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INFLUENCE OF POLYMER-SURFACTANT ADDITIVES ON PRESSURE DROPS IN PIPE FLOW

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Abstract. The aim of this paper was to present the possibility to enhance the drag reduction effect in pipe flow by simultaneous addition of high molecular polymers and surfactants to the transported liquid medium.

The mechanism of drag reduction by polymeric and micellar aggregates was presented. Qualitative analysis of polymer and micellar additives influence on the shape and character of flow resistance curves was performed. Multicomponent polymer-micellar solution flow resistance curves were compared with the appropriate single additive polymer or surfactant solution flow resistance curves.

The results indicate that the presence of polymer-micellar aggregates causes flow laminarization in the initial phase of turbulent flow, leading to the extension of the stable transition zone. Simultaneous addition of surfactant with salt and a high molecular polymer to the solvent significantly reduces mechanical degradation of the internal structure of polymer-micellar solution.

Keywords. Drag reduction, flow resistance, internal friction, pipe flow, polymer, surfactant, aggregate.

INTRODUCTION

The discovery of the abnormal drag reduction phenomenon in pipe flow by adding trace amounts of high molecular weight polymers or surfactants to the solvent was an inspiring starting point in researches of hydraulic transport possibilities with simultaneous significant cost reduction. Within the framework of the scientific discipline of technical rheology, a large-scale study was performed, whose aim was either reducing the cost of the liquid flow in the pipeline or increasing the flow efficiency/flow rate without the necessity of increasing the power demand. It is commonly known that drag reduction effect is caused by high molecular weight polymers, surfactants, fine solid particles and fibrous structure additives [1-7].

In scientific research as well as in engineering applications, the most commonly used drag reduction agents are high molecular weight polymers and surfactants. Adding even a small amount of these substances to the transported solvent induces significant and extremely advantageous, from the energetic point of view, reductions of pressure losses caused by fluid internal friction in the turbulent range of flow. This results in a significant increase in the flow rate without the necessity of increasing the power demand, or vice versa – to reduce the power demand while maintaining a constant flow rate. Therefore, it provides large potential possibilities for application of this effect in different industry branches, particularly in oil industry [3, 8], or in heating [9], fire-fighting [10], transport of slurries, sludge and brines [2, 11], while increasing the efficiency of sewerage and anti-flood systems in time of heavy rainfall [12]. The drag reduction effect caused by polymers was utilized in designing an industrial installation for crude oil transportation in Norway, USA and India [2, 3, 8].

The new internal structure, which occurs when special additives are introduced into the solution, was perceived to be the cause of the drag reduction effect. The addition of surfactants agents into the solvent results in micelles structure formation. In case of application of a high molecular weight polymer as a drag reducing additive, formation of macromolecules is observed.

At no motion condition, when the fluid is at rest, the above mentioned structures are chaotic. Only during fluid flow shearing, both macromolecules and micelles start to arrange in a characteristic orientation, in accordance with the principle of minimum resistance. Solution concentrations are very small. In case of high molecular polymers it is order of magnitude of several or several dozen of ppm, and for surfactants it is order of tenths of mM/dm^3. Furthermore, in order to obtain more favourable conditions for the formation of micelles, small amounts of electrolytes are added into the solution. Salts (e.g. sodium salicylate or sodium bromide) or alcohols (e.g. α – naphthol) are the typically used electrolytes.

The effect of drag reduction of flow by high molecular polymers or surfactants has also some limitations resulting from the properties of additives. The main disadvantage of high molecular polymers is their susceptibility to mechanical and thermal degradation. In case of surfactant solutions it is a certain critical Reynolds number. When exceeded, micelles orientation is lost, and the drag reduction effect collapses. The number depends not only on the pipe's diameter, but also on the solution concentration.

An important distinguishing factor for the phenomenon of drag reduction caused by surfactant additives comparing to drag reduction effect induced by high molecular polymers is the reversibility of solution degradation [1, 13]. In case where the value of Re number falls below critical Re value, the drag reduction effect occurs again. Moreover, the drag reduction effect in surfactant solution is not weakened in time of long-term liquid pumping comparing to the polymer solution. This is a great advantage for the transport of liquids over long distances.

