

MIXING TIME IN IONIC AND NON-IONIC POLYMER SOLUTIONS

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Abstract. The paper deals with experimental studies directed on the determination of mixing time t_m for ionic and non-ionic polymer solutions. The polymer used was polyacrylamide, partially hydrolyzed polyacrylamide, guar gum and carboxymethylcellulose sodium salt. The differences in mixing process between the systems studied has been observed. Probably it results from different internal microstructure of solutions which is built up by stretch polymer chains. This microstructure in spatial network form leads to disturbances in transition of vortices from large scale to small scale and thus, to dumping a turbulence, that will increase the time needed for the homogenization of a system.

Key words: Mixing time; non-Newtonian fluid; Viscoelastic; Polymer solution; polyelectrolytes;

1. INTRODUCTION

Mixing time is a fundamental parameter for evaluation the homogeneity of systems in agitated vessels. Rheologically complex fluids are commonly used in many technologies and chemical or food process industries. Mixing time in non-Newtonian fluids has been the subject of studies in few papers [1-4]. Ford and Ulbrecht [3] carried out the studies of the mixing time for viscoelasticity fluids (aqueous solutions of polyacrylamide and carboxymethylcellulose sodium salt) in the vessel equipped with helical screw impeller. Similarly, Slemenik and Žumer [2,4] studied the mixing time for carboxymethylcellulose sodium salt and xantan gum solutions in the agitated vessel equipped with Rushton turbine and helical ribbon impeller in the laminar flow regime ($0.5 < Re < 50$). They showed, that the mixing time is dependent on the type and number of impellers, rheological properties of the fluid and the size of the vessel. Broniarz-Press and Woziwodzki [1] analyzed the dependence of the mixing time on the impeller bottom clearance for a single impeller and on the distance between impellers for dual impeller non-aerated systems. The aqueous solutions of carboxymethylcellulose sodium salt of various molecular weights (250,000 and 700,000) as well as conductometric method, have been used. Karcz and Szoplik [5,6] studied the effects of eccentricity and pumping mode of the impeller, and position of the tracer dosage point into the liquid on mixing time for non-Newtonian fluid. In this paper, mixing time in polyelectrolyte and non-ionic polymer solutions has been studied.

In the majority of papers [5,6] the mixing time t_m has been presented in the connection with energy dissipation coefficient:

$$\varepsilon = \frac{P}{\rho V} \quad (1)$$

or with Reynolds number which for Newtonian fluids is defined as follows:

$$Re = \frac{nd^2\rho}{\eta} \quad (2)$$

For shear-thinning media the formula of the Reynolds number proposed by Metzner and Otto Re_{MO} [7], has been used:

$$Re_{MO} = \frac{nd^2\rho}{\eta_a} \quad (3)$$

Metzner and Otto [7] have found that the average shear rate in the agitated vessel is proportional to impeller speed in the tank:

$$\dot{\gamma}_m \propto n \quad (4)$$

The proportionality coefficient B^* can be written as:

$$\dot{\gamma}_m = B^* \cdot n \quad (5)$$

Constant B^* is characteristic for a given type of the agitated geometric system and for a given fluid group. Gluz i Pavlushenko [8] gave the value $B^* = 4\pi$ to be valid for all impeller types. For fluids described by power-law model the apparent viscosity can be defined as:

$$\eta_a = K \cdot \dot{\gamma}_m^{m-1} \quad (6)$$

hence the Reynolds number takes the form:

$$Re_{MO} = (B^*)^{1-m} \frac{n^{2-m} d^2 \rho}{K} \quad (7)$$

To correlate the experimental data it is convenient to use the dimensionless mixing number [9]:

$$t_m \cdot n = \text{const} \quad (8)$$

On the basis of experimental data it has been found that in the turbulent regime this number has a constant value at fixed geometrical parameters of the tank.

2. EXPERIMENTAL

The main element of the test installation was the cylindrical tank of diameter of 0.19 m equipped with Rushton turbine. The measurements were performed at following geometrical characteristics of stirred vessel: $H/T = 1$, $h/T = 1/3$, $D/T = 1/3$ and $b/D = 1/10$.

