

Pressure Drop in Aqueous Surfactant Solution Flow through Pipes in SIS Structure Degradation Zone

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Abstract: -The paper describes chemical and rheologic properties of solutions of polymer additives and cationic surfactants while they flow through pipes in a laminar and turbulent zone and their influence on drag reduction. Surface active additives or aqueous solutions of surfactants form rod-like micelles, associated into an intermolecular SIS structure that absorbs the turbulence energy at the passage through a pipe, thus influencing the reduction in pressure drop or drag reduction. The influence of the velocity of aqueous solution of surface active additives is analysed in pipes in the Re number range, where high shear stress leads to a degradation of the surfactant intermolecular SIS structure and the drag reduction effect disappears. The pressure drop and drag reduction rate diagrams as functions of aqueous surfactant solution flow velocity and Re number are based on computer calculations.

Key-words: -Fluid dynamics, surfactants, pressure drop, shear stress, drag coefficient, drag reduction

1 Introduction

It has been known for several centuries that even small concentrations (a few $\mu\text{g/g}$) of polymer or surface active additives in a fluid substantially reduce drag in turbulent flow in pipes compared to a pure fluid. This phenomenon was first introduced by Toms [1] in 1948, which attracted the researchers' attention only in the 1960s when the drag reduction phenomenon with additives became the subject of numerous research studies. Such increased interest and the scope of research did not solely result from the importance of this phenomenon in fluid mechanics theory and rheology but from the fact that the practical applications of additives allow substantial savings in energy consumption [2,3].

2 Formation of Viscoelastic Micellar Structure

When surface active additives are dissolved in water the hydrophilic part is oriented towards and the hydrophobic part from the water phase. Two mechanisms exist for reduction of energetically unfavourable hydrocarbon-water interface. According to the first mechanism, the hydrophobic part is oriented towards the non-polar phase, e.g. gas, non-polar solid or hydrophobic liquid phase. According to the second mechanism, however, the molecules of additive form aggregates known as

micelles [4]. The hydrophilic parts of molecules form a shield in the micelle around the hydrophobic parts located in the micelle core which results in a reduction of the total surface around the hydrophobic part. At low concentrations, the micelles take a spherical shape. In geometrical terms, it is impossible for a hydrophilic group to fully cover the entire micelle surface, which is why a part of the hydrocarbon chain is still in contact with water. As the system seeks to further reduce the interface, this results in the transformation into the rod-like micelles. The investigations into drag reduction using surface active additives have shown that the presence of rod-like micelles is considered to be a necessary condition for drag reducing effect [5].

Micelles are agglomerates containing between 30 and 200 molecules [6]. In accordance with the rule that »like dissolves like« the non-polar parts of molecules are located in the centre of the micelle, the polar ends of the molecules are oriented towards the surface and remain in contact with the water. These energetically favourable agglomerates are formed when the first critical micelle concentration (CMC_1) is exceeded. The surfactant solubility increases when CMC_1 is attained. The solubility of individual surfactant molecules is low, whereas micelles are highly soluble [7]. The CMC_1 concentration depends on the size of the hydrophobic part of the molecule and only slightly on the hydrophilic group. The CMC_1 values are

determined for numerous surfactants and published in different publications [8]. At a concentration above CMC_1 , the micelles are always in a thermodynamic equilibrium with individual molecules. Every surfactant molecule is retained in a micelle or in a solution for a specific short period of time. The time period during which a molecule is held in a micelle depends on the length of the alkyl chain and the concentration of oppositely-charged ions [9]. A surfactant with 12 carbon atoms is retained in a micelle approximately 10 μ s. The retention time is extended three times with every additional carbon atom. Micelles may take different shapes, i.e. spherical, bubble-like, rod-like or flat. The electronic microscope images have shown structures of rod-like micelles in a temperature range in which drag reduction occurs, whereas in a temperature range in which no drag reduction occurs, bubble-like micelle microstructures have prevailed [10]. This confirms the generally accepted theory that the necessary condition for drag reduction is the presence of rod-like micelles in a surface active additive solution.

