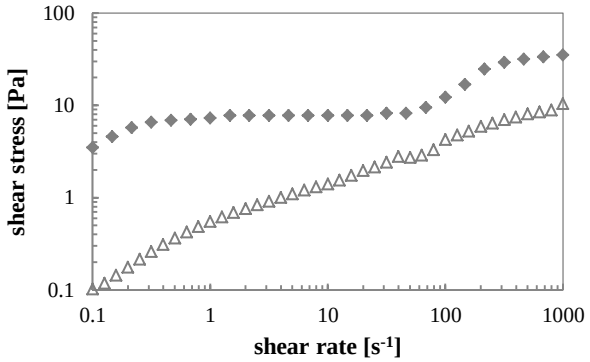

Fig.2 Flow curves for the solutions of CTAB/NaSal 40/40 mM (♦) and CTAB/NaSal 10/40 mM (Δ) at T = 295 K

The rheological time-dependent behaviours at constant shear stress and shear rate were corresponding to the effective shear rate reached the single particle falling down.

It has been shown (Fig.3) that shear rate growth upon creep test at discrete shear stress above the shear stress plateau does not appear the shear rate oscillations. After certain time the characteristic rapidly rise of apparent shear rate over the time is observed. It reflects as entanglement-disentanglement transition (EDT) [12].

On the other hand in the solution B it is possible to observe that shear stress functions change harmonic with the time (Fig. 4). Using the Fourier transform the stress oscillation was determined with the dominant frequency and in accordance to [13] comparison was carried out basing on only one sinusoidal function.

The time-dependent behaviour of the solutions tested can be connected with the change in the internal structure of wormlike micelles due to flow or can suggest the strong memory effects in viscoelastic materials [14,15]. The temporal instabilities were observed in the shear-thickening micellar solutions. Nowadays, such effect for the

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shear-thinning micellar systems is poorly described and studied.

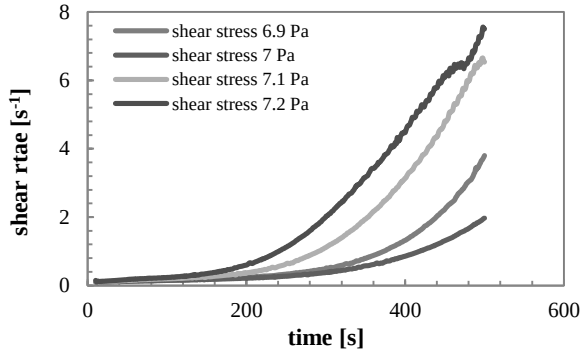

Fig.3 Creep test experiment at discrete applied shear stresses for CTAB/NaSal 40/40 mM

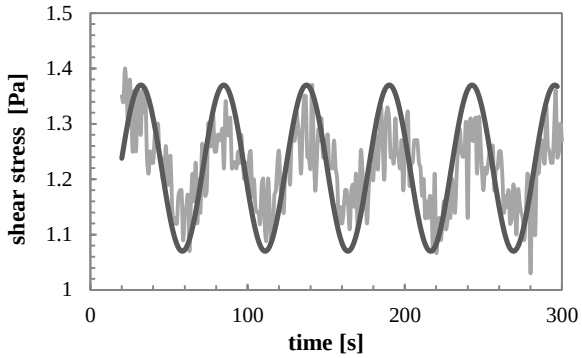

Fig.4 Shear stress oscillations vs. time at constant shear rate (6.75 s^{-1}) for the micellar solution B

The experimental setup of sedimentation consisted of a rectangular container from Plexiglas with inner edge lengths 0.15×0.15×0.6 [m]. The movement of spheres was recorded with CCD camera. The experiments were performed using steel spheres of the density 7800 kg/m^3 of diameters of 10 [mm] for solution A and 4 [mm] for liquid B, respectively. The measurements run started by placing the sphere on the immersed platform equipped with few gaps with various initial separate distances. Time interval between each measurement was 30 minutes to fully relax and homogenize the liquid.

In the Fig. 5 the most representative experimental data as a function of the position vs. time for the suspending particle in CTAB/NaSal 40/40 mM are presented. The falling sphere does not tend to achieve the terminal velocity and moves with the transient oscillations.

