Comparative assessment of drag reduction efficiencies of polymer solutions and surfactants at low temperatures

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Abstract. The antiturbulent efficiency of solutions of high molecular weight polymers and that of micellar systems of surfactants are compared. The effect of the structural organization of polymer solutions and colloidal systems on their antiturbulent efficiency is shown. Hydrodynamic and physicochemical approaches are used to interpret the experimental results. It is shown that the use of polymers as drag reducing agents in main oil pipelines is more preferable at low liquid temperatures in northern latitudes (the Arctic).

1. Introduction

By dissolving the polymers, homogeneous solutions are formed, which have some properties of colloid systems (low diffusion rate of polymer macromolecules with immobilized solvent and dispersed phase particles of colloid systems, small values of osmotic pressure, etc.). This can be explained by similarity of their structural-mechanical characteristics and the large size of polymer molecules and micelles (~100·10⁻⁹ m), in comparison with the small molecular size (~1·10⁻⁹ m) of the dispersion medium (solvent).

One more feature that binds colloid particles with macromolecules is their ability to reduce hydrodynamic resistance. This phenomenon, called the Toms effect (TE), manifests in increasing turbulent flow rate of the polymer solutions in comparison with the flow rate of the initial solvent [1]. It has also been found that colloid systems, having aqueous or hydrocarbon dispersion medium, are also capable to reduce hydrodynamic resistance.

The Toms effect is currently widely used in various fields, for example, in the oil industry. The oil-soluble polymers of different chemical nature (polyisoprene, polybutadiene, polyisobutylene, polyolefins, etc.) are used to intensify the industrial pumping of oil and petroleum products. The turbulent flow solutions of hydrocarbon liquids regularities are of practical and theoretical interest as well.

The aim of this paper is to establish functional connections between hydrodynamic flow parameters, physical and chemical properties of the solutions, their structure and antiturbulent efficiency of polymer solutions and surface-active substances (SAS). Transferring the TE on the quantitative level will allow us to estimate a priori the efficiency of antiturbulent additives.
2. Experimental section
Laminar flow of liquid in the cylindrical channel becomes turbulent at a Reynolds Number that is greater than the critical value \( Re_c = 2UR_w \nu^{-1} \geq 2300 \). Changing a flow regime is accompanied by a coefficient increase in hydrodynamic resistance \( \lambda \). This leads to the energy expenditures growth for pumping liquids in the turbulent regime. Regardless of the flow regime, the functional linkage between the volume flow rate \( (Q) \) and set pressure drop \( (\Delta P) \) is described by the Darcy-Weisbach equation

\[
\Delta P = \frac{\lambda}{4\pi^2 R_w} \rho \nu^2,
\]

where \( Q = \pi R^2 U \) – volume flow rate; \( U \) – the average linear liquid velocity; \( \Delta P = P_1 - P_2 \) – friction pressure drop in the pipe with the length \( L \) and radius \( R_w \); \( \rho \) – the liquid density; \( \nu = \eta / \rho \) – dynamic and kinematic viscosity, respectively.

The fluidity experiment testing of various liquids (one-component solvents, polymer solutions and colloid systems) has been carried out using a laboratory turbulent rheometer (tube radius \( R_w = 1.1 \times 10^{-3} \) m, length \( L = 0.8 \) m). A turbulent rheometer is similar in design to a capillary viscometer and that allows us to take measurements in laminar and turbulent flow regime [2]. By passing the liquid through a cylindrical channel during the experiment, the turbulent rheometer measured volume flow rate \( Q \) and pressure drop \( \Delta P \). The viscosity values, density, and temperature of solutions and solvents are known prior to the experiments. The polycarbonate solutions (a repeating unit formula of the polymer chain \((-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-)_n\) in petrol (concentration \( C = 100 \) g/m\(^3\) and \( C = 200 \) g/m\(^3\), a molecular mass of \( M_r = 1.1 \times 10^6 \)) and solutions of oil-soluble SAS (\( C = 1000 \) g/m\(^3\), and \( C = 2000 \) g/m\(^3\)) have been investigated. As SAS, aluminum salts of higher carboxylic acids (formula \( \text{Al(OH}(\text{RCOO})_2)_n \), where \( R = (\text{CH}_2)_{10-20} \) have been used. These SAS are also called «aluminum soap» (Al-soap). The results of hydrodynamic experiments (Figure 1) are represented as a variation \( \lambda = f(Re) \). The analysis of experimental data and variation \( \lambda = f(Re) \) showed that the coefficients of hydrodynamic resistance \( \lambda \) in laminar flow region for Newtonian liquids (water, oil, gasoline, etc.) lie on the Poiseuille curve (Figure 1, curve 1). The transition to turbulent flow regime occurs in Reynolds number range from \( Re \cdot 10^{-3} = 2,0 - 3,0 \). It is accompanied by sensible increase in hydrodynamic resistance and the transition magnitude values \( \lambda \) from the Poiseuille curve onto the empirical Blasius curve (Figure 1, curve 2), typical for the flow of Newtonian liquids at \( Re \cdot 10^{-3} > 0,3 \).

