Mixing time of surface active agent solutions
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# Mixing time of surface active agent solutions

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## Abstract

One of the basic properties of the surfactant solutions is their ability to reduce the interfacial tension and form the micelle associates. The phenomenon depends on the surfactant concentration in a solution and surfactant structure as well as on the kind and the concentration of salt present. The paper deals with the experimental studies directed to mixing time in drag reducing micellar solutions. It has been shown that in TTAB/NaSal aqueous solutions agitated the dumping of turbulent vortex in microscale exists. The effects of the decrease of mass transport in the tank volume and increase of the mixing time, have been observed too.

Keywords: mixing time, energy dissipated, surfactant solution, conductometric method, optical method

## 1. Introduction

One of the fundamental properties of surfactants is their ability to reduce interfacial tension and form the micelle associates. Surfactant molecules under appropriate conditions (depending on chemical structure, solution concentration, type and concentration of salt with counter- or co-ion present) can assemble in a reversible process to form various structures in solutions. In a dilute solution the molecules of surfactant cover the interface with the hydrophilic part uniaxially oriented to water or with the hydrophobic part oriented to the inpolar solvent. After the total interphase surface packing reached a certain characteristic transition concentration (critical micelle concentration $CMC_1$) single monomers exist inside the solution. Above the value of $CMC_1$ dilute aqueous solutions of a given surface-active agent build up the spherical micelle structures. The increase of concentration of the surface-active agent in solutions causes the transformation of micelles from a spherical to a cylindrical structure. The transformation takes place when the solution concentration is equal to the so-called second critical micelle concentration ($CMC_2$). It has been shown that the further increase of surfactant concentration causes the superposition of micelles, decrease of micelle diameter and increase of their length (Zielinski, 2000). For the

cetyltrimethylammonium bromide, for example, in water, increasing concentration gives spherical micelles at the critical micellar concentration $CMC_1$ and after, elongated micelles, more or less flexible, which leads near 0.7 M (at 298K) to a nematic phase followed by a hexagonal one. At low concentration of CTAB, the addition of a simple salt (like potassium bromide) facilitates the growing of the micelle, giving a rodlike system. The addition of an organic compound like organic salt (sodium salicylate) is even more effective to promote the growth of micelle size. The solutions with rod-like micelles, similar to high-molecular polymer solutions, show the ability of drag reduction in turbulent pipe flow. Both types of the active additives found the application not only in drag reduction in turbulent pipe flow, but also in crude oil production (Chen *et al.*, 2005), as thickener media of cosmetics, detergents and cleaners etc. (Zielinski, 2000; Yang, 2002; and Zakin *et al.*, 1998).

An analysis of mixing time was a subject of lot of studies (Nienow, 1997; Bujalski *et al.*, 2002; Szoplik and Karcz, 2006). Unfortunately, the studies published were not focused on the mixing time of surfactant solutions. The aim of the present were is to study the mixing time of drag-reducing surfactant solutions.

At $Re > 6400 \cdot Ne^{-1/3}$ mixing time in a tank equipped with Rushton turbine for Newtonian fluids agitated can be determined from the Ruszkowski (1994) relationship:

$$t_{95} = 5.9 D^{2/3} \varepsilon^{-1/3} \left( \frac{D}{d} \right)^{1/3} \qquad (1)$$

where $\varepsilon$ is energy dissipation coefficient:

$$\varepsilon = \frac{P}{\rho V} \qquad (2)$$

In the paper the experimental studies directed to determination the mixing time $t_m$ for tetradecylotrimethyloammonium bromide (TTAB) aqueous solutions in the agitated vessel equipped with turbine impeller of six straight blades, have been presented. Sodium bromide (NaBr) and sodium salicylate (NaSal) were used as additives promoting the micelle association process. In order to estimate the mixing time the optical method accompanied with the numerical analysis of a film, has been chosen.

## 2. Experimental

The test installation is presented in Figure 1. Its main element was the cylindrical tank of diameter of 0.19 m (1) equipped with Rushton turbine (3). The measurements were performed at following geometrical characteristics of stirred vessel: $H = D = 1$, $h/D = 1/3$ and $b/D = 1/10$. Rotational speed of impeller was measured using inductive sensor (7). The torque moment measurements permitted to determine the power consumption.