In the study the aqueous solutions of polymers soluble in water were used: carboxymethylcellulose sodium salt (Na-CMC), of molecular weight of $M_w = 700,000$, guar gum (GG), polyacrylamide (Rokrysol WF1) of molecular mass $M_w = 4.4 \cdot 10^6$ and of polydispersity of 4.7 and partially hydrolyzed polyacrylamide of molecular weight of $M_w = 4.4 \cdot 10^6$ and of polydispersity of 3.0 (Rokrysol WF2). Guar gum and Rokrysol WF1 are the non-ionic polymers, while Na-CMC and Rokrysol WF2 belong to anionic polymer group. All tested polymer solutions were power-law fluids. In the study the model Newtonian fluids were distilled water and glycerine aqueous solution of the concentration of 47%. The characteristics of fluids used in the study are presented in Table 1.

Table 1. Characteristics of the solutions used in the study

Solution	$C_{p,p}$ [%]	$\eta \cdot 10^3$ [Pa·s]	m	K [Pa·s ^m]	Density ρ [kg/m ³]
Water	0	1	1	0.001	998.2
aqueous glycerol solution (47%)	47	4.640	1	–	1117
Rokrysol WF1	0.1	–	0.869	0.00792	998
	0.2	–	0.508	0.197	1000
Rokrysol WF2	0.05	–	0.701	0.025	998
	0.1	–	0.548	0.142	998
	0.2	–	0.504	0.389	1000
carboxymethylcellulose sodium slat (Na-CMC)	0.05	–	0.758	0.016	1000
	0.1	–	0.626	0.117	1000
guar gum (GG)	0.2	–	0.613	0.198	1000
	0.2	–	0.679	0.036	1000
	0.25	–	0.599	0.082	1000
	0.3	–	0.593	0.173	1000
	0.4	–	0.548	0.357	1000

Two methods (optical and conductometric) were applied to evaluate the mixing time in the fluids studied. In the conductometric method 10 cm³ of aqueous solution of sodium chloride (NaCl, 0.1M) was injected. The tracer was introduced through the hole in central part of the tank bottom. Conductometric electrode was placed in the upper part of the vessel. The time-effect of conductance changes has been observed. The mixing time was the time value when the conductance was lower than 2% of the final one. In the first stage of experimental studies on mixing time the conductometric method for water, glycerol and guar gum aqueous solutions was used. The results permitted to verify the correctness of the data obtained with these ones observed using the optical method. The addition of the salt into polymer solution brings about the changes in the rheological properties of the polyelectrolyte solutions. This observation was the reason of the selection of optical method based on numerical analysis of films as the main one. The tracer (ultramarine polymer solution, 4%) was introduced into the tank (20 cm³). The digital camera Konica Minolta Dimage A200 was the main apparatus from which the films were imported to Corel PHOTO-PAINT 11 program. Next, the frame corresponding to the moment of the tracer injection has been found. The frame was marked at the height of 16 cm (from tank bottom) and of area about 2×2 cm. In order to evaluate the mean depth of blue colour in the frame chosen the HISTOGRAM command has been used. The moment when the system received full homogeneity and the changes in mean depth of blue colour in a frame became lower than 2%, has been determined. The mixing time value

was calculated on the basis of the number of frames recorded from the moment of dye injection and divided by film recording velocity (15 frames per second).

In Figure 1 the relationships of dimensionless mixing number $t_m \cdot n$ vs. Reynolds number for non-ionic polymer solutions (Rokrysol WF1 and guar gum) have been presented. It results from the experimental points that dimensionless mixing number for a given polymer concentration is independent of Reynolds number value. The run of these relations is analogous to Newtonian fluids. It is seen from Figure 1 that for Rokrysol WF1 solutions (Figure 1a) the dimensionless mixing number extended from about 40 to 60, while for guar gum solutions (Figure 1b) of concentrations about 0.2 and 0.4 percent is increased from 21 to 31 level.