The phase diagram of surface active additive aqueous solutions shows that the micelle formation does not solely depend on the surfactant solution concentration but also on temperature. The Kraft point is defined as the temperature above which the surfactant solubility markedly increases and represents an equilibrium between the phases of pure component, water solution of individual molecules and water solution of micelles [11]. If the temperature is lower than the Kraft point the surfactant may take the form of crystals or gel. At temperatures above the Kraft point and the concentrations higher than CMC_1 , the spherical micelle structures are formed in the aqueous surfactant solution with a diameter approximately twice the length of an individual molecule. If the surfactant concentration in the solution continues to increase the average number of additive molecules in the spherical micelle structure grows until the entire micelle volume is completely filled with hydrocarbon chains. The CMC_1 concentration displays only little temperature dependence. The hydrophobic core in spherical micelles is not completely isolated from the external aqueous phase as the non-polar groups repel each other due to identical charges. The electrostatic repulsion between the non-polar groups of molecules decreases as a result of the transformation into rod-like micelles, which occurs when the second critical micelle concentration (CMC_2) is exceeded. At the concentrations above CMC_2 , rod-like micelles are formed in aqueous solutions of

surfactants, because such geometrical shape is energetically more favourable, allowing the integration of a larger number of micelles in an identical volume [5]. With increasing surfactant concentration, the rod-like micelles grow in length. The CMC_2 concentration is strongly temperature dependent.

Low-concentration aqueous surfactant solutions that form spherical micelles behave similarly as the water and do not perform the drag reducing effect. At concentrations higher than CMC_2 , the rod-like micelles are formed in the additive solution, exhibiting a viscoelastic behaviour [12]. Extensive research has shown that rod-like micelles do not directly reduce drag, but rather that larger supramolecular micelle structures are required, formed of micelle clusters under the influence of shear stresses in a turbulent flow. The rod-like micelle cells are aligned under the shear stress in the flow direction and form a viscoelastic three-dimensional network structure known as »Shear Induced State« (SIS) which expands the buffer layer and reduces the layer of turbulent main-stream flow [12]. The SIS structures absorb the kinetic energy from the turbulent whirls thus reducing the energy dissipation as the fluid flows through the pipe. Fig. 1 shows the viscoelastic micellar SIS structure and the alignment of rod-like micelles under shear stress effect.

At the concentrations around CMC_2 , only few relatively small rod-like micelle aggregates are formed having a limited capability of forming the oriented network SIS structures, which is why their drag reduction effect is small. Therefore, for satisfactory reduction of drag a higher concentration is required causing permanently aligned viscoelastic micellar SIS structures suppressing the formation of turbulent whirls.

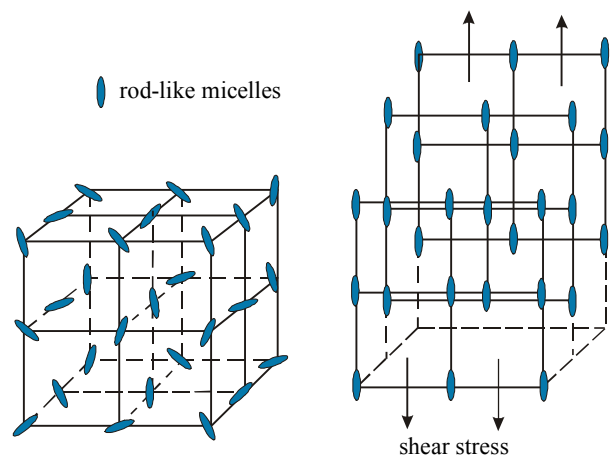


Fig 1: Viscoelastic supramolecular structure of micelles (SIS) [12]

The experiments have shown that for efficient drag reduction the mass parts ranging between 0.01 mg/g and 0.2 mg/g are required which, compared to the polymer additives, represents a 2-times higher concentration. The reason lies in a smaller molar mass of the surface active additives. Higher concentration naturally results in higher surfactant solution viscosity.

3 Drag Reduction Principles

The solutions of high-molecular-weight polymers feature drag reduction already at very small concentrations, which is why the difference between the viscosity of their solutions and the viscosity of pure fluid (solvent) is negligibly small. The surface active additives introduced into the fluid increase the viscosity and the difference between both viscosities is no longer negligible. Since the determination of viscosity of a surfactant solution is very difficult with the latter being a complex shear stress function in the laminar and a modified turbulence structure in the turbulent flow, the physical properties of the solvent are used in the computations. In this way the determination of flow pressure conditions of various additive solutions and the comparison with the empirical equation of minimal drag asymptote may be much easier. It should be noted, however, that diagram $\lambda = f(Re)$ applies only to a specific pipe diameter.

