

Sedimentation in micellar solutions of tetradecyltrimethylammonium bromide

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Abstract

In the paper the results of experimental studies on the sedimentation process of barium carbonate (of mean particles diameter of 25 [μm]) in aqueous solutions of tetradecyltrimethylammonium bromide, have been presented. As the additives assisting in micellar association the sodium bromide and sodium salicylate, have been used. The sedimentation tests were carried out in the transparent cylinder of 1 dm³ volume and height of 34 [cm]. It has been shown that in tetradecyltrimethylammonium bromide solutions of concentrations of 1·CMC and 2·CMC, the sedimentation process proceeds faster than in clear water. The reason of that observation can be a fact that the cationic surfactants are adsorbed on the barium carbonate molecule surface. As the result it causes the both, reduced surface charge and decreased repulsion between particles. Aggregation is induced by the hydrophobic interactions between particles. It will facilitate the approach of molecules to each other and the greater agglomerates are formed. For the sake of bigger mass, the molecules fall faster. Growth of the TTAB concentration to 10·CMC level and addition of sodium bromide into a solution causes slowing down the sedimentation process. It is the result of the growth in fluid density and viscosity. The sedimentation velocity for barium carbonate falling in TTAB/NaSal system was lower than this one in the clear solvent observed. Density of this solution was comparable with water density, whereas the growth of the viscosity of solution has been observed. It can be the result of the decrease of sedimentation velocity.

Keywords: sedimentation, surfactant solution, tetradecyltrimethylammonium bromide

1. Introduction

The study of behaviour of aqueous colloids in presence of cationic surfactant or polymer is actively pursued by many investigators. Rubio and Goldfarb (1970) reported the greater aggregation effect on colloidal silica in the hexadecyltrimethylammonium bromide as compared to salts. Zukang *et al.* (1990)

studied the structure of silica aggregates in the presence of cationic surfactant using the neutron scattering technique. Roldugina *et al.* (2000) studied the effect of surfactant concentration on average number of silica particles aggregates in flocks. Simultaneous aggregation and sedimentation of silica particles in presence of surfactant and salts have been studied by Gupta and Basu (2005). In the present work the sedimentation of barium carbonate particles in micellar aqueous solution of tetradecyltrimethylammonium bromide has been investigated.

In dilute solution the molecules of surfactant cover the interface with the hydrophilic part uniaxially oriented to water. Above the value of CMC the surfactant builds up the spherical micellar structures. The increase of concentration of surface-active agent in a solution causes the transformation of micelles from spherical form to a rodlike structure. The transformation takes place when the solution concentration is equal to so-called second critical micelle concentration (CMC₂). The sphere-rod transition of the alkyltrimethylammonium halides micelles can be caused by addition of salt too. At a certain threshold micelle concentration, rodlike micelles interact, overlap and entangle together to form a network (Imae and Ikeda, 1986). The longest micellar associates (called wormlike or threadlike micelles) in alkyltrimethylammonium halides solutions with added sodium salicylate, have been formed (Qi and Zakin, 2002).

2. Experimental

The sedimentation tests were carried out in the transparent cylinder of 1 [dm³] volume and height of 34 [cm]. The cylinder was located in a glass tank of the thermostat to stabilize the temperature (25±1°C). The changes of the height of the interface between the clear liquid and the suspension were measured in time.

The velocity of settling of the interface was calculated from equation

$$w = \frac{\Delta h}{\Delta t} \quad (1)$$

where Δh is a change in the height of the suspension in time Δt . Solid concentration of suspension was calculated from equation

$$c = \frac{c_o \cdot h_o}{h} \quad (2)$$

where c_o is an initial concentration of suspension equal to 100 [kg/m³] and h_o is an initial height of suspension.

The liquids studied were the aqueous solutions of cationic surface active agent: tetradecyltrimethylammonium bromide (TTAB). The compounds used for surfactant solutions modification were sodium bromide (NaBr) and sodium salicylate (NaSal). As the disperse phase barium carbonate particles were used in the experiments. The properties of barium carbonate are shown in Table 1.

