



Aggregation Properties of Triton X-100 in a Mixture of Ordinary and Heavy Water

Victor P. Arkhipov¹ · Ruslan V. Arkhipov² · Natalia Kuzina¹ · Ekaterina V. Petrova³ · Andrei Filippov⁴

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Abstract

The dynamic and aggregation properties of Triton X-100 in a mixture of ordinary and heavy water in a wide temperature range from room temperature to the cloud point and above were studied. The ratio of ordinary and heavy water was calculated in such a way as to ensure equal densities of Triton X-100 and the water mixture. This made it possible to exclude the effects of sedimentation and study the evolution of Triton X-100 micelles and aggregates, without complication by the effects of spatial phase separation above the cloud point. Self-diffusion coefficients of Triton X-100 molecules were measured by NMR, and the effective hydrodynamic radii of micelles and aggregates were calculated using the Stokes–Einstein relation. The anomalous temperature behavior of the diffusion coefficient of Triton X-100 molecules is explained by changes in the sizes of diffusing objects during their evolution from micelles to dehydrated aggregates below the cloud point and by changes in the sizes of aggregates above the cloud point. The results of the NMR studies are confirmed by data obtained by dynamic light scattering.

1 Introduction

Nonionic surfactants in aqueous solutions at temperatures above the cloud point lose their solubility in water due to the breaking of hydrogen bonds between the oxygen atoms of the oxyethylene fragments of the surfactant molecules and the hydrogen of the

✉ Andrei Filippov
Andrei.Filippov@ltu.se

¹ Department of Physics, Kazan National Research Technological University, 420015 Kazan, Russian Federation

² Institute of Physics, Kazan Federal University, 420008 Kazan, Russian Federation

³ Department of Analytical Chemistry, Kazan National Research Technological University, 420015 Kazan, Russian Federation

⁴ Chemistry of Interfaces, Luleå University of Technology, 97187 Luleå, Sweden

water molecules [1, 2]. A homogeneous micellar solution at the cloud point is separated into two phases that are depleted and enriched with surfactant. The surfactant-depleted phase contains surfactants with a concentration equal to the critical micelle concentration (CMC), while the surfactant-enriched phase contains aggregates of dehydrated surfactant molecules [3]. The effective sizes of such aggregates at the cloud point reach values on the order of 10^2 nm [4]. Due to incoherent light scattering, the solution becomes cloudy, and due to sedimentation phenomena, the enriched and depleted surfactant phases are separated spatially [5, 6]. The clouding phenomenon underlies the micellar extraction method with a non-ionic surfactant-enriched phase, a method known as cloud point extraction CPE [7–11].

The temperature evolution of surfactant micelles in aqueous solutions has been studied from room temperature to temperatures near the cloud point [12–16]. With rare exceptions [17], studies above cloud point, to the best of the authors' knowledge, have not been performed due to sedimentation phenomena arising from the difference in densities of nonionic surfactants and water. It is possible to eliminate sedimentation, that is, the settling (or floating) of particles in a dispersion medium under the action of gravity, if the densities of the dispersion medium and the dispersed phase are equal to each other. So, if the density of surfactants is higher than the density of ordinary H_2O water but less than the density of heavy D_2O water, then, using a mixture of ordinary and heavy water, it is possible to achieve the necessary equal densities of surfactants and an aqueous mixture. The study of the evolution of micelles and aggregates of non-ionic surfactants near and above the cloud point can be useful in understanding and optimizing CPE processes, an important advantage of which is environmental safety.

The purpose of this work was to study the dynamic and aggregation properties of aqueous solutions of the nonionic surfactant Triton X-100 in a wide temperature range of 295–350 K, both below and above the cloud point. To eliminate the effects of sedimentation, a mixture of $\text{H}_2\text{O} + \text{D}_2\text{O}$ with a density equal to that of Triton X-100 was used as a dispersion medium. The main research method was NMR diffusometry. The self-diffusion coefficients of water molecules and Triton X-100 were measured selectively on a Bruker-Avance NMR spectrometer (^1H -400 MHz). The effective hydrodynamic radii of micelles and aggregates were calculated from the measured diffusion coefficient of Triton X-100 molecules using the Stokes–Einstein relation. The cloud point was determined visually, and dynamic light scattering was used to provide an independent determination of the sizes of the micelles and aggregates. Unlike the NMR diffusometry method, the DLS method is based on the phenomenon of mutual diffusion and complements the capabilities of the NMR method. The aggregation numbers were calculated using the approximation of the spherical shape of micelles and aggregates. All studies were performed at a constant concentration of Triton X-100 in solutions, $C = 1$ wt%.