INFLUENCE OF ANALYSED ADDITIVES INTERNAL STRUCTURE ON PIPE FLOW RESISTANCE

CHAIN STRUCTURE OF POLYMER MACROMOLECULES

Adding a small amount of a polymer to the solvent (usually water) causes a change of the internal structure of the solution creating so called macromolecules. Due to the characteristic chain structure of polymers in solutions, macromolecules form different conformations. They can take shape of randomly coiled spherical structures or stretched elastic threads. Macromolecules in a solution of low concentration (c<0,1%) form spherical polymer coils - fig.1(a). Their influence on the rheological properties of the solution is negligible. Rheological changes are noticed only when the polymer macromolecules take the form of elastic fibres – fig.1(b).

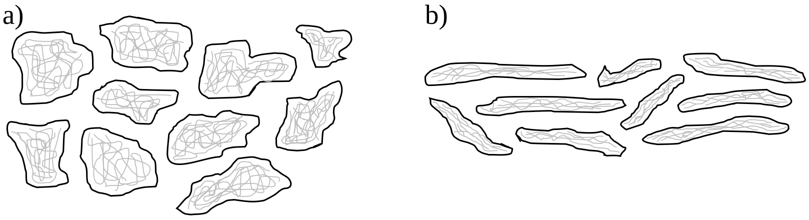

Figure 1. Polymer macromolecules: a) in shape of coiled spherical balls, b) in shape of elastic threads

This effect occurs upon increasing the polymer concentration in the solution. Such a solution exhibits non-Newtonian and viscoelastic characteristics. Changes in its viscosity are also observable. By the application of slight shear stress to the solution induced by simple solution shearing, the polymer threads are stretched and start to arrange in a characteristic orientation, in accordance with the principle of minimum resistance – fig.2.

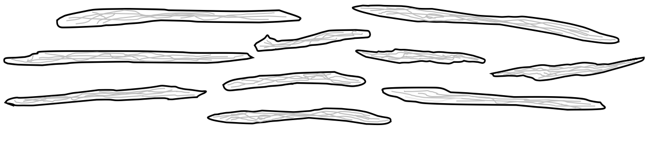

Figure 2. Macromolecules of polymer elongated under the shear stress

Molecules with such conformation contribute to velocity fluctuation suppression in turbulent range of flow causing its laminarization and reducing fluid flow pressure losses at the same time. Having exceeded a certain critical value of shear stress at pipe wall the polymer chains are ripped apart and an irreversible degradation of polymer macromolecule structure is observed [5,7,14]. It should also be noted that the polymer macromolecules are also susceptible to irreversible thermal degradation for solution temperatures exceeding 40°C [1]. Due to the mechanical and thermal degradation of the polymer solution, the drag reduction effect gradually vanishes.

The effect of abnormally reduced friction losses in turbulent flow can appear in different ranges of the Reynolds number, while the shape and location of friction losses curve depends not only on the Reynolds number definition, but most of all on the pipe diameter value, solution concentration, type of the drag reducer applied, its molecular structure and conformation, intermolecular bonds of the applied chemical additive, its molecular weight, rate of solution degradation, etc.

The source of the Toms effect is lying in different rheological properties of Toms liquid comparing to the properties of purely viscous liquid. The presence of elastic polymer macromolecules in the solvent leads to a locally distorted averaged linear velocity profile and a deformation of power of the low empirical Ostwald - de Waele formula [7]. It allows to assume the real flow of the polymer solution to the flow of the so-called *pseudo purely viscous liquid*, defined as a *purely viscous* suspension of stiff molecules with dimensions of nondeformed polymer macromolecules. A new hypothesis [9] was formulated as a consequence of comparing the distorted Toms liquid velocity profiles and the corresponding velocity profiles of the pseudo purely viscous liquid. According to this hypothesis, during the flow of the polymer solution an additional negative shear stress is observed. It is induced by the polymer's elastic properties and the reduction of power law consistency constant value associated with this effect. The hypothesis of additional shear stress explains all effects accompanying the Toms phenomenon.