Table 1. Properties of barium carbonate

	Property	Value
1.	Density of solid, ρ_s	4430 [kg/m ³]
2.	Bulk density	350 [kg/m ³]
3.	Solubility in water (20°C)	0.02 [g/dm ³]
4.	Mean particles diameter	25 [μm]

The critical surfactant concentration used in the experiments has been determined from literature data (Imae and Ikeda, 1986). In Tables 2-4 the properties of surfactant solution in which the surfactant builds up the micelles are presented:

- spherical – Table 2 (the surfactant concentration is expressed in terms of critical micelle concentration),
- rodlike (TTAB/NaBr system) – Table 3,
- rodlike (wormlike) (TTAB/NaSal system) – Table 4.

Additionally, the sedimentation tests in distilled water and sodium bromide solution were carried out.

Table 2. Characteristics of TTAB solution (spherical micelles)

	Concentration of TTAB	Concentration of TTAB $C_{V,s} \cdot 10^3$ [g/cm ³]	Concentration of NaBr $C_{M,sl}$ M	$\eta \cdot 10^3$ [Pa·s]	ρ [kg/m ³]	σ [mN/m]
1	1·CMC	1.3	–	0.89	997	40.5
2	2·CMC	2.6	–	0.93	997	39.8
3	10·CMC	13.0	–	1.03	997	38.5
4	10·CMC	1.5	0.1	1.05	1006	37.2

Table 3. Characteristics of TTAB/NaBr aqueous solution (rodlike micelles)

	Concentration of TTAB $C_{V,s} \cdot 10^3$ [g/cm ³]	Concentration of NaBr $C_{M,sl}$ M	Molecular weight of micelles, M [kg/kmol]	$\eta \cdot 10^3$ [Pa·s]	ρ [kg/m ³]	σ [mN/m]
1	8.05	1	485,000	1.09	1107	36.0
2	2.97	2	1,240,000	1.15	1147	36.1

Table 4. Characteristics of TTAB/NaSal aqueous solution

	Concentration of TTAB $C_{V,s} \cdot 10^4$ [g/cm ³]	Concentration of NaSal $C_{M,sl} \cdot 10^4$ M	Concentration of TTAB C_p [ppm]	$\eta \cdot 10^3$ [Pa·s]	ρ [kg/m ³]	σ [mN/m]
1	4.01	2.38	400	1.14	997	35.7
2	8.02	4.76	800	1.60	997	35.3

In Fig. 1 sedimentation curves for barium carbonate in distilled water and TTAB aqueous solution are presented. It has been shown that in tetradecyltrimethylammonium bromide solutions of concentrations of 1·CMC and

2·CMC, the sedimentation process proceeds faster than in clear water. The growth of the TTAB concentration to 10·CMC level in a solution causes slowing down the sedimentation process (Figs. 1 and 2).