Two methods (optical and conductometrical) were applied to evaluate the mixing time in the fluids studied. In both of them the tracer (10 ml 0.1M NaCl) was introduced through the hole in central part of the tank bottom. The conductance changes were measured using conductometer CPC-551, connected with an electrode (2) of constant $l = 51 \pm 1$ m$^{-1}$. The mixing time was the time value, when the conductance was lower than 2% of the final one. In optical method the ultramarine as the dye was used because the preliminary tests showed that it has no effect on rheological and physical properties of fluids studied.
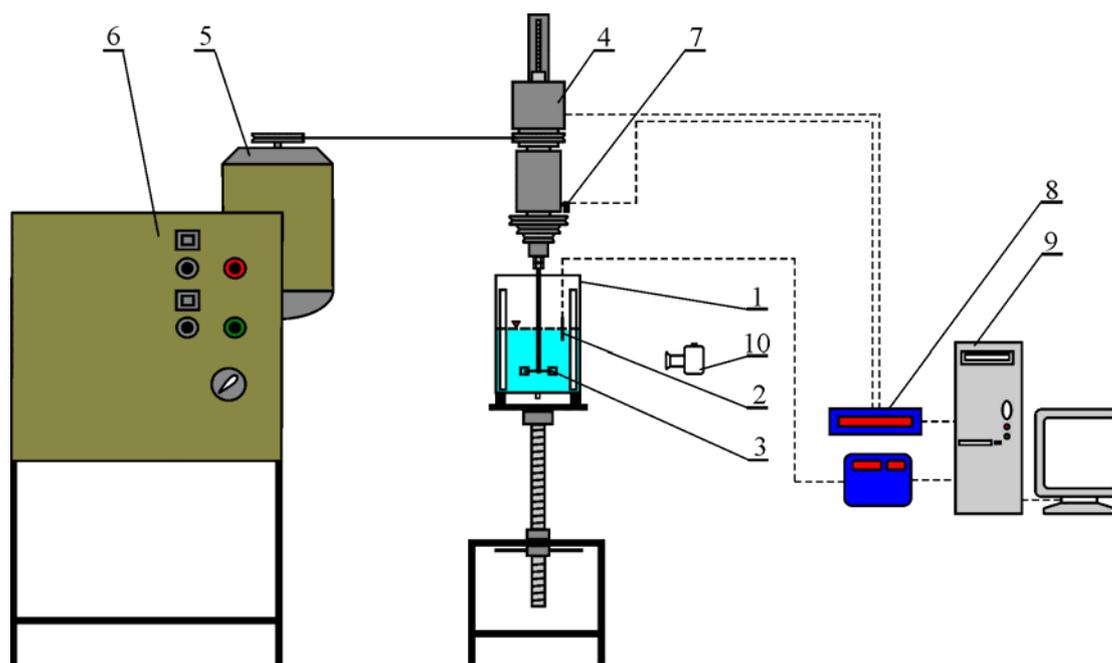


Fig. 1. Experimental set-up: 1 – tank, 2 – conductometric electrode, 3 – impeller, 4 – torque meter, 5 – motor, 6 – control system, 7 – rotational speed detector, 8 – ALFA 2000S meter, 9 – computer PC, 10 – digital apparatus

In the measurements the aqueous solutions of cationic surfactant tetradecyltrimethylammonium bromide (TTAB) with addition of sodium bromide (NaBr) or sodium salicylate (NaSal) of various concentrations were used. In optical method the pigment ultramarine (loftsman) has been applied. To check the correctness of the results obtained the conductometric technique has been used, additionally.

In the study the model Newtonian fluids were distilled water and glycerin aqueous solution of concentration of 47%. The characteristics of fluids used in the study are presented in Table 1.

On the ground of numerical analysis of photos and films the variant of optical method for mixing time evaluation has been developed. The photos and films were performed using the numerical apparatus Konica Minolta Dimage A200. PHOTO-PAINT 11 program was applied.

| Solution | $C_{p,s}$ [ppm] | $C_{p,sl}$ [%] | Viscosity $\eta \cdot 10^3$ [Pa·s] | Density $\rho$ [kg/m$^3$] |
|---|---|---|---|---|
| Water | 0 | 0 | 1 | 998.2 |
| aqueous glycerol solution (47%) | – | – | 4.640 | 1117 |
| TTAB+NaSal | 100 | 0.0095 | 1.003 | 998 |
| | 200 | 0.019 | 1.042 | 998 |
| | 300 | 0.028 | 1.057 | 998 |
| | 400 | 0.038 | 1.150 | 998 |
| | 600 | 0.057 | 1.284 | 1000 |
| TTAB+NaBr | 80 | 2.06 | 0.991 | 1011 |
| | 800 | 20.6 | 0.999 | 1011 |
| | 1950 | 41.2 | 1.874 | 1303 |