MICELLAR STRUCTURE OF SURFACTANTS

The drag reduction effect caused by small amounts of surfactant addition is particularly interesting from a cognitive point of view, as well as its utilitarian character. Unlike the Toms effect, it is not susceptible to mechanical degradation [1, 2, 13]. Surfactants added to the solvent (usually water) create a low concentrated solution. When the surfactant concentration exceeds a certain critical level of concentration, individual surfactant molecules start to organize into new structures called *micelles*. This concentration of structure transition is called *first critical micelle concentration CMC*. The so-formed single micelle consists of several dozen to several thousand individual surfactant molecules. The drag reduction effect in the flow of such a micellar solution takes place only when cylindrical threadlike/rodlike micelles are present in the solution – fig. 3

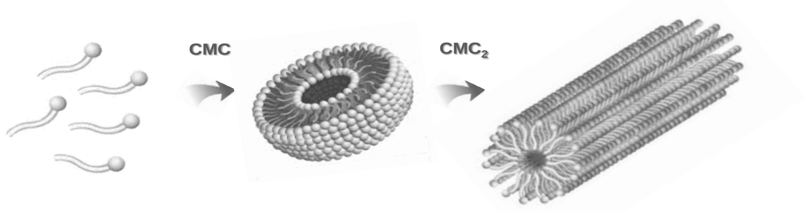

Figure 3. Formation of spherical and cylindrical/threadlike micelle structures in aqueous solution of surfactant

The length of rodlike micelles is in the range of 25÷200[nm], and their diameter is in the range of 2÷5[nm]. The time of micelles formation varies from milliseconds to hours. Threadlike micelles are formed when the surfactant concentration exceeds *second critical micelle concentration* CMC_2. Both *CMC* and CMC_2 values depend on the type of surfactant and temperature – fig.4.

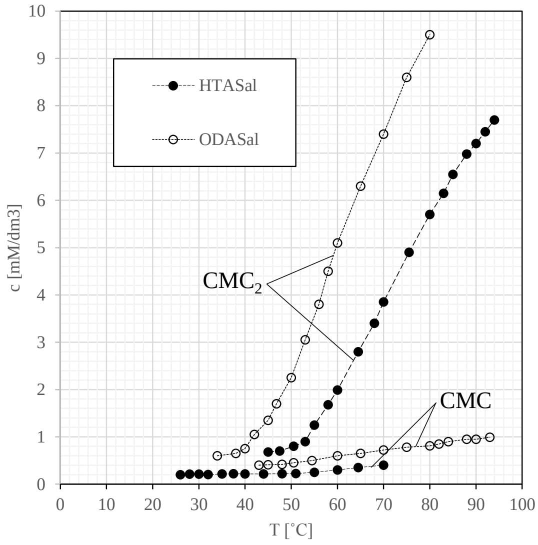

Figure 4. Critical concentration CMC and CMC_2 of aqueous solution of surfactant in temperature function [15]

Reformation of spherical micelles into threadlike micelles can be induced by adding a small amount of electrolytes (e.g. salts or alcohols) [15, 16].

Under the shear stress caused by the solution flow, the rodlike micelles start to arrange in a characteristic orientation which produces the drag reduction effect. According to [17] the drag reduction effect is caused by the viscosity anisotropy in the boundary layer. On the other hand, in [13-15] the friction losses reduction effect is explained by the characteristic orientation of threadlike micelles in the flow direction.

Under the shear stress micelles are untangled and oriented toward the flow direction. It impedes the development and relocation of vortices in the direction perpendicular to the flow direction, thereby decreasing the amplitude and frequency of turbulent fluctuation. Hence turbulence intensity and turbulent energy dissipation are reduced.

Beyond a certain critical value of the shear stress on the wall the drag reduction effect disappears. Micelles lose orientation in the flow direction. Comparing to a polymer solution, a micellar solution is insusceptible to mechanical and thermal degradation [1].

According to the functional relationship of the friction coefficient derived in [13,14], after exceeding a certain critical Reynolds number value a sudden increase in the flow resistance is observed. This critical value of Re number also defines the flow conditions at which the maximal drag reduction is obtained. The presented concept assumes that the drag reduction effect appears only in presence of threadlike micelles. In the laminar flow micelles arrange in the orientation parallel to the main flow direction. The flow resistance in this range of flow can be assigned using the same equations, which are valid for the laminar flow of non-Newtonian purely viscous liquid. Exceeding *the first critical Reynolds number* causes appearance of the laminar flow disturbances which are suppressed by threadlike micelles oriented in the flow direction.

The flow resistance in this range of flow is only slightly larger than the flow resistance in the laminar range and significantly smaller comparing to the flow resistance in the turbulent zone. Exceeding *the second critical Reynolds number* leads to the loss of rodlike micelles specific orientation. Micelles then coil into a globular shape structure. This causes a sudden increase in the flow resistance and the disappearance of the drag reduction effect.