Fitting these experimental data's with the linear function is possible to calculate the transient deviation from the monotonous movement and estimate the average velocity (Fig.6)

$$\Delta s = s_{\exp} - s_{fit} \quad (1)$$

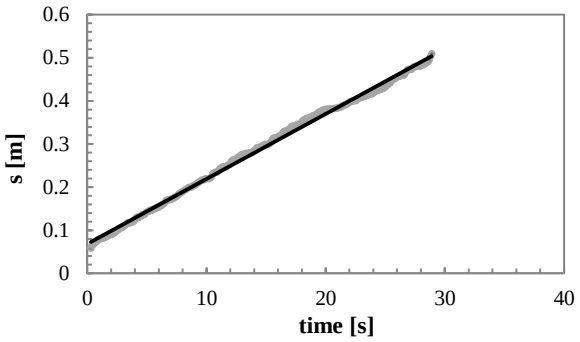

Fig.5 Position vs. time for the motion of single steel sphere of d = 10 mm in CTAB/NaSal 40/40 mM solution

The average falling velocity of single particle determined in CTAB/NaSal 40/40 mM solution is equal to v = 0.015 [m/s] and in CTAB/NaSal 10/40 mM solution v = 0.03 [m/s], respectively. The flow of the single particle is characterized by the Reynolds number Re_A = 0.003 and Re_B = 0.15, correspondently.

Using the relevant control parameter; effective shear rate $\dot{\gamma}_{eff}$ defined as the radio of average velocity to the diameter of sphere, in CTAB/NaSal 40/40 mM solution ($\dot{\gamma}_{eff}$ = 1.5 [s^{-1}]), it has been shown that the particle moves in the stress plateau regime. In the second case the particle at $\dot{\gamma}_{eff}$ = 7.5 [s^{-1}] falls still in the shear-thinning regime. Connecting these observations with the dynamic rheological properties of the systems tested, the Deborah number was calculated. It is equal to *De* = 6.75 in CTAB/NaSal 40/40 mM and to *De* = 9.75 in CTAB/NaSal 10/40 mM solutions, respectively. According to [10] the values of Deborah number reached the regime at which the sphere starts to fluctuate ($De \geq 4$).

The calculated transient deviations Δs nonlinearly changed with local maxima and minima, what corresponds indeed with the alternately acceleration and deceleration of phases (Fig. 6). The Fast Fourier Transform (FFT) analysis pointed out a dominant peak with the frequencies of f = 0.13 [1/s] in CTAB/NaSal 40/40 mM and f = 0.3 [1/s] in the CTAB/NaSal 10/40 mM.

To describe the dynamics of the attraction between two falling side-by-side spheres was used the dimensionless parameter S/D, where D is the particle diameter and S is calculated from the coordinates of the position between 2 particles

$$S = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} \quad (2)$$

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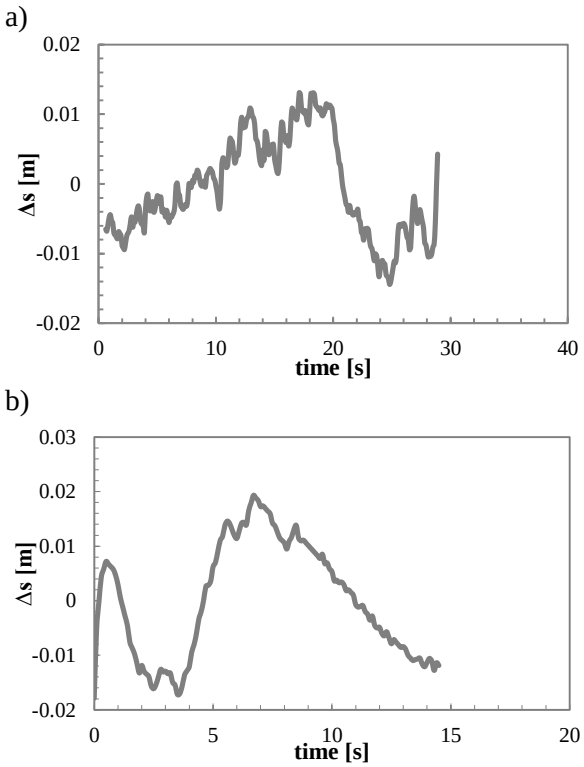

Fig.6 Deviations from the monotonous movement *Δs* for the falling of single sphere in CTAB/NaSal solutions:
a) 40/40 mM, b) 10/40 mM