Table 1. Characteristics of the solutions used in the study

## 3. Result and discussion

The experimental data on the mixing time of complex fluids agitated were analyzed in connection with energy dissipated (2) and Reynolds number for Newtonian model fluids:

$$Re = \frac{nd^2\rho}{\eta} \tag{3}$$

In Fig. 2 the comparison of authors' experimental data for distilled water and glycerol solution obtained in both, conductometric and optical techniques, with those ones resulted from relation (1), has been presented. From the patterns shown it can be stated that experimental data for water in majority confirm the proposal (1), but in glycerol solution only two experimental data obtained are accordant. In latter case it might be due to the fact that the Ruszkowski relationship was limited to the values of $Re > 6400\ Ne^{-0.33}$ and only the points mentioned above satisfied the condition given above.
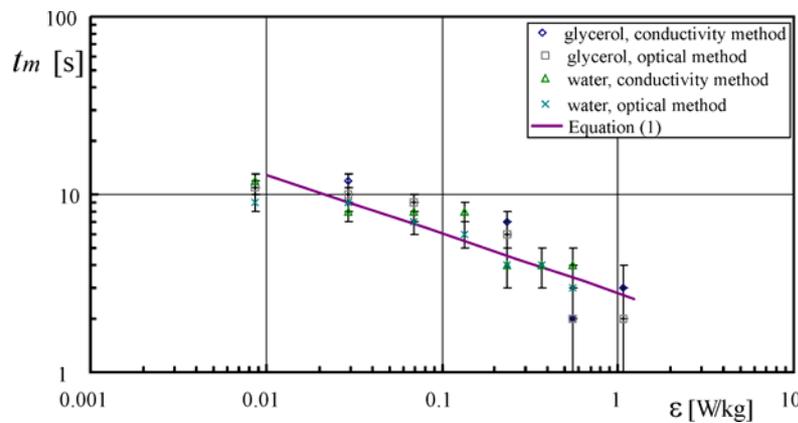


Fig. 2. Comparison of the experimental data with resulted from relationship (1)

In Fig. 3a the mixing time $t_m$ dependent on energy dissipation coefficient $\varepsilon$ for TTAB/NaBr solutions has been presented. According to literature data (Imae and Ikeda, 1986) in these solutions, the spherical micelles (80 and 800 ppm) and cylindrical micelles (1950 ppm) can be formed. It is evident, that experimental points for surface active agents solutions underlying the line of Ruszkowski equation (1), and in the range of $\varepsilon \geq 0.28$ lie in the region of measurement error. In the range of measurement error, the differences between mixing time for concentrations of TTAB/NaBr in a solution studied, were not appreciable. Totally different patterns of relation $t_m = f(\varepsilon)$ for TTAB/NaSal solutions system have been obtained (Fig. 3b). For surfactant solution concentration equal to 100 ppm the experimental points run below Ruszkowski proposal (1), similarly like it was observed in TTAB/NaBr system (Fig. 3a).
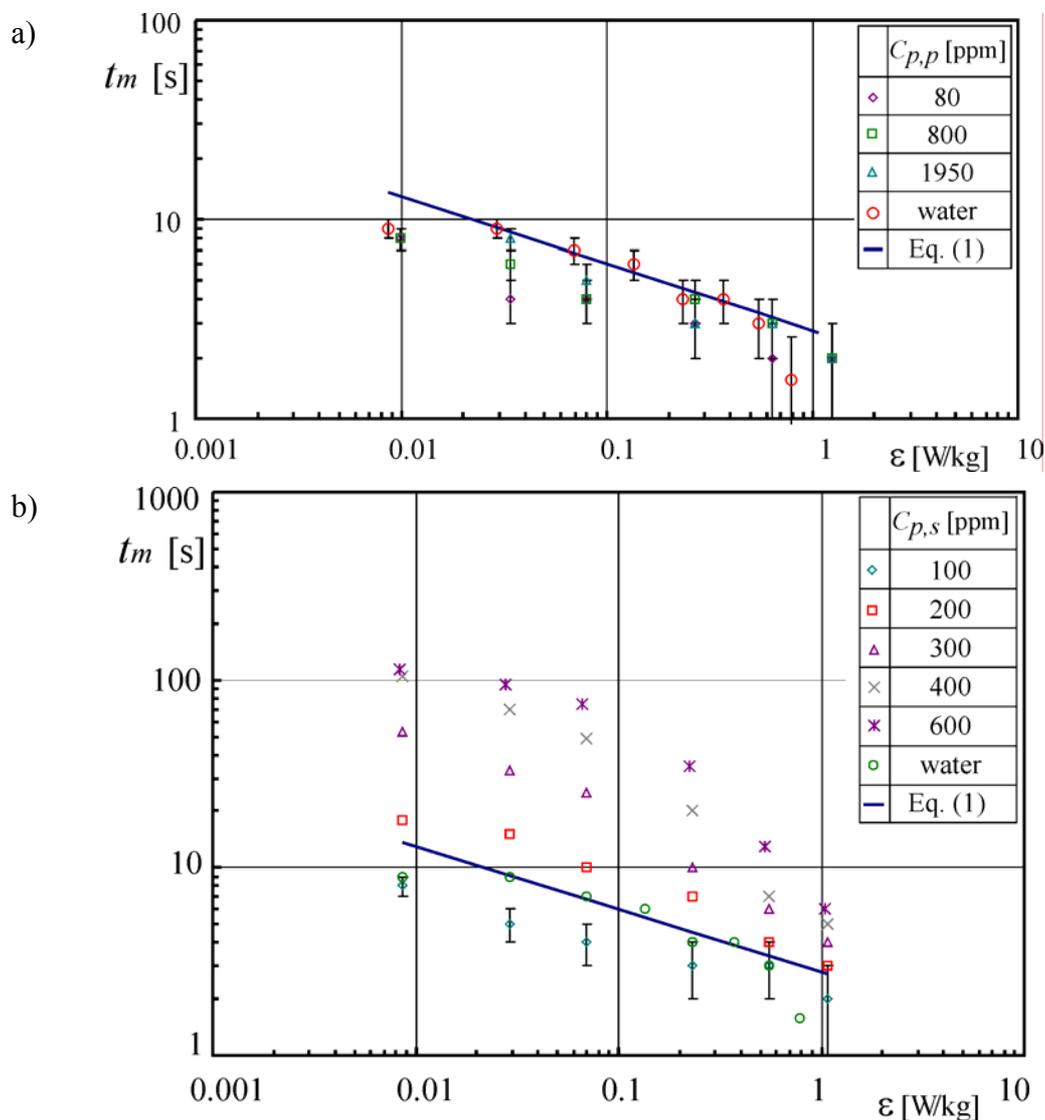