Figure 1 shows that the current non-Newtonian liquids (polycarbonate solutions and Al-soap) in a turbulent regime reduce the drag coefficient \( \lambda \) (the Toms effect).
For laminar flow regime, values $\lambda$ for the investigated solutions (as for Newtonian liquids) lie on the Poiseuille curve (curve 1), but for turbulent flow regime values $\lambda$ are located in the area (curves 3-7), bounded by Blasius curve above, and the hypothetical extension of the Poiseuille curve in turbulent flow below. Thus, the drag reduction coefficient $\lambda$ is acceptable only for the turbulent regime. The greater the concentration ($C$) of a dissolved additive and higher a molecular weight ($M_r$) of the polymer sample is, the greater a reducing effect $\lambda$ is.

It should be noticed, that minimum values of drag coefficient $\lambda$ of polymer solutions turbulent flow, are limited by the Virk asymptote $\lambda = 2.36 \cdot Re^{-0.58}$. It is shown, that under no circumstances they may fall within the area below the Poiseuille curve in the turbulent region (Figure 1, curve 1). In other words, the effect of antiturbulent additives comes up to a partial flow laminarization.

The Toms effect ($DR, \%$) is accepted to estimate quantitatively by relative change in the drag coefficient, expressed as a percentage:

$$DR, \% = \frac{\lambda_S - \lambda_P}{\lambda_S} \cdot 100\%,$$

where $\lambda_S$– the drag coefficient of a the pure solvent; $\lambda_P$– the drag coefficient of the solution with the additive.

The coefficient $\lambda_S$ and $\lambda_P$ can be calculated from the transformed Darcy-Weisbach formula

$$\lambda = \frac{4\pi^2 R_W^5}{L \rho} \frac{\Delta P}{Q^2}.$$

In accordance with the Darcy-Weisbach equation (1) a reduction in the drag coefficient $\lambda$ provided $\Delta P = const$ should be accompanied by an increase in the volume flow of solution additives $Q_p$ as compared to a rate of liquid without additives $Q_S$ on the value $\Delta Q = Q_p - Q_S$. Using these experimentally determined values one can calculate the Toms effect ($\Delta P = const$) in the expression (3):

$$DR, \% = \left[1 - \frac{Q_S^2}{(Q_S + \Delta Q)^2}\right] \cdot 100\%.$$

The effect size of drag reduction with the Reynolds number increase approaches to its maximum value $DR_{MAX} \sim 75\%$. The antiturbulent additives Baker, Necadd, X-Pand, Liquid Power on the base of oil-soluble high molecular weight polymers ($M_r \sim 10 \cdot 10^6$) (which are currently widely used in the world of industrial oil pumping) have such a high effect size. It is enough to add 5-10 grams (5-10 ppm) of polymer per 1 tonne of oil to achieve the maxi effect size.

To compare the efficiency of different antiturbulent additives, one can use a graph variation of the effect size on the additives concentration $DR = f(C)$. As it seen from a typical figure, 2, the effect size increases rapidly and reaches its maxi value ($DR_{MAX}$) at an «optimal» concentration ($C_{opt}$) when the additive concentration increase occurs. By further concentration increasing, the effect is being reduced. Figure 2 shows that it is required 10 times less polyisoprene ($C_{opt, 1} = 200 \text{ g/m}^3$), than the oil-soluble SAS ($C_{opt, 2} = 2000 \text{ g/m}^3$) for the maxi effect size. The smaller the value of «optimal» concentration is, the more effective antiturbulent additives are.