Drag reduction in a turbulent flow of additive solution in a pipe is shown as a change in flow-pressure conditions. At a constant pressure drop the flow increases while the additive is introduced and conversely, at a constant flow the pressure drop is reduced. The drag reduction rate (DR) is defined at a constant flow by the ratio between the pressure drop for the liquid with additive introduced and the pressure drop for the pure fluid flow:

$$DR = \left(1 - \frac{\Delta p_a}{\Delta p_v} \right) 100\% \quad (1)$$

DR may also be expressed as a relationship between the drag coefficients:

$$DR = \left(1 - \frac{\lambda_a}{\lambda_v} \right) 100\% \quad (2)$$

Drag reduction occurs when DR is positive. The higher the DR value the larger the drag reduction [13].

3.1 Influence of Pipe Diameter on Drag Reduction

In surfactant solutions the critical value of shear stress is achieved at very low Re numbers, at which the drag coefficient in a turbulent flow exhibits a gradual deviation from the extended laminar flow curve. Drag reduction increases until the shear stress reaches a critical value. At the critical value of shear stress, mechanical degradation of the micellar SIS structure occurs and drag coefficient starts to rise quickly until the value, indicated on the Karman's curve, is attained. The diagram in Fig. 2 shows that in the flow of the aqueous Habon-G surfactant solution through 4- and 6-mm pipes the critical shear velocity value is exceeded already at low Re numbers, at which the SIS structure of the surfactant is degraded and the drag reduction effect disappears. In higher diameter pipes the critical shear velocity is attained only at much higher Re numbers. In 10 mm and 20 mm pipes the degradation occurs at even lower Re numbers, whereas in a pipe with the internal diameter of 39.4 mm and more it occurs only at $Re > 10^5$.

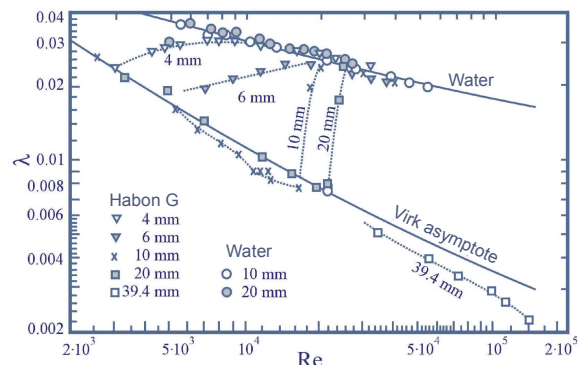


Fig. 2: Drag coefficient depending on Re number of 500 ppm Habon G solution [16]

4 Pressure Drop in Surfactant SIS Structure Degradation Range

In aqueous surfactant solutions the critical value of shear velocity is attained at relatively low Re numbers. Drag reduction increases until the critical value of shear velocity is attained, at which the surfactant SIS micellar structure is degraded and the drag effect disappears. In larger diameter pipes the critical shear velocity is achieved only at much higher Re numbers, whereas in smaller diameter pipes the surfactant SIS micellar structure occurs already at lower Re numbers.

A computation made for the pipes with inner diameter of 4 mm, 6 mm, 10 mm and 20 mm served for the comparison between the pressure

drop per meter of pipe in pure water flow and the flow of 500 ppm Habon G solution [9]. A computer software application has been developed for computation purposes, with the computation results presented in Fig. 3 to 10. The following equations have been used for the computation of drag coefficient depending on pipe inner diameter:

In the laminar flow $Re < 2300$ the Hagan-Poiseuille equation [3,8] was used for drag coefficient determination. For the transitional and turbulent range of $Re > 2300$ the Blasius equation [3, 8] was used.

In order to determine the drag coefficient for the flow of 500 ppm Habon G solution [9] ($Re > 2300$) the Virk equation (4) was used in the explicit form.