Fig. 3. Comparison of the mixing times for surfactant solutions with mixing times for distilled water:
a) TTAB/NaBr, b) TTAB/NaSal

The concurrence of experimental points for the both systems analyzed results from the fact, that in TTAB/NaSal solution at the surfactant concentration 100 ppm only spherical micelles or relatively short cylindrical micelles can be present. At higher TTAB/NaSal concentrations the considerable increase of mixing time with surfactant concentration increase is evident. The literature data showed, that in quaternary ammonium salt with sodium salicylate, the unusually long rodlike micelles, called also wormlike micelles or thread micelles, have been formed (Qi and Zakin, 2002). The growth of mixing time was connected with micelle association. It is additionally seen from the patterns in Fig. 3b that with the increase of energy dissipation coefficient $\varepsilon$, the decrease in differences between mixing times is observed. At the rotational speed of impeller $n = 2$ s$^{-1}$ the mixing time for water is equal 9 s and increases to value of 113 s for surfactant solution of concentration of 600 ppm. The increase is twelve times. At the rotational impeller speed n = 10 s$^{-1}$ the mixing time changed from 2 to 6 s (3 times). The changes observed in mixing time with increasing rotational impeller speed can be explained by the changes of flow in straight pipe characteristics (Ohlendorf *et al.*, 1986).
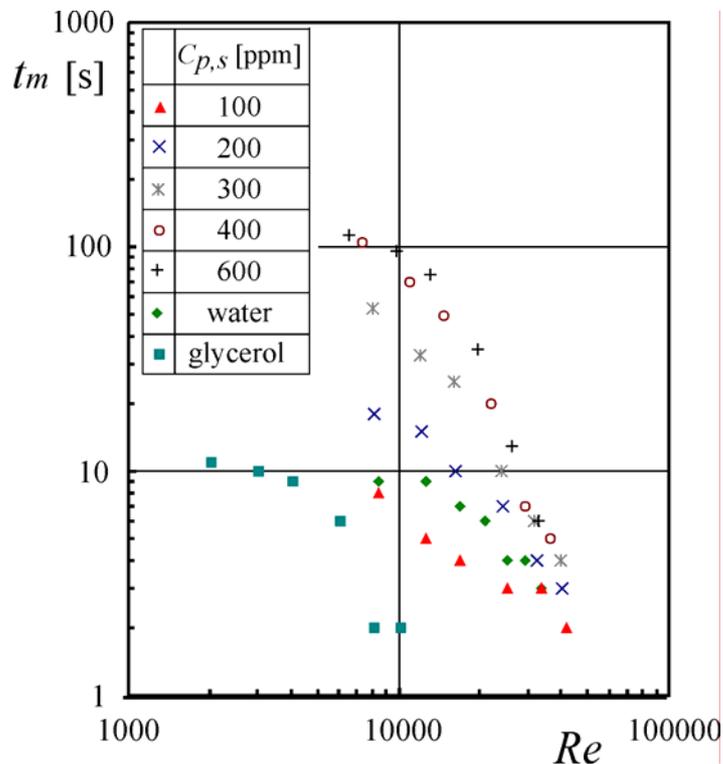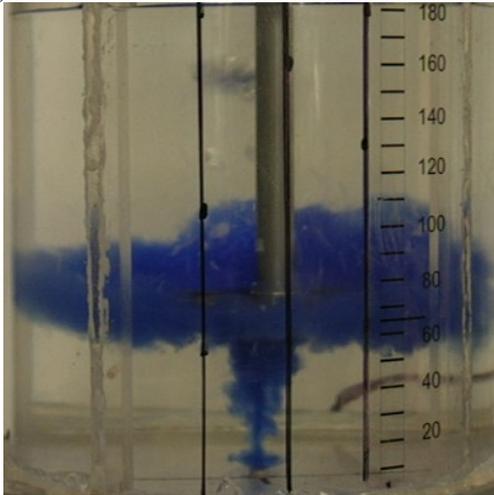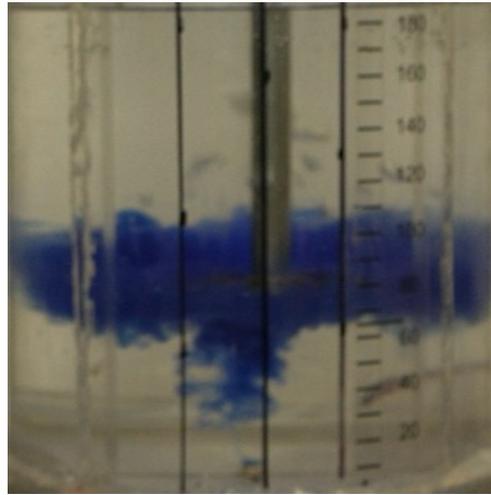