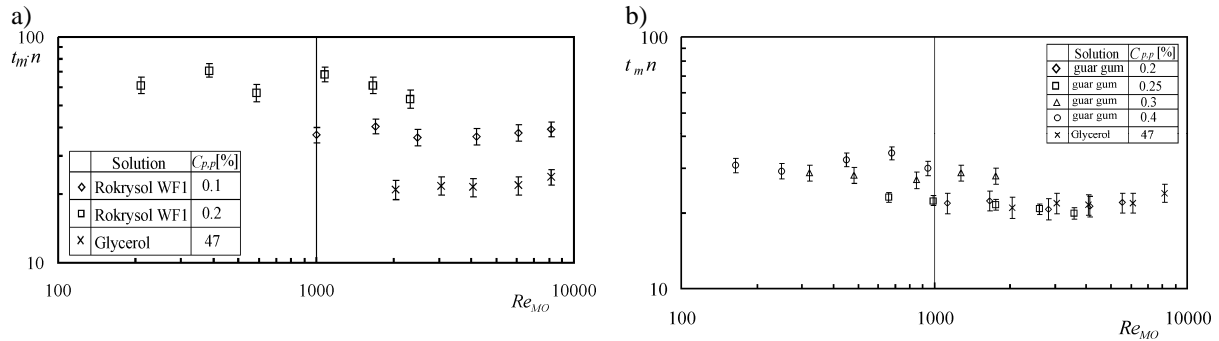


Fig. 1. Relation of dimensionless mixing number vs. Reynolds number for aqueous solutions of non-ionic polymers:

a) Rokrysol WF1 solutions, b) guar gum solutions

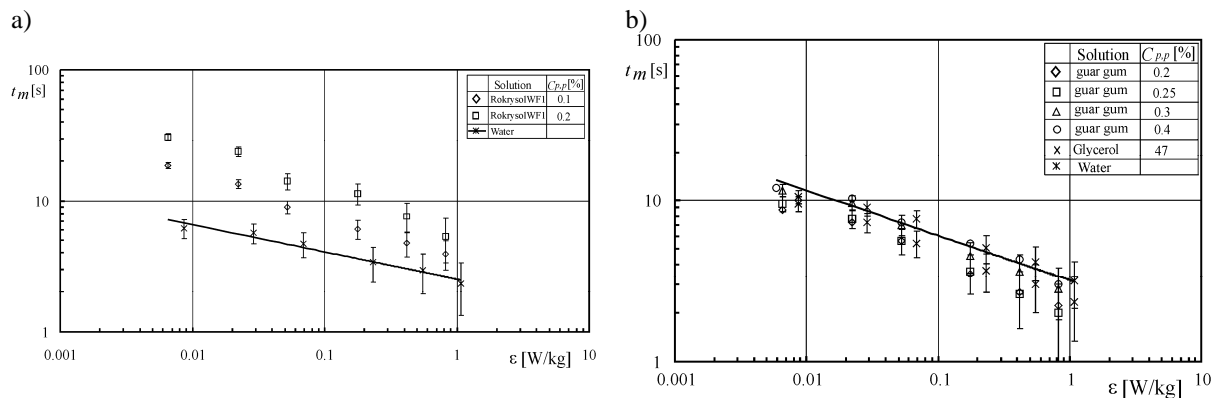


Fig. 2. Mixing time t_m vs. energy dissipation coefficient ϵ for aqueous solutions of non-ionic polymers:

a) Rokrysol WF1 solutions, b) guar gum solutions

In Figure 2 the mixing time t_m relationship on energy dissipation coefficient ϵ has been presented. The experimental data showed that for Rokrysol WF1 solutions the considerable increase in mixing time compared with the clear water and glycerol solution has been observed. In guar gum solutions the values of mixing time were of the similar level as observed in Newtonian fluids. In order to analyse the viscosity effect on mixing time in Rokrysol WF1 and guar gum solutions, the average apparent viscosities at the shear rate value $\dot{\gamma} = 31.4 \text{ s}^{-1}$ were determined from equation (5) for impeller speed $n = 10 \text{ s}^{-1}$. For Rokrysol WF1 solutions the average viscosity values were 0.008 [Pa·s] at 0.1 % concentration and 0.036 [Pa·s] at 0.2 % concentration. Values of the viscosity of guar gum solutions of 0.2 % and 0.4 % concentrations were equal to 0.012 and 0.0752 [Pa·s], respectively. So, as the guar gum solutions had higher viscosity than Rokrysol WF1 solutions, whereas the mixing times

obtained were longer, the increase in mixing time should not be connected with viscosity increase.