EXPERIMENTAL ANALYSES OF FLOW RESISTANCE CURVES

Measurements were performed using modern capillary-pipe rheometer, designed and constructed in the Division of Fluid Mechanics laboratory at the Cracow University of Technology [18]. After the preliminary study, the following drag reducers were used for experimental analysis: the non-ionic polymer with high molecular weight $M_v=8\cdot10^6$ –

poly(ethylene oxide) – $[CH_2\ CH_2\ O]_n$ (PEO) and the cationic surfactant – cetyltrimetyl ammonium bromide – $[CH_3(CH_2)_{i5}N(CH_3)_3]$+Br~ (CTAB).

In order to lower the CMC value, salt sodium salicylate $C_7H_5NaO_3$ (NaSal) was used. Distilled water was used as the solvent.

After the application of the appropriate additives to the solvent, solutions were mixed gently so as not to cause mechanical degradation of polymer chains. Mixtures were left at rest for 24 hours before measurements. Adiabatic steady flow of homogenous solutions were examined in 8 different straight pipes with diameters between 1.8[mm] and 21[mm], in temperature equal to 25˚C.

In order to perform a better interpretation of the effect of the simultaneous addition of the polymer, the surfactant and salt, comparing to the adequate addition of pure polymer or pure surfactant, measurement data was presented in the modified system of “pseudorheostable” numbers [Re_M, c_{fM}], and described by formulas (1) and (2) [7]:

$$\mathbf{c}_{fM} = \frac{\frac{D\Delta p}{4L}}{\frac{\rho u_m^2}{2}}\left[\frac{2(n+1)}{3n+1}\right]^{2,5} \tag{1}$$

$$\mathbf{Re}_{\mathbf{M}} = \frac{D^n u_m^{2-n}\rho}{K\left(\frac{3n+1}{4n}\right)^n 8^{n-1}}\left[\frac{2(n+1)}{3n+1}\right]^{-2,5} \tag{2}$$

where: D is pipe diameter, ρ is fluid density and n and K are respectively flow index and consistency constant of power-law fluid model.

The flow resistance curves of rheostable (purely viscous) non-Newtonian fluids in such defined dimensionless numbers system are boiled down to a single curve – in the whole range of the modified Reynolds number (2) – identical to the classical Newtonian curve described in the laminar range by Fanning equation and in the turbulent flow by Blasius formula. The choice of such a coordinate system was dictated additionally by the fact that it facilitates the identification and description of the characteristic drag reduction flow zones. In this modified system of pseudorheostable numbers [Re_M, c_{fM}] each deviation of the experimental flow resistance curve which indicates abnormal drag reduction from pseudorheostable Blasius curve, allows the identification of specific additives' influence (polymers or/and surfactants with salt) on a range of analyses of the drag reduction effect.

Representative flow resistance curves of the analysed polymer-micellar solution and the corresponding purely polymer solution and purely micellar solution are presented in fig.5.

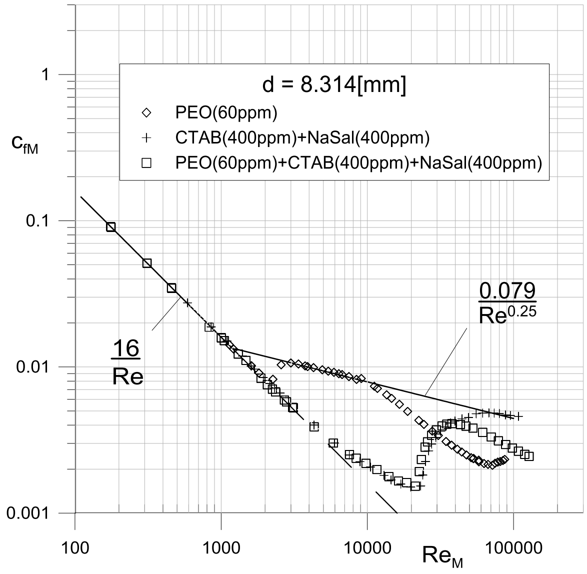

Figure 5. The flow resistance curves of polymer, surfactant and polymer-surfactant water solutions, defined in the system of cardinal numbers (1) and (2)

The analysis of presented flow resistance curves indicates that in the laminar range of flow simultaneous addition of polymer and surfactant to the solvent causes inconsiderable increase of flow resistance and significant extension of the stable transitional zone of flow. The existence of the third significantly extended reduction zone is also observed, in which the viscoelastic properties of the solution are the dominant factor. It is particularly well illustrated by fig.6.