For this reason, antiturbulent additives based on polymers, versus SAS, find wide application in pipeline transportation of crude oil.

**Figure 2.** Variation of the Toms effect magnitude and antiturbulent additives concentration (polyisoprene solutions (1) and SAS (2) in gasoline).
A significant drawback of the formulas (2) and (3) is the absence of strongly expressed functional dependence of the effect (DR) on the physicochemical properties of the solvent and solutions thereof. Moreover, these expressions do not allow us to forecast the effect size a priori.

3. Physicochemical description of the turbulent flow of polymer solutions and colloidal systems

To explain the reason of the different antiturbulent efficiency for polymers and SAS, we should drill down the structure of polymer solutions and colloid systems. The macromolecules, which consist of a large number of monomeric units, linked by covalent bonds, have a specific structure in a solution. The polymer chains are coiled in loose skeins, which volume depends on molar mass of the polymer (M) and intrinsic viscosity [\eta] of polymer solution. It can be calculated by the formula

$$V_w = M[\eta]/N_A,$$

which is a consequence of the well-known equation of Fox-Flory

$$h M^{\frac{1}{2}} = M[\eta]/\Phi.$$  

The coils of macromolecules always hold within themselves a certain amount of a solvent. Each monomeric unit of a polymer chain, depending on the thermodynamic quality of the solvent, is surrounded by dozens or even hundreds of the solvent molecules. According to the geometric dimensions, the solvent molecules are comparable to monomeric units. In the volume of the macromolecular coil with immobilized solvent at a fraction of the polymer chain dimensions, the solvent molecules are comparable to monomeric units. In the volume of the macromolecular coil with immobilized solvent at a fraction of the polymer chain dimensions, the solvent molecules are comparable to monomeric units. In the volume of the macromolecular coil with immobilized solvent at a fraction of the polymer chain dimensions, the solvent molecules are comparable to monomeric units.

The coils elasticity coefficient \(G\) in the equation (5) is crucial, which characterizes the elastic properties of macromolecular coils with immobilized solvent. Therefore, the smaller the elasticity of macromolecular coils is, the greater the volumetric speed gain of polymer solution turbulent flow is, in
comparison with the flow rate of the pure solvent. In its turn, the lower the coils elasticity is, the more
their volumes (molecular mass) are. The experimental data on the dependence of volumetric speed gain
($\Delta Q$) on various parameters ($\tau_w, T, C$), which confirm the validity of the theoretical equation (5) are
shown in paper.\(^5\)

The volume flow increment $\Delta Q$ is included in the equation (3), so the increase in this value must be
accompanied by an increase in the effect of drag reduction $DR$. The function of $\Delta Q = f(C)$, as well as
the dependence of $DR = f(C)$ for dilute solutions, with concentration growth, is increased according to
linear law, reaching its maximum at the same value of «optimal» concentration ($C_{opt}$) and then slowly
decreases in the concentrated solutions areas.\(^5\)

It is known that the properties of polymer solutions are determined not by the value of the
concentration of dissolved polymer ($C$), but the value of the volume fraction $\psi = \frac{\sum V_k}{V_o}$ occupied
by all the macromolecular coils in the total volume of the $V_o$. The structure of the polymer solution changes
depending on the volume fraction of macromolecular coils if the dissolved polymer concentration increases.

Figure 3 schematically demonstrates polymer solutions of different concentrations. The
macromolecules are separated by solvent layers and have unperturbed equilibrium dimensions ($V_k = const$
) in the dilute solution with volume fraction of coils smaller than one (Figure 3, state 1). «Maximally dense packing principle» is realized with increasing concentration of macromolecules in a
certain moment (Figure 3, condition 2), where in the volume fraction of the coils in the solution becomes
approximately equal to one $\psi \approx 1$. The macromolecular coils with immobilized solvent are in close
contact, but they do not deform each other yet. This concentration is called «optimal». With further
concentration increase the coils begin to discriminate against each other, i.e. become compressed and
reduced in volume. In the result we observe the polymer component content increase in the coil and its
rigidity increases as well. Thus, the changes of the solution structure should lead to a change in its fluidity
that is predicted by the equation (5) and confirmed experimentally.