The following approximation equations were used to determine the drag coefficient in the SIS structure degradation range: The polynomial for the computation of the drag coefficient of a 4 mm pipe in the SIS structure degradation range:

$$\lambda = 0.0158 + 0.352 \cdot 10^{-5} \cdot q_v - 0.207 \cdot 10^{-9} \cdot q_v^2 \quad (3)$$

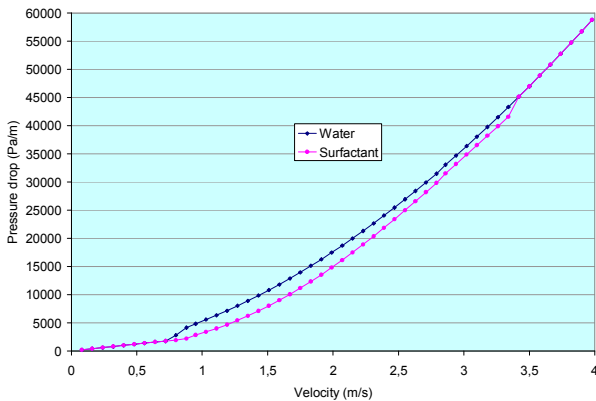


Fig. 3: Pressure drop per meter in a 4 mm pipe

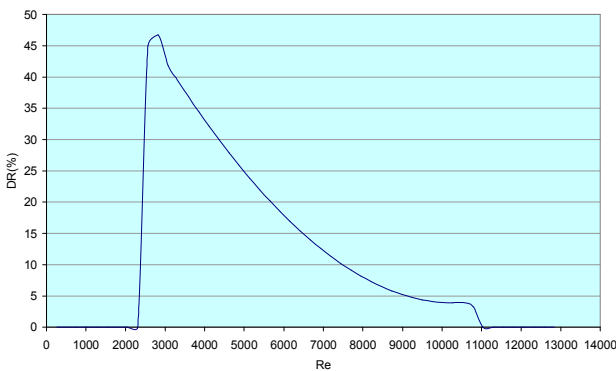


Fig. 4: Drag reduction rate (DR) depending on Re number in a 4 mm pipe

The polynomial for the computation of the drag coefficient of a 6 mm pipe in the SIS structure degradation range:

$$\lambda = 0.0234 - 0.197 \cdot 10^{-5} \cdot q_v + 0.193 \cdot 10^{-9} \cdot q_v^2 \quad (4)$$

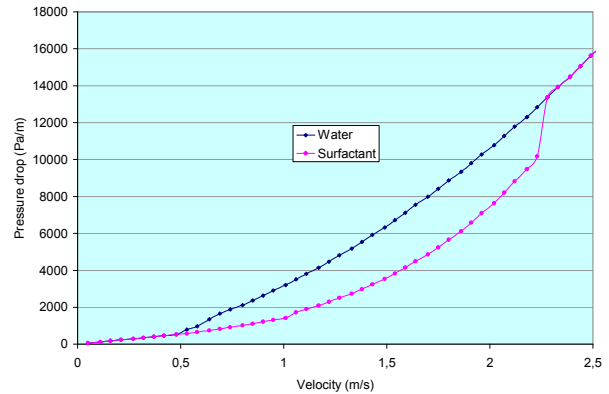


Fig. 5: Pressure drop per meter in a 6 mm pipe

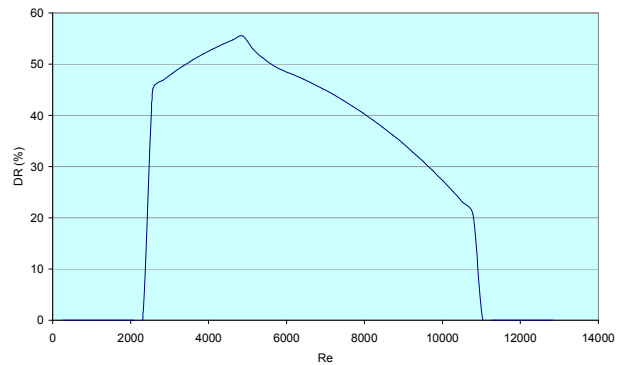


Fig. 6: Drag reduction rate (DR) depending on Re number in a 6 mm pipe

The polynomial for the computation of the drag coefficient of a 10 mm pipe in the SIS structure degradation range:

$$\lambda = -0.349 + 0.106 \cdot 10^{-5} \cdot q_v + 0.3 \cdot 10^{-8} \cdot q_v^2 \quad (5)$$