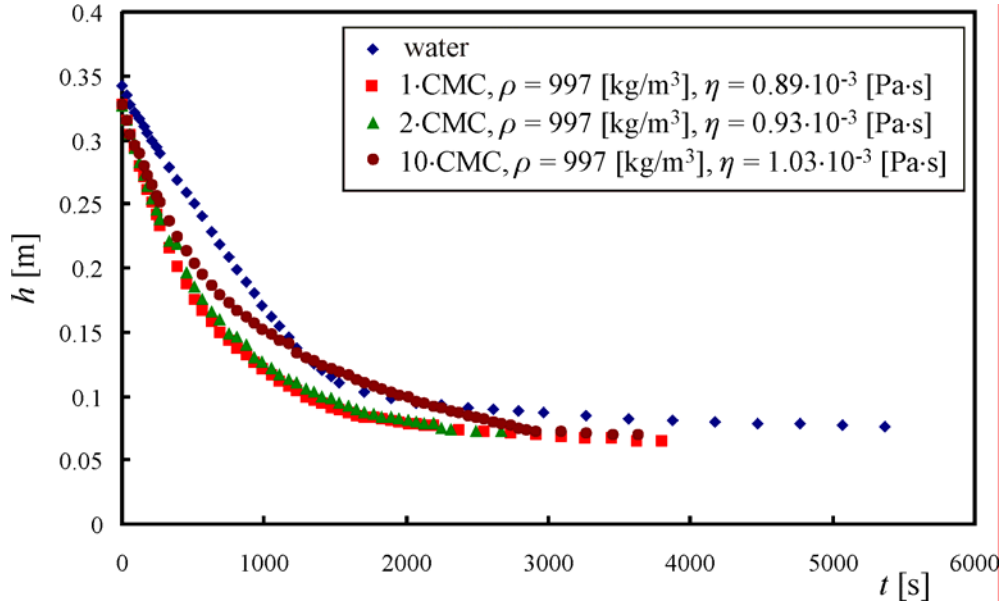


Fig. 1. Sedimentation curves of barium carbonate in TTAB solution in clear water

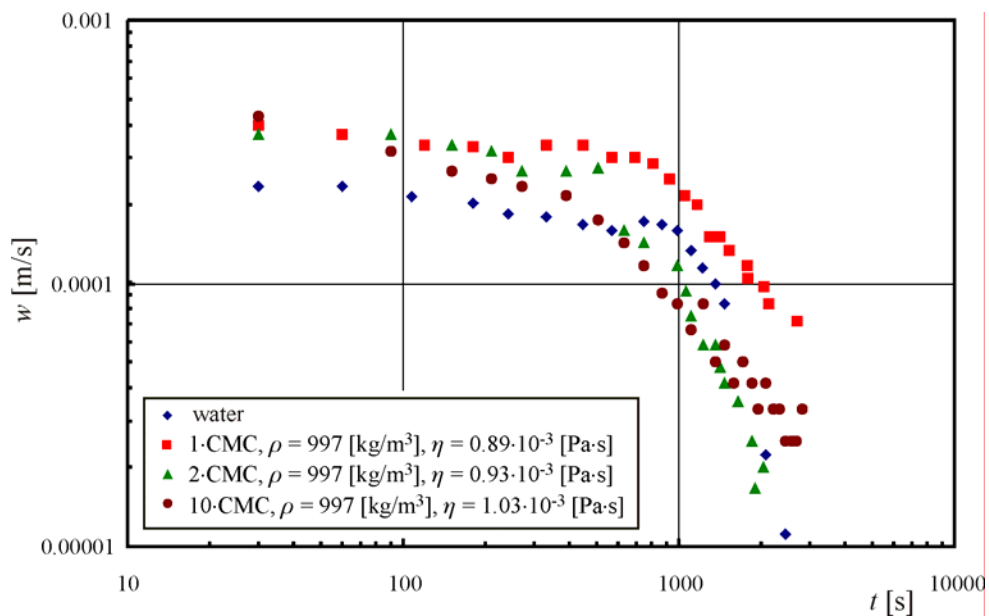


Fig. 2. Plot of the velocity of settling vs. time of sedimentation for settling of barium carbonate in TTAB solutions

The above-mentioned changes in sedimentation of suspension studied, can be explained on the basis of barium carbonate surface-cationic surfactant interactions.

Due to negative surface charge on the barium carbonate surface the adsorption of cationic surfactants onto the barium carbonate surface takes place. The hydrophilic polar group of the surfactant adsorbs onto the surface of barium carbonate by ion exchange mechanism while the hydrophobic part of the surfactant points outward (Fig. 3a). Thus barium carbonate surface is rendered to be hydrophobic due to the adsorption of the cationic surfactant onto surface of barium carbonate. Sedimentation rate increases rapidly at the concentration of TTAB equal to $1 \cdot \text{CMC}$ because of the hydrophobic interactions between particles and their aggregation. Hydrophobic interaction forces have been found to be of long range and 10 – 100 times stronger in comparison with van der Waals forces (Zukang *et al.*, 1990). Aggregation is induced by the hydrophobic interactions between particles.