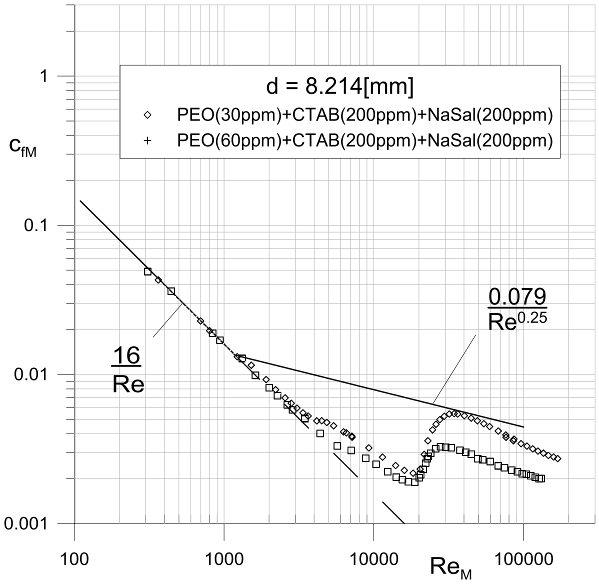

Figure 6. Comparison of the flow resistance curves of polymer-surfactant water solutions for different polymer concentration

In comparison to a purely micellar solution, the collapse of drag reduction is normally observed in this region. It should also be noted that addition to the micellar solution of even small amounts of high molecular weight polymer (about 10[ppm]) causes a reduction of the non-Newtonian properties of the solution.

The results of drag reduction measurements analysis indicate the effect of pipe diameter influence on drag reduction efficiency. Increasing the pipe diameter d results in clear extension of the stable transitional zone towards higher values of the Reynolds number. Moreover, decreasing the pipe diameter value d results in an increase of the drag reduction effect in the third additional turbulent range of flow – fig.7.

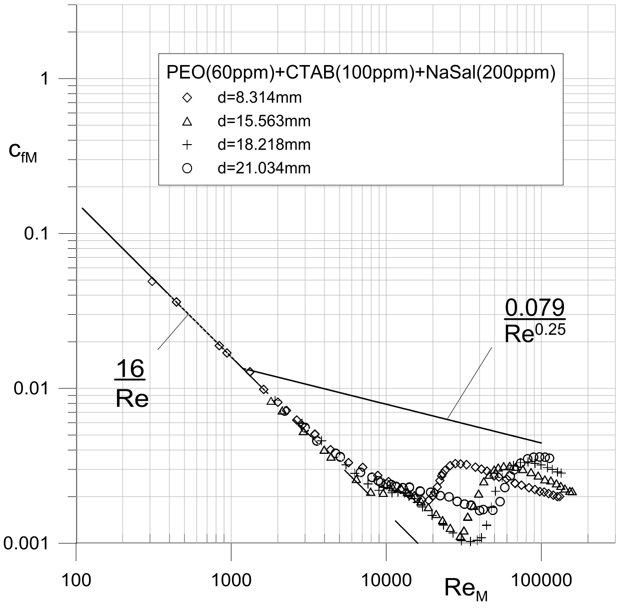

Figure 7. Pipe diameter effect on the flow resistance curves of polymer-surfactant water solutions

HYPOTETIC MECHANIZM OF DRAG REDUCTION CAUSED BY POLYMER-MICELLAR ADDITIVES

Simultaneous introduction of small amounts of polymer and surfactant additives to the solvent provides initiation of micellarization process at much lower concentration, comparing CMC. This concentration is called *the critical aggregation concentration* (CAC) [13, 19].

In case of an ionic surfactant mixed with a counter charged polyelectrolyte only a small part of the polyelectrolyte is adsorbed by the surfaces of the micelles. Furthermore, CAC has a lower order of magnitude than the original CMC due to the following facts:

- electrostatic interaction occurs between the electrolyte and the surface of the micelles,
- no concentration of surfactant counter-ions on the micelles surface appears; their place is taken by the polyelectrolyte,
- highly charged polyelectrolytes can trigger a certain amount of concentrated counter-ions, as they combine with the micelles.