Fig. 4. Relation of mixing time vs. Reynolds number $t_m$ = f(*Re*) for TTAB/NaSal solutions

In paper (Ohlendorf *et al.*, 1986) it was suggested that the presence of long rodlike micelles leads to turbulent drag reduction that is connected with the quenching of wires.
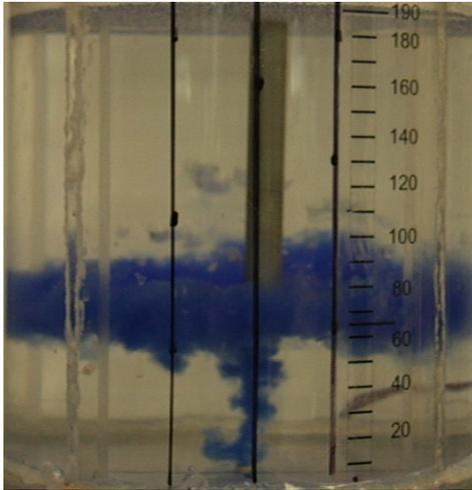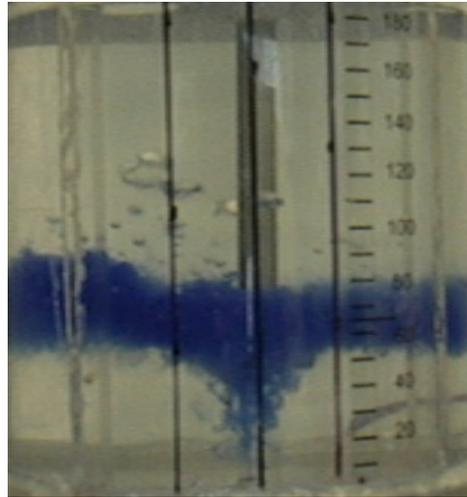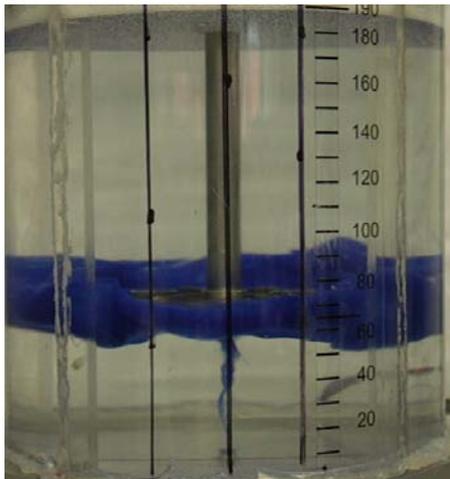
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a)  *Re* = 8433