2 Experimental Part

Materials. Non-ionic surfactant Triton X-100, Sigma-Aldrich laboratory grade, cloud point 65 °C in ordinary water was used [18]. Distilled and additionally deionized water H_2O and deuterated water D_2O (degree of substitution 99.9%, Sigma)

were used to prepare solutions with a solvent density equal to that of Triton X-100. The densities of ordinary water, heavy water and Triton X-100 at a temperature of 20 °C are 0.9982; 1.1056 and 1.0650 g/ml, respectively [19, 20]. The samples were thoroughly mixed and allowed to settle for 2 days before measurements.

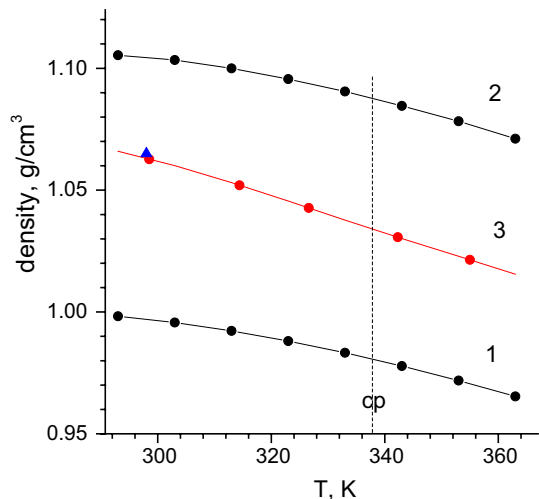
Density The density of Triton X-100 as a function of temperature was measured by the standard pycnometric method [21] using a glass pycnometer. Boiled distilled, degassed ordinary water was used as the reference liquid. The densities of ordinary and heavy water [19], as well as the density of Triton X-100 measured by us, depending on the temperature, are presented in Fig. 1. As can be seen from Fig. 1, the densities of water and Triton X-100 naturally decrease with increasing temperature but are not completely sybatic. The data obtained make it possible to calculate the ratio of ordinary and heavy water, which is necessary to obtain equal densities of the aqueous mixture and the Triton X-100. The optimal ratio of H₂O:D₂O at temperatures near and above the cloud point is 0.48:0.52 in weight fractions or in volume fractions of 0.51:0.49—this ensures equality of the densities of Triton X-100 and the aqueous mixture at a temperature of 343 K.

NMR diffusometry. The self-diffusion coefficients of Triton X-100 molecules were measured on a Bruker-Avance NMR spectrometer (¹H-400 MHz) using a pulsed magnetic field gradient and a stimulated spin echo pulse sequence [22]. The amplitude of the stimulated spin echo signal is determined by the expression:

$$A(\tau, \tau_1, g, \delta) \propto \exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1}\right) \exp(-\gamma^2 g^2 \delta^2 D t_d), \quad (1)$$

where T_1 and T_2 are times of spin–lattice and spin–spin relaxation, τ , τ_1 are time intervals in the pulse sequence, γ is the proton gyromagnetic ratio, g and δ are amplitude and duration of the magnetic field gradient pulse, D is the diffusion coefficient,

Fig. 1 Densities: 1-ordinary water [19], 2-heavy water [19], 3—Triton X-100, down triangle – density of Triton X-100 at 298 K [20]



$t_d = (\Delta - \delta/3)$ is the diffusion time, $\Delta = (\tau + \tau_f)$. The measurements were performed at a fixed diffusion time $t_d = 49$ ms and duration of the gradient pulse $\delta = 1$ ms, number of scans $NS = 4$. To obtain the diffusion decay of the spin echo signal, the amplitude of the impulse gradient was varied (16 values). In measurements of the D of Triton X-100, the maximum amplitude of the gradient pulses was 6–8 T/m, while in measurements of the D of water, it was 0.5–0.8 T/m. The maximum amplitude of the gradient pulses was set individually in each measurement, depending on the value of the D . The necessary condition is to obtain at least tenfold diffusion decay of the spin echo signal. The repetition time RT between successive scans required to restore magnetization was set to 5 s, in accordance with the spin–lattice relaxation time of Triton X-100 oxyethylene protons $T_1 \approx 0.5$ s at 25 °C and $T_1 \approx 1$ s at 80 °C.

Processing of diffusion decays and the determination of the self-diffusion coefficients D were carried out using Bruker TopSpin 3.5 software [23]. The measurement error of the D did not exceed 5–6%. The temperature was set and controlled with an accuracy of 0.1 °C. The temperature sensor of the spectrometer was calibrated using a reference sample of ethylene glycol [24]. The ^1H NMR spectrum of Triton X-100 in D_2O solutions presented in Fig. 2: phenylene protons (6.9; 7.3 ppm), oxyethylene protons (4.15; 3.8 and 3.7 ppm), alkyl protons (1.75; 1.2 and 0.8 ppm). Self-diffusion coefficients were determined from the decays of the integral intensities of the lines of protons of oxyethylene groups, as the most intense lines in the spectra.

Figure 3 shows diffusion decays of the echo signal for oxyethylene groups of Triton X-100 in the