In a dilute solution ($\psi << 1$) due to the low concentrations ($C$) value of $C \cdot [\eta] << 1$, and then the
denominator of the formula $\Psi = C \cdot [\eta]/(1 + C \cdot [\eta])$ in the equation (5) is equal to one. Consequently,
a velocity increment’s linear dependence on concentration should be performed for the dilute solution
$\Delta Q = \frac{\pi R_w^2 \tau_w}{\sqrt{\rho G}} [\eta] C = const \cdot C$.

There is a compression of coils and increase of their resilience in the concentrated polymer solution
(Figure 3, state 3) for $C \cdot [\eta] >> 1$ and $\psi = 1$. This should be accompanied by a decrease in the volume flow increment
proportionally $G^{1/2}$, i.e. the monotonous drop effect takes place
in accordance with $\Delta Q = \frac{\pi R_w^2 \tau_w}{\sqrt{\rho G}} = \frac{const}{\sqrt{G}}$.

**Figure 3.** The structure of the polymer solution: 1 – a dilute solution ($0 < \Psi < 1; C < C_{opt}, V_k = const$);
2 – an «optimal» concentration solution ($\Psi \approx 1; C = C_{opt}, G_1 V_k = const; G_2 \approx G_1$);
3 – a concentrated solution ($\Psi = 1; C > C_{opt}, V_j < V_k; G_3 > G_1 \approx G_2$)

These theoretical considerations are confirmed experimentally for all known twines a polymer – a
solvent. The «optimal» concentration $C_{opt}$ differs for various polymers. The greater the volume of coils
is, the less $C_{opt}$ is, and it is more profit able to use high molecular weight polymer sample in industrial
practice.

The main drawback of high-molecular polymers ($M_t > 1 \cdot 10^6$) is their irreversible destruction when
they are injected into the flow with high shear stress if they are used as drag reducing agents. Breaking
covalent links between adjacent monomeric units is accompanied by a decrease in polymer chain length
and coil volume, which reduces the Toms effect until its complete disappearance [5]. The polymer
destruction is signified during liquids passage through industrial pumps on main product pipelines. So,
it is necessary to add a fresh portion of antiturbulent additives after the passage of liquids through the pumping stations.

A somewhat different picture is observed in colloid systems. Surface-active substances dispersed (dissolved) up to separate molecules of relatively small molecular weight \((M_\text{r} \approx 200 - 500)\) in dilute solutions. By increasing the content of SAS and after reaching the critical concentration for micelle formation (CCM) in the solution, the aggregates are formed. The aggregates composed of a large number of SAS molecules, which are structured in ordered associates (micelles). Consequently, achieving CCM, the homogeneous SAS solutions drop into heterogeneous systems. It was established experimentally that the hydrodynamic resistance may reduce SAS solutions only after reaching the CCM, i.e. the concentrated solutions, where large enough micelles have already been formed.

Surface-active substances molecules possess a polar group and a non-polar hydrocarbon radical, i.e. have a diphilic structure. Therefore, the micelle structure depends on the polarity of dispersing medium. For example, in a hydrocarbon (non-polar) dispersing medium the polar functional groups of the SAS molecules are located in the micelle core and linked by intermolecular forces (the ordering and strength of arising associates depend on them). The hydrocarbon «tails» of diphilic SAS molecules on the micelleperiphery provide solubility in the nonpolar medium. The strength of such supramolecular structures is low because of the low intermolecular interaction energy. But due to the tight convergence of SAS molecules in the formed micelles, their coefficient of elasticity \(G_{\text{SAS}}\) is much greater than the polymeric macromolecular coils coefficient of elasticity \(G_{\text{POLY}}\). Therefore, in accordance with equation (5), the effectiveness of antiturbulent rigid micelles is significantly lower than with the macromolecular coils with immobilized solvent. There is no condition 3 in micellar solutions. Instead, the volumetric structured system is formed that can run only after its destruction under large external force.

4. Conclusions
1. On the basis of the thermodynamic and physicochemical approaches, the functional dependence of polymer solutions’ and surface active substances’ antiturbulent efficiency on the hydrodynamic flow parameters, physicochemical solutions properties and their structures is established.
2. The reasons of varying antiturbulent efficiency of polymers and surface active substances were validated theoretically. The high antiturbulent efficiency of polymer solutions is the result of a low elasticity of macromolecular coils which elasticity has the entropic nature. Significantly less efficiency of colloid systems is due to the high rigidity of the micelles of surface-active substances solutions which elasticity has the energy nature.

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