b)  *Re* = 2034

c)  *Re* = 8621

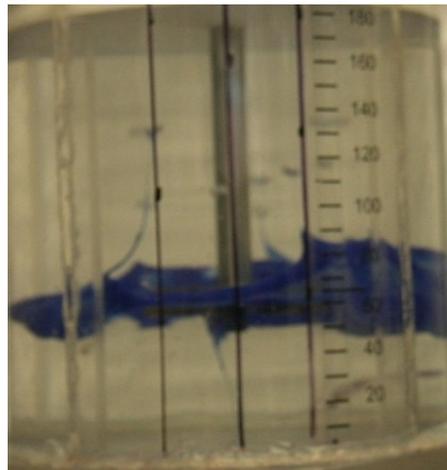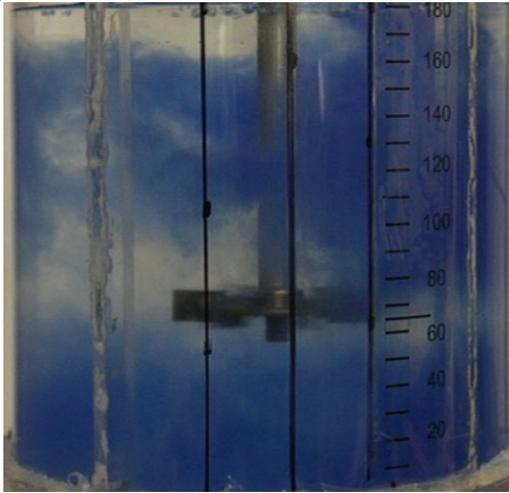d)  *Re* = 5888
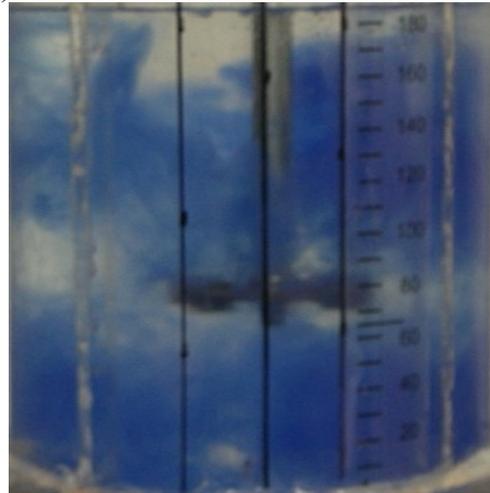
e)  *Re* = 7978

f)  *Re* = 6581

Fig. 5. Comparison of the injection moment of dye for rotational impeller speed $n = 2$ [s$^{-1}$] for solutions:
a) distilled water, b) 47% glycerol, c) 80 ppm TTAB/2.06 NaBr, d) 1950 ppm TTAB/41.2 NaBr, e) 300 ppm TTAB, f) 600 ppm TTAB

a)  *Re* = 8433

b)  *Re* = 2034

c)  *Re* = 8621

d)  *Re* = 5888
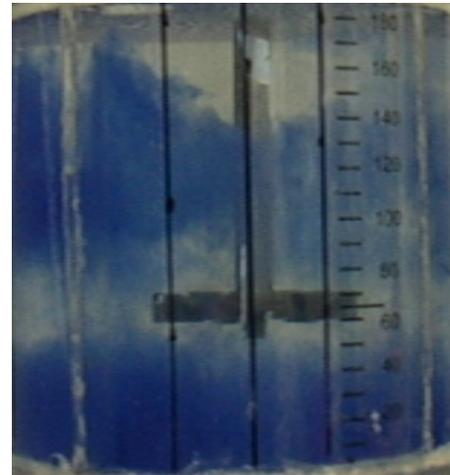
e)  *Re* = 7978
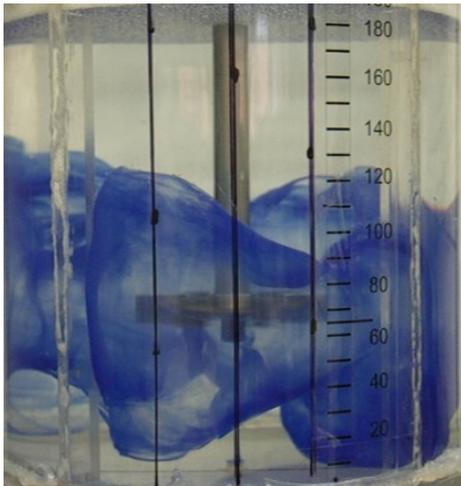
f)  *Re* = 6581
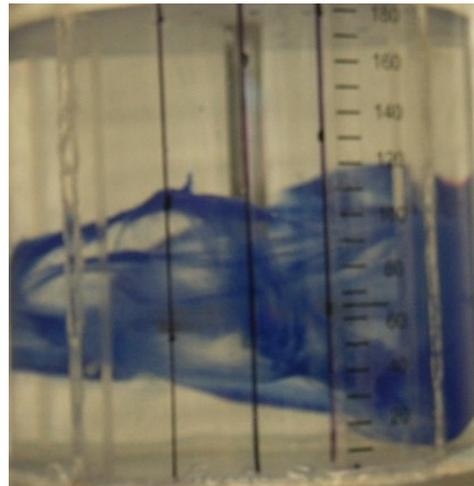
Fig. 6. Comparison of the images of dye distribution in the tank region after 2s from the injection dye moment for rotational impeller speed $n = 2$ [s$^{-1}$] for solutions: a) distilled water, b) 47% glycerol, c) 80 ppm TTAB/2.06 NaBr, d) 1950 ppm TTAB/41.2 NaBr, e) 300 ppm TTAB, f) 600 ppm TTAB