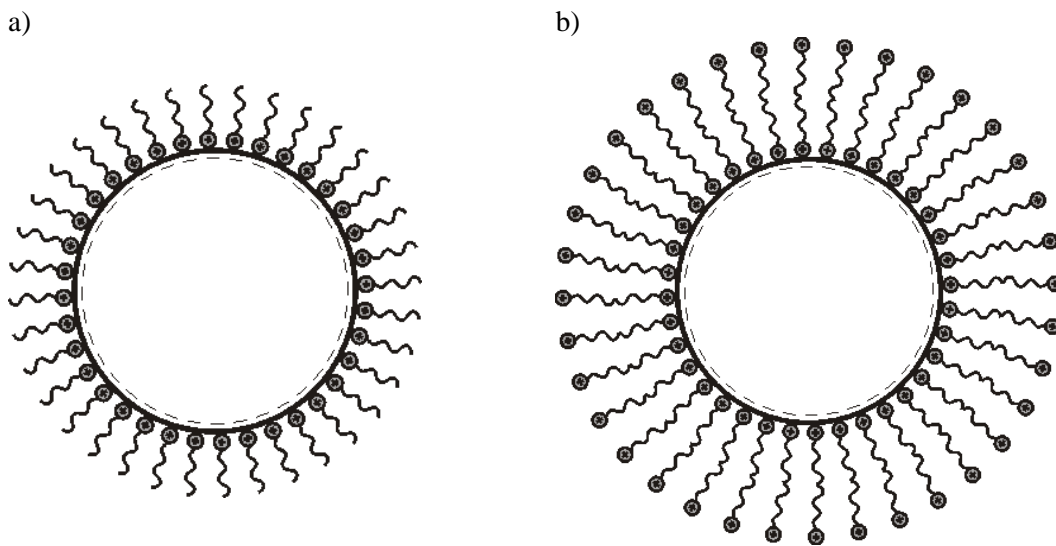


Fig. 3. Scheme of possible mechanism of cationic surfactant adsorption: a) monolayer adsorbed on negatively charged silica surface at a relatively lower concentration, b) two layers of surfactant (hemimicelles) at high surfactant concentration

It will facilitate the approach of molecules to each other and the greater agglomerates are formed. For the sake of bigger mass, the molecules fall faster. At higher concentration of cationic surfactant the hemimicelles (Gupta and Basu, 2005) are formed (Fig. 3b). Hemimicelles are surfactant bilayers formed on the surface of solid. Thus, the particle surfaces become hydrophilic. It leads to the disintegration of barium carbonate aggregates and decrease of sedimentation rate.

In the Fig. 4 the relationship of the concentration of solid vs. time of sedimentation has been presented. It is seen that a final concentration of sediment in clear water is equal to $447 \text{ [kg/m}^3\text{]}$ while in surfactant solution it is equal to $503 \text{ [kg/m}^3\text{]}$. Additionally, the final compression of settlings after $t = 3800 \text{ [s]}$ in surfactant solutions and after $t = 5370 \text{ [s]}$ in clear water, has been observed. It results from these data that the addition of surfactant will increase and accelerate the compression of sediment.

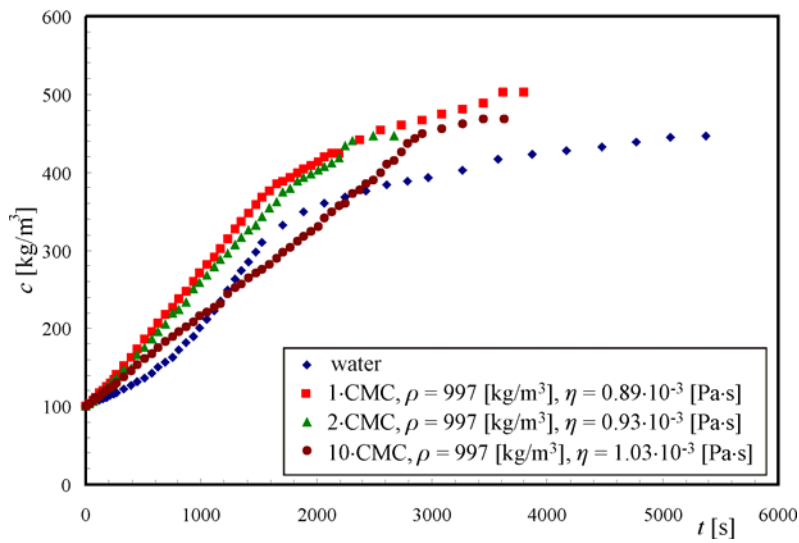


Fig. 4. Plot of concentration of suspension vs. time sedimentation for settling of barium carbonate in TTAB solutions

In Fig. 5 the comparison of the sedimentation curves for TTAB solutions in clear water and with NaBr addition has been presented. It results from the analysis of the plots, that the addition of salt to surfactant solution caused displacement in sedimentation curves towards higher values of suspension height. In the range of the sediment compression the experimental points for both surfactant solutions lie in the same height. The changes in sedimentation process for surfactant solution of concentration equal of 10-CMC with NaBr addition can be connected with increase in fluid density. The growth of density of liquid have the lesser influence on compression sediment process than on sedimentation rate in constant velocity zone.