In the initial state, there is a long highly charged polyelectrolyte chain with a great number of concentrated counter-ions. The final state of the mixture has single threadlike micelles with a part of polymer macromolecule chain coiled around rigid micelles – fig. 8(a). According to [13, 19, 20], these molecules form the so-called *aggregates*.

Such newly created polymer-micellar solution can be characterized by a lower susceptibility to mechanical degradation during flow or its degradation can be almost invisible. Schematically illustrated aggregates (fig. 8(a)) subjected to the shear stress take orientations consistent with the aforementioned principle of minimum resistance – fig. 8(b). With increasing value of the Reynolds number, internal friction forces stretch and extend the aggregates leading to the laminarization of the initial phase of the turbulent flow.

Therefore, it may be hypothesized that the rigid rodlike micelles, which create the core of the aggregates, are responsible for reducing the flow resistance in the extended transitional zone between the laminar and turbulent flow.

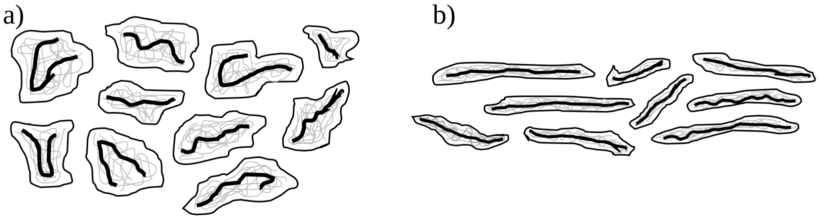

Figure 8. Polymer-micellar aggregate: a) in shape of spherical balls, b) during shear stress action

The aggregates and micelles are responsible for transmission of internal friction in the liquid. The value of the critical Reynolds number for which the transition to the turbulent zone is observed is greater for polymer-micellar solutions. This means that the stable transition zone is extended. The reason for such behaviour can be the partial disintegration of aggregates to original forms, i.e. micelles (formed from the surfactant) and macromolecules (formed from the polymer) due to a significant increase of the shear rate. From this moment, both micelles and macromolecules interact separately on the transported solution causing a further drag reduction effect. Passing further in the turbulent range of flow micelles lose their orientation and no longer have a major impact on the drag reduction. A key role is played in this zone by the polymer. Not having undergone an earlier degradation, the polymer macromolecules still cause the low reduction.

In drag reduction caused by the use of polymer-surfactant solution, one cannot talk about the so-called *collapse of the drag reduction.* It occurs permanently over a wide range of Reynolds numbers. In the turbulent zone polymer macromolecules undergo a certain mechanical degradation. Decreasing the shear rate leads to the reconstruction of the solution's internal structure. As a result of electrostatic interaction, the recreated micelles are combined with the polymer chains by coiling around them. These chains are much shorter and such newly created aggregates do not have the same rheological properties as the original ones. This results in a slight increase of the flow resistance in comparison with a freshly prepared solution.

CONCLUSIONS

The experimental analysis of the influence of simultaneous addition of polymer and surfactant additives to a water solvent indicates that in the laminar range of flow the simultaneous addition of a polymer and a surfactant to the solvent causes an inconsiderable increase of the flow resistance comparing to the pure solvent's flow resistance. A significant extension of the stable transitional zone of flow has been observed, however. The analysis of experimental flow resistance curves (fig.5–fig.7) allows to observe the existence of the third significantly extended reduction zone in the turbulent range of flow. In this zone the viscoelastic properties of the solution are the dominant factor. It is found that in this zone the drag reduction is influenced by the polymer concentration in the solvent. The higher concentration of polymer in the solution is applied, the greater drag reduction in the flow is obtained.

The results of drag reduction measurements analysis indicate the effect of the pipe diameter change on the drag reduction. Increasing the pipe diameter d results in clear extension of the stable transitional zone towards higher values of the Reynolds number, while decreasing the pipe diameter value induces an increase of the drag reduction effect in the third additional turbulent range of flow.

Simultaneous addition of a polymer and a surfactant with salt significantly reduces the mechanical degradation of the polymer-micellar solution's internal structure.

The comparison analysis indicates that polymer-micellar solutions combine and intensify the positive features of their pure polymer and micellar equivalents. Moreover, they provide efficient reduction of flow resistance in a wider range of the Reynolds number.

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