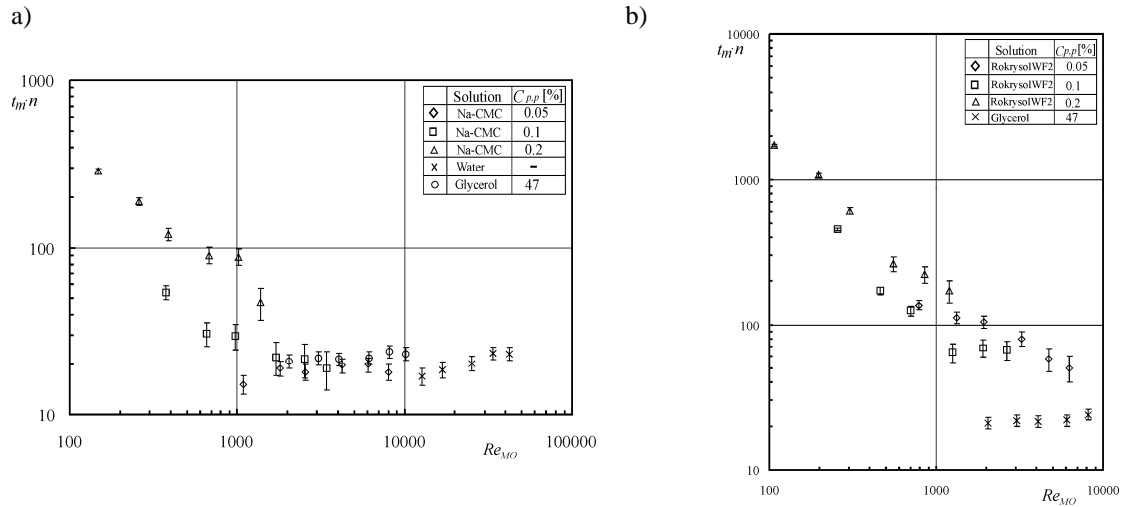


Fig. 3. Dimensionless mixing time vs. Reynolds number for aqueous solutions of polyelectrolytes: a) Na-CMC solutions, b) Rokrysol WF2 solutions

In Figure 3 the relationships of $t_m \cdot n = f(Re)$ for aqueous solutions of polyelectrolytes studied have been presented. It has been shown that for Na-CMC aqueous solution of concentration of 0.05 % the mixing time number is independent of Reynolds number. The similar effect was observed in Newtonian liquids and aqueous solutions of non-ionic polymers studied. In Na-CMC solutions of $C_{p,p} > 0.05$ % and Rokrysol WF2 solutions studied the decrease of the mixing time number with the increase of Reynolds number has been observed. The mixing time values in Rokrysol WF2 solutions observed were higher than in Na-CMC solutions of comparable viscosity (Figure 4). It results from Figure 4 that in Na-CMC 0.05 % solutions the mixing times are comparable with values obtained for clear water, in the range of energy dissipation studied. For Na-CMC solutions of concentration greater than 0.05 % and all Rokrysol WF2 solutions used the meaningful increase of the mixing time in relation to clear water has been observed. Apparent viscosity at rotational speed impeller of $n = 10 \text{ s}^{-1}$ for Na-CMC and Rokrysol WF2 solutions of concentration of 0.2% was $\eta_a \approx 0.07 \text{ [Pa}\cdot\text{s]}$.