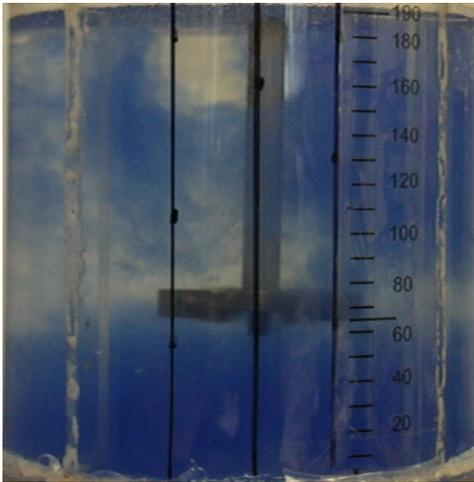Fig. 7. Comparison of the images of dye distribution in the tank region after 5s from the injection dye moment for rotational impeller speed *n* = 2 [s⁻¹] for solutions: a) distilled water, b) 47% glycerol, c) 80 ppm TTAB/2.06 NaBr, d) 1950 ppm TTAB/41.2 NaBr, e) 300 ppm TTAB, f) 600 ppm TTAB
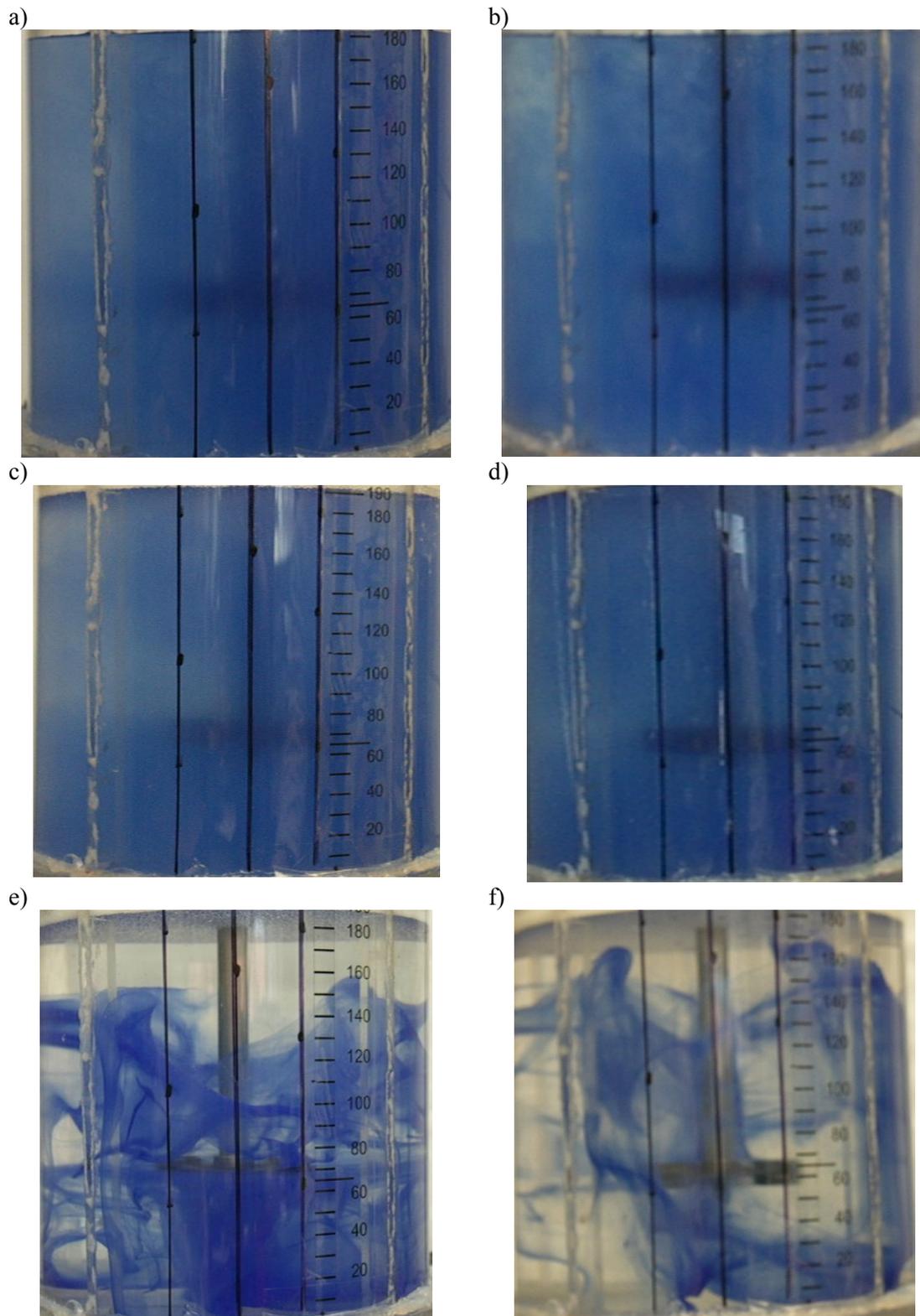
Drag reduction exists only in a limited range of the Reynolds number. After exceeding the critical value of Reynolds number, the pressure drop returns to the level characteristic for clear solvent. It can be connected with increase in shear stresses, with breakdown of internal micelle structure as well as flow stabilization. Similarly, in a case of mixing process, the increase in impeller rotational speed causes the increase of stresses in solution. It leads to break-up of micelle associates. It manifests in smaller differences between mixing time in clear solvent and TTAB/NaSal solution.