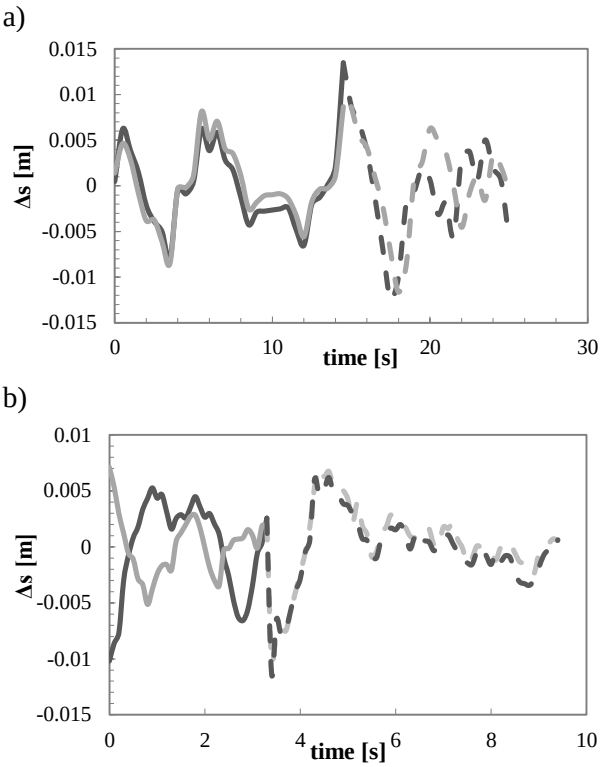

Fig.7 Temporal deviations from the monotonous movement of the separate particles (undashed lines) and the dumbbell (dashed lines) at:
a) S/D = 5.5 in CTAB/NaSal 40/40 mM,
b) S/D = 7 in CTAB/NaSal 10/40 mM

In the Fig.7 are presented the temporal deviations from the monotonous movement. From the data obtained in solution A (Fig.7a) it is possible to estimate that the time and the locations of flow instabilities for separate particles appear in the similar way. In the second solution (Fig.7b) was observed that the fluctuations appear random and occurs the alternately acceleration and deceleration. The particles do not move parallel. Shortly before the collision both spheres meaningfully accelerate and then interfere and the dumbbell further fluctuates. However the oscillations of dumbbell in CTAB/NaSal 40/40 mM occur even often, but compared to the first part of the motion, the amplitude is being smaller. While the falling dumbbell in CTAB/NaSal 10/40 mM already moves with the constant velocity, the oscillations are damped in time.

The analysis the average velocities of the particles and dumbbell points out the presence of leader and trailing particle (Fig.8). The velocity of the leader sphere is higher than the second one. The attractive interactions between two falling side-by-side spheres cause the increase of the velocity of each particle before the collision. The dumbbell falls with the velocities much higher than the single sphere, suggesting the influence of the shear-thinning properties of the medium. However the average velocity of the dumbbell is being higher already two times in comparison with velocity of single falling particle.

If the initial separate distance S/D is enough small, then the particles need the short time period to attract, similarly as in the polymer solutions. When this parameter is increasing, the separate distance is changing monotonously with the time (Fig.9).

The distance between particles is increasing because of alternately deceleration and acceleration of particles (Fig.7b), but finally takes place the collision. After the contact, the dumbbell seems to behave a long body, but during the sedimentation the particles rotate around each other. It affects the oscillation of the S/D parameter around the value 1.

At the critical separation distance $S/D^* \cong 6$ the particles fall separately in the CTAB/NaSal 40/40 mM solution, although after some time this parameter is slowly decreasing (Fig.9a). Comparing the results presented in Fig.9 the attraction between falling side-by-side particle is stronger in the CTAB/NaSal 10/40 mM system ($S/D^* \geq 8$). In this micellar solution, initially the separation distance for $S/D \geq 8$ is changing nonlinearly.

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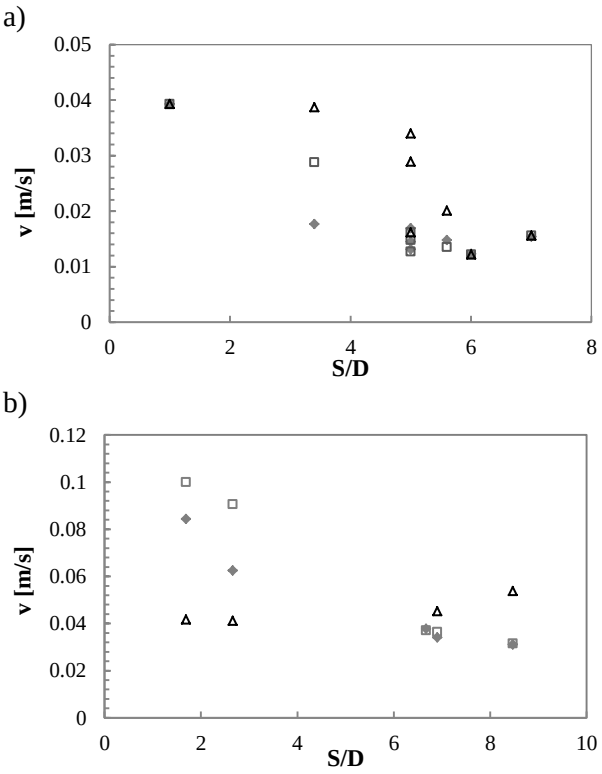
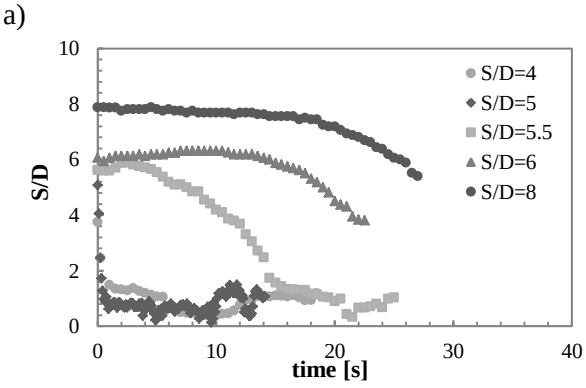