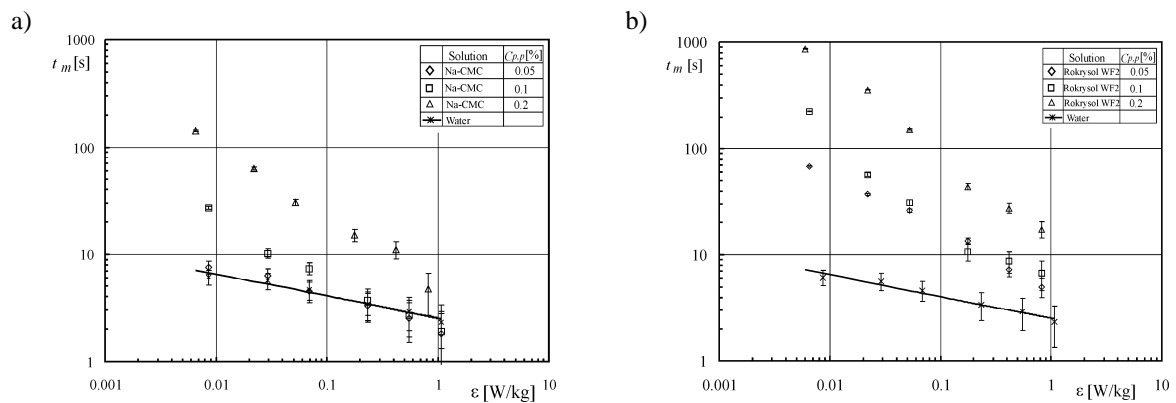


Fig. 4. Mixing time t_m vs. energy dissipation coefficient ϵ for polyelectrolyte solutions: a) Na-CMC solutions, b) Rokrysol WF2 solutions

In Figure 5 the results of dynamic rheological measurements of aqueous polymer solution have been presented. Measurements were carried out in a controlled stress rheometer RS1 (Thermo Haake, Karlsruhe, Germany), using cone plate geometry of 6 cm diameter, monitored by a RheoWin software package (version 3.61, Thermo Haake). The viscoelastic properties of fluids in the relationships of storage modulus G' vs. frequency ω are presented in Figure 5a. It is seen that for Rokrysol WF2 and Na-CMC solutions the values of storage modulus are higher than the values obtained for Rokrysol WF1 and guar gum, in the range of frequency studied. That fact indicates the formation of a considerably stronger internal structure in ionic polymer solutions. It results from the relationship $\eta' = f(\omega)$ shown in Figure 5b that for guar gum solution the absolute viscosity takes the values comparable to these ones in Na-CMC solution of concentration 0.2% as well in Rokrysol WF2 solution of concentration 0.1%. In Figure 6 the relations of $t_m \cdot n = f(Re)$ are shown for solutions, which rheological properties were presented above. For guar gum solution about concentration 0.3% the lowest values of the mixing time have been obtained.