It is noteworthy, that the range of Reynolds number, in which the measurement of mixing time for TTAB/NaSal solutions has been performed, comply with the range of Reynolds number Re in which the mixing time in clear water has been studied (Fig. 4).

The reason of considerable elongation of the homogenization time in micellar solutions for TTAB/NaSal system can be partially explained on the basis of images in Figures 5-7. Fig. 5 brings the photos of the agitated vessel filled with different solutions used in the study, at the moment of injection of a dye into the tank. In cases of distilled water, 47% glycerol solution and TTAB/NaBr system the boundaries of dye are evidently "fuzzy". It indicates the presence of fine turbulent vortices in solutions which have the essential role in mass convection bringing the system to a state of homogeneity. Totally different image for TTAB/NaSal system of concentrations of 300 and 600 ppm (Fig. 5e,f) has been observed. The boundaries of a range occupied through dye are sharp, that testifies for the lack of fine vortices in solution and delay in mass transfer processes.

Additionally, in Figs 5-6 the Reynolds number values have been presented. The lowest Reynolds number value ($Re = 2034$) pertains to glycerol solution, and the highest value ($Re = 8433$) to distilled water. Values of Re for TTAB/NaSal system of concentrations of 300 and 600 ppm ($Re$ equal to 7978 and 6581, respectively) are situated between the values for distilled water and glycerol solution. Therefore, the differences in turbulence intensity are not due to the influence of viscosity of the solution, dumping the turbulence.

From the comparison of images shown in Figs. 6 and 7 (photos were carried out after 2 and 5 s from the moment of injection the dye) it is evident that in TTAB/NaSal system the characteristic trails have been formed, which should be connected with general circulation of fluid generated through impeller. In typical case of mixing for Newtonian fluids, the large scale vortices should break up into the smaller parts, thus intensifying the mixing process. However, the pictures of TTAB/NaSal system do not exhibit the latter stage.

The influence of long rodlike micelles formed in that solution is, thus, connected with interference in a transition of large scale vortices to a smaller scale. The physical nature of this process demands further investigations.

## 5. Conclusions

The comparative measurements of the mixing time performed by conductometrical and optical methods proved the usability of an evolved method of digital photos analysis for the evaluation of mixing time in a tank equipped with turbine impellers. It was found that significant differences between mixing times for TTAB/NaBr system and clear solvent, as well as for surfactant solutions, where spherical and cylindrical micelles have been formed, do not exist. For determination the mixing time in these solutions in technical calculations the Ruszkowski relationship (1) can be used. The strong increase of mixing time for aqueous tetradecyltrimethylammonium bromide solutions with sodium salicylate above the concentration of 200 ppm surfactant, has been observed. According to literature data, in these solutions the long wormlike micelles have been formed. The analysis of images showed that in TTAB/NaSal system the dumping of turbulence in small scales vortices takes place. It leads to reduction of mass transport rates in tank volume and also to increase in mixing time.

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