Fig.8 The velocity of the particles (♦ and □) before and after the collision (Δ) as a function of the initial separate distance in the solutions of:
a) CTAB/NaSal 40/40 mM,
b) CTAB/NaSal 10/40 mM

Also observing the shape of trajectory the falling particles was noted the dependency on the initial separation distance. As the initial distance is enough small the particles attract simultaneously to each other. Whereas as the distance is being bigger only the trailing sphere changes her path and approaches the leader sphere, which fall down the straight line (Fig.10).

According to [16] the path of the leading sphere remains straight independent of the initial separation distance.



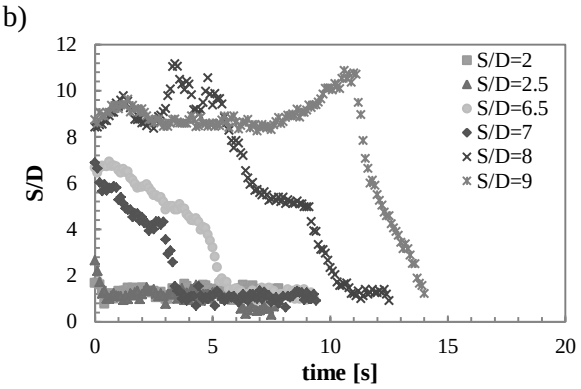


Fig.9 The change of the dimensionless distance between particles S/D as the function of time in the solutions of:
a) CTAB/NaSal 40/40 mM,
b) CTAB/NaSal 10/40 mM

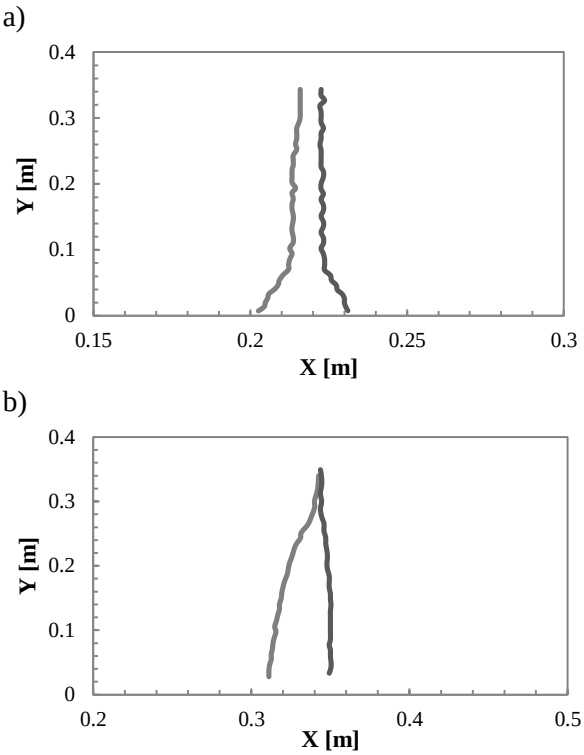


Fig.10 The trajectory of the motion of side-by-side particles in wormlike micellar solutions with molar ratio 1:1:
a) S/D = 3, b) S/D=5

4 Conclusion

The interactions between falling particles in side-by-side configuration present the complex behaviour: rotation as well as the oscillation of the dumbbells. Similarly to the polymer solutions the attractive forces have been meaningfully influenced on the interaction between falling particles. According to

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the rheological measurements it is believed that the oscillations are directly associated with the structural transition in the micellar network. In contrary to the non-Newtonian fluids without the micelles the movement of dumbbells influences stronger the time-dependent properties of the micellar solutions. Basing on the detailed rheological measurements the continuous relaxation processes, control the sedimentation and also the transient fluctuations were identified.

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