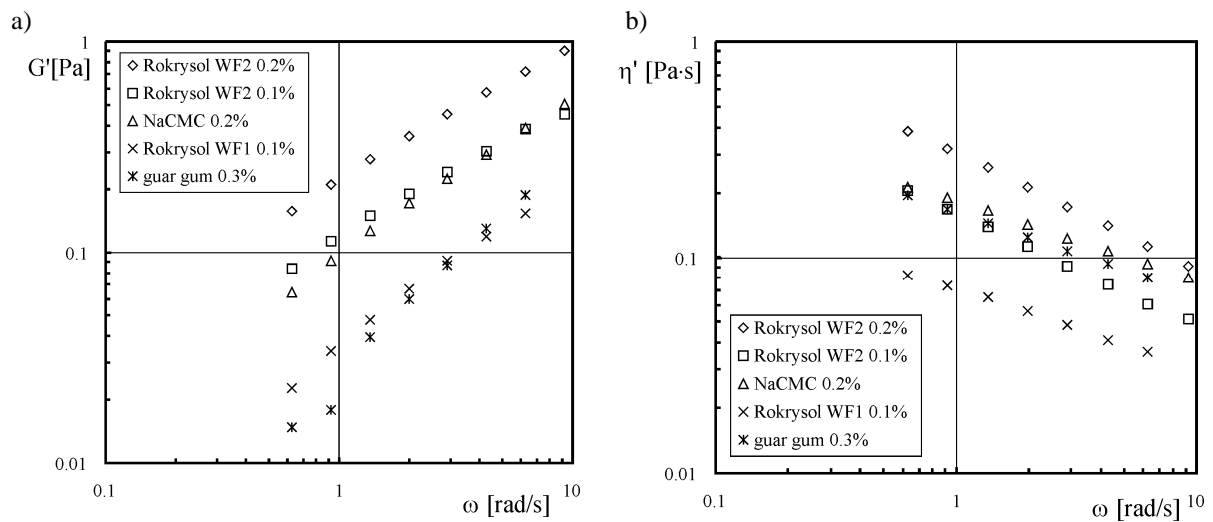


Fig. 5. The results of oscillatory measurements: a) storage modulus G' as a function of frequency ω in the linear viscoelastic regime, b) dynamic viscosity η' vs. frequency ω

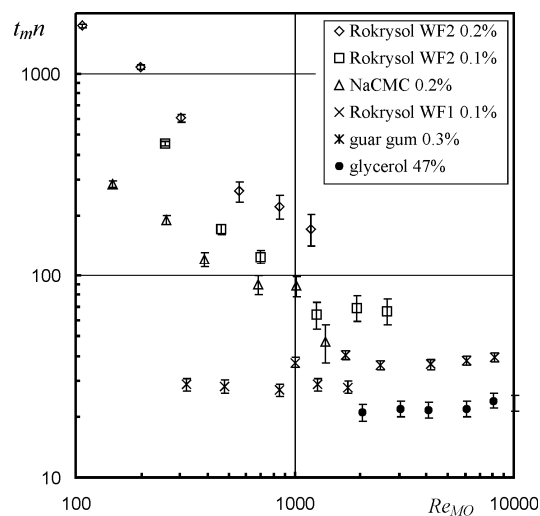


Fig. 6. Comparison dimensionless mixing time vs. Reynolds number for ionic and non-ionic aqueous solutions