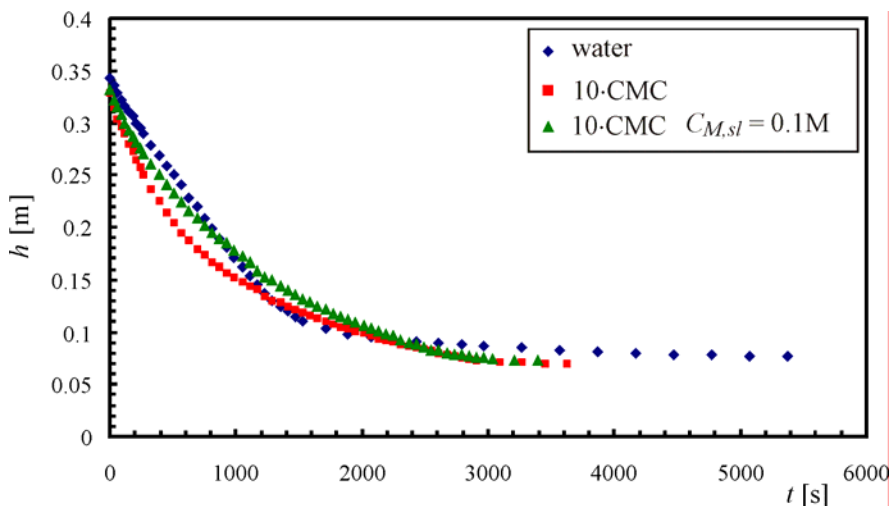


Fig. 5. Sedimentation curves of barium carbonate in TTAB solution in clear water and with NaBr addition

Fig. 6 shows sedimentation curves in TTAB solutions in which rodlike micelles are formed (Imae and Ikeda, 1986). The sphere-rod transition of micelles was induced by NaBr addition (Table 3). Additionally, in the Fig. 6 the results for sedimentation of barium carbonate in 2M NaBr solution have been presented. The run of experimental points is surprising. The sedimentation rate is the greatest in 2M sodium bromide solution and the least in TTAB/NaBr solution of 2M salt concentration.

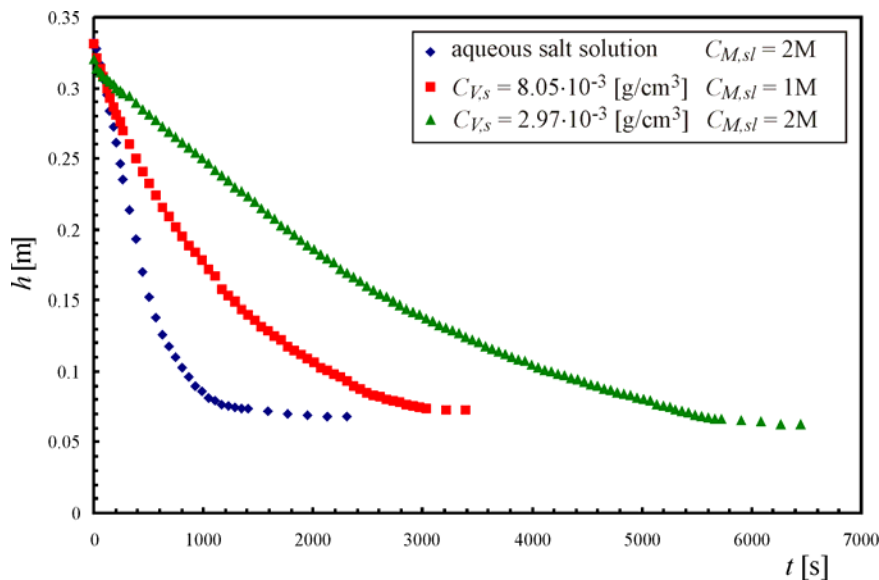


Fig. 6. Sedimentation curves of barium carbonate in TTAB/NaBr solutions

It results from the data presented in Table 3 that the molecular weight of the rodlike micelles formed in TTAB solution of concentration of $8.05 \cdot 10^{-3}$ [g/cm³] in 1M NaBr is $M = 485,000$, whereas in TTAB solution of concentration of $2.97 \cdot 10^{-3}$ [g/cm³] in 2M NaBr the micelles have the molecular weight $M = 1,240,000$ (Imae and Ikeda, 1986). The density of TTAB/2M NaBr solution was comparable with density of 2M NaBr solution ($\rho = 1147$ [kg/m³]). The decrease in sedimentation rate is possibly caused by a presence of rodlike micelles. However, additional studies are required for explanation the effects observed in sedimentation rate.