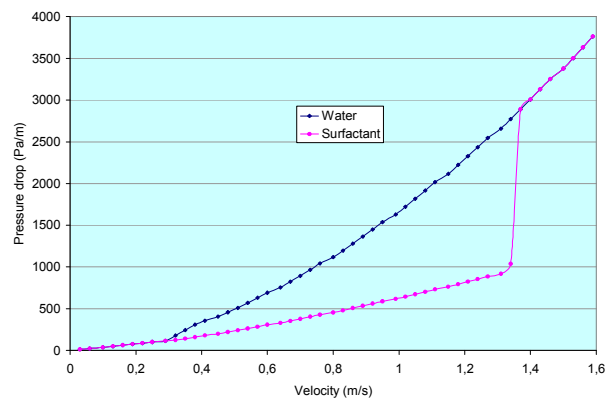


Fig. 7: Pressure drop per meter in a 10 mm pipe

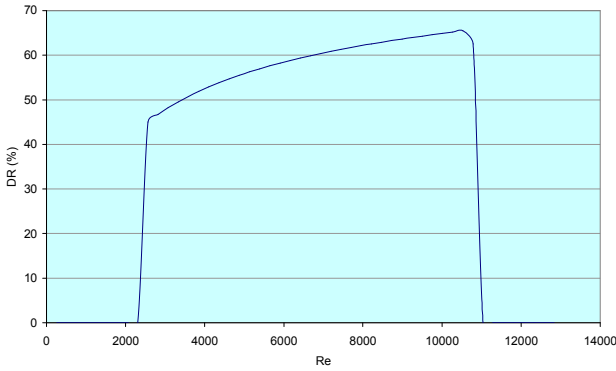


Fig. 8: Drag reduction rate (DR) depending on Re number in a 10 mm pipe

The polynomial for the computation of the drag coefficient of a 20 mm pipe in the SIS structure degradation range:

$$\lambda = 22.7 - 0.405 \cdot 10^{-2} \cdot q_v + 0.181 \cdot 10^{-6} \cdot q_v^2 \quad (6)$$

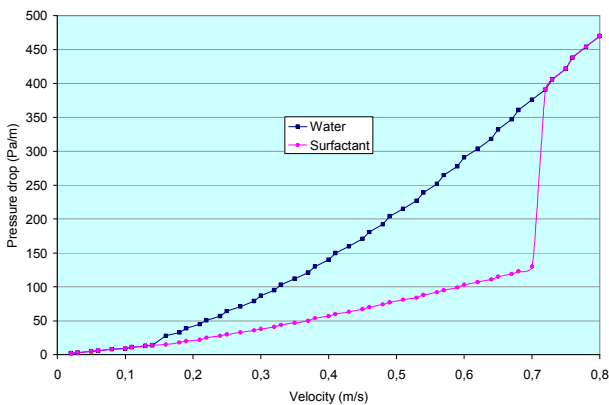


Fig. 9: Pressure drop per Velocity in a 20 mm pipe

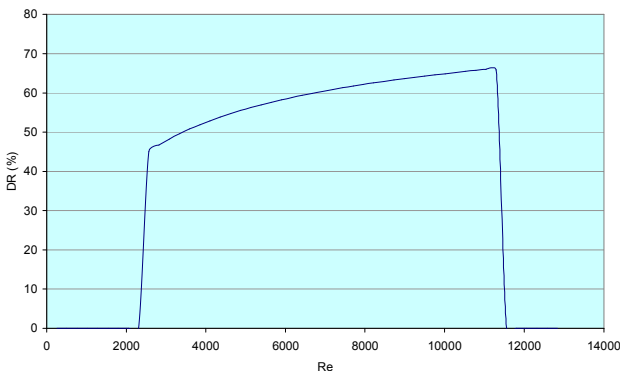


Fig. 10: Drag reduction rate (DR) depending on Re number in a 20 mm pipe

6 Conclusion

The application of additives in pipe-flow systems allows drag reduction and consequently lower

energy consumption or improved system performance [3]. Two groups of chemical compounds, i.e. polymers and surfactants represent commercially available additives. Contrary to polymers, which are irreversibly degraded at high shear stress, the mechanical degradation of surfactants is reversible.

This ability of surface active additives allows their application in circular distribution pipe systems whose dimensions should be such as not to exceed the critical Re number value, since high shear stresses lead to the degradation of the intermolecular SIS structure of surfactant micelles and the drag reduction effect disappears.

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