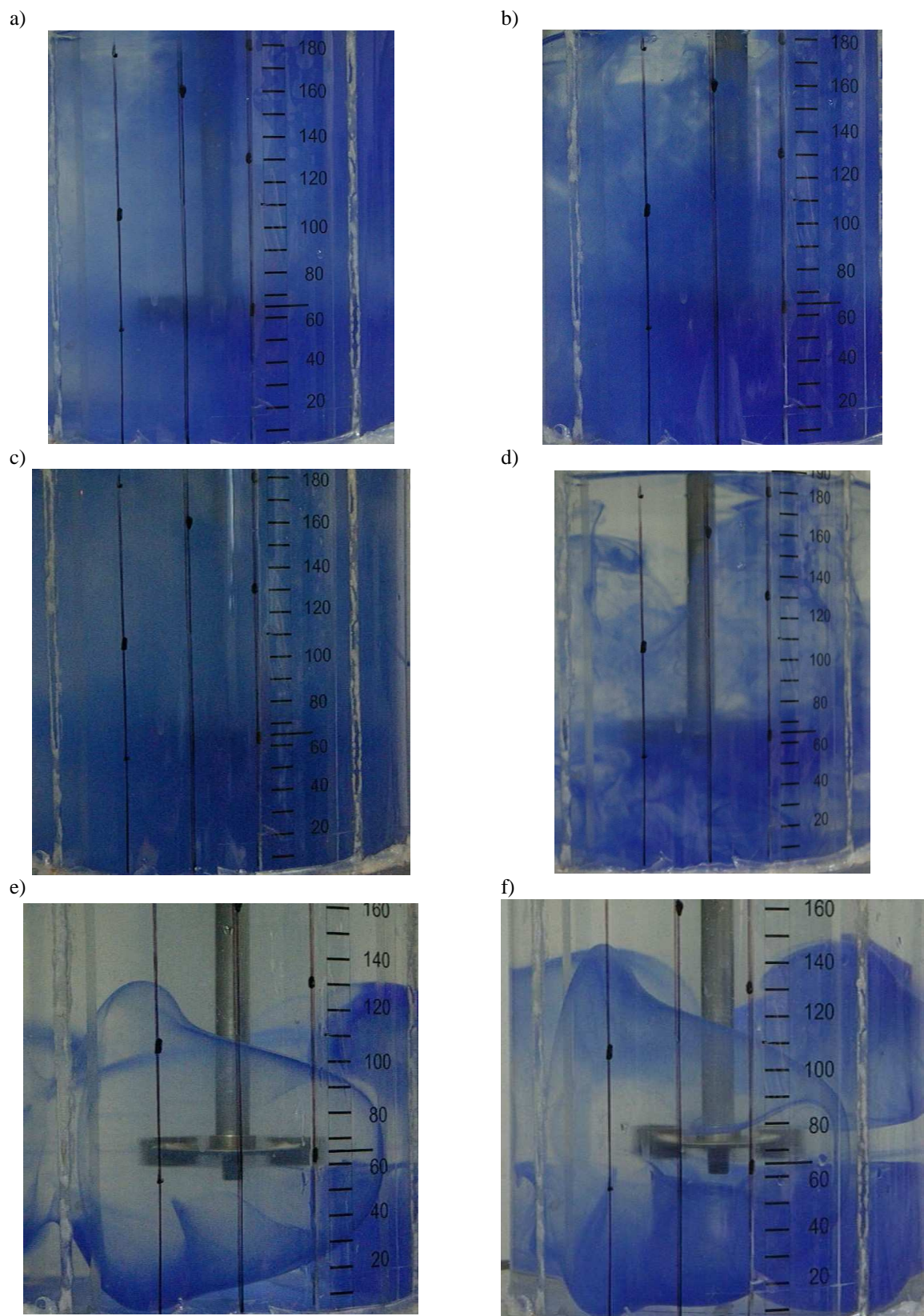


Fig. 7. Comparison of the images of dye distribution in the tank region after 2 s from the dye injection moment at rotational impeller speed $n = 3 \text{ [s}^{-1}\text{]}$ for solutions: a) distilled water, b) 47% glycerol, c) Guar Gum 0.4 [%], d) Na-CMC 0.2 [%], e) Rokrysol WF2 0.2 [%], f) Rokrysol WF1 0.1 [%]

Additional information about the effect of the polymer additives on mixing time in the solution can be obtained from the images shown in Figure 7. It is seen from the patterns that the dye distributions in the tank when the Newtonian fluids and guar gum solutions were agitated, are very close. The dyes of the band structure have been formed. The lack of characteristic fuzzy limits of dye for Newtonian fluids and guar gum solutions has been observed. So, the decay of vortices of large scale is evident. It should be underlined that for Rokrysol WF1 solutions the image obtained may be regarded as transitional one having the common features with guar gum, Rokrysol WF2 as well as Na-CMC aqueous solutions.

It follows from the analysis of experimental data that the increase of the mixing time in polymer solutions can not be connected with the increase of viscosity in these solutions. The effect observed can be a result either of an existence (or lack) of the viscoelastic properties, or specific configuration of polymer in the solutions studied. Non-ionic polymers show the tendency to build up the coiled bundles in a solution. In the solutions of the relatively low concentrations they do not show the mutual splicing of their chains and spatial network forming. Polyelectrolytes have more „rigid” chains in the solutions, therefore their chains occur in more elongated forms. It causes the mutually splicing chains and spatial network in polyelectrolytes that is very often connected with the viscoelastic properties of the solutions.

3. CONCLUSION

The analysis of images showed that in Na-CMC and Rokrysol WF2 systems the disturbances in transition of vortices from large scale to small scale which are dumping a turbulence take place, thus increasing the time needed for the homogenization of system. The differences in interactions of anionic and non-ionic polymers for mixing time can be connected with their macromolecular configuration in solution. The absence of monominal charges in polymer chain causes their stretching and occurrence in a solution in more stretched form. Such chains have a tendency to form spatial network, that leads to dumping of turbulence. Non-ionic polymers occur in solution in coiled ball, the mutual splicing of which in dilute solutions is weak. It has not much influence to flow character and mixing time.

4. REFERENCES

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