In Fig. 7 the experimental results of sedimentation process of barium carbonate in tetradecyltrimethylammonium bromide solutions with sodium salicylate additive have been presented. According to literature data (Walker, 2001) in these type of solutions, the rodlike micelles of very long sizes (called *wormlike*) can be formed. The run of sedimentation curves shown in Fig. 7 indicates the complex character of this process in TTAB/NaSal solutions. In the case of solution of concentration $4,01 \cdot 10^{-4}$ [g/cm³] the whole sedimentation curve runs above the settling curve in clear water. At the concentration of $8,02 \cdot 10^{-4}$ [g/cm³] in the range of constant sedimentation rate the experimental points overlap with points characteristic for sedimentation in clear water. Further the decrease in sedimentation rate can be observed. Additionally, the direct relationship between changes in course of sedimentation curves and the

concentration of surface active agent in solution does not exist. Experimental points for settling of barium carbonate particles in TTAB solution of concentration $8,02 \cdot 10^{-4}$ [g/cm³] lie below the points obtained for solution of $4,01 \cdot 10^{-4}$ [g/cm³] concentration. In the range of sediment compression the experimental points overlap.

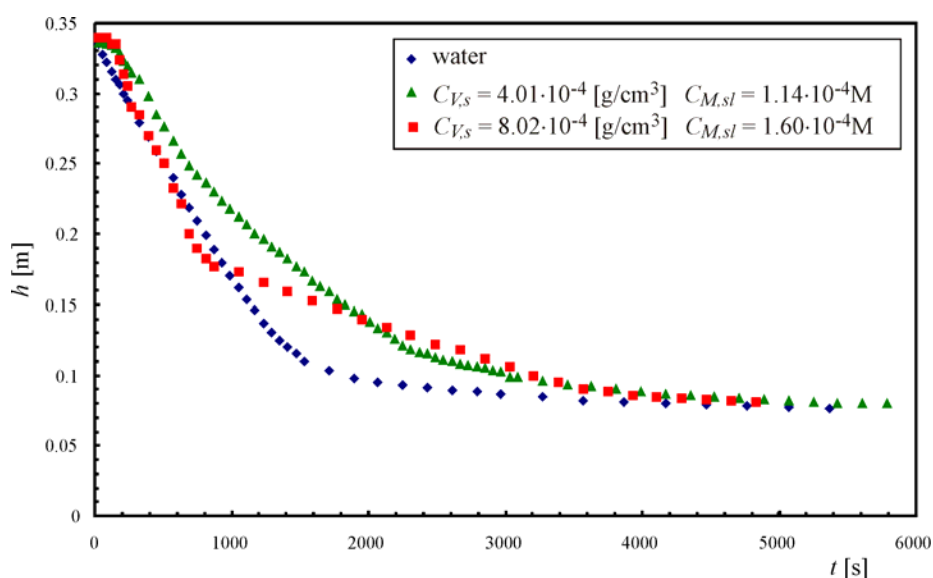


Fig. 7. Sedimentation curves of barium carbonate in TTAB/NaSal solutions

The observed decrease in sedimentation rate of barium carbonate particles in TTAB/NaSal solutions can be explained by the growth of viscosity (Table 4). However, the viscosity of TTAB/NaSal solution increases with the increase of concentration of surfactant. The change in viscosity do not cause the decrease in sedimentation rate. Therefore, the changes presented are probably connected with aggregation of particles in TTAB/NaSal solutions. For that reason, the explanation of changes taking place in sedimentation process in TTAB solutions with NaSal addition is not possible without preliminary investigation of aggregation process.

3. Conclusions

The experimental results showed that in the studied range of surfactant concentration due to aggregation of particles the sedimentation rate of barium carbonate particles is highest at 1-CMC TTAB concentration. In the presence of both TTAB and NaBr the sedimentation rate decreases. Large decrease of sedimentation rate in TTAB/NaBr solutions, in which the rodlike micelles are formed, was observed. The run of sedimentation curves of TTAB/NaSal solutions indicates the complex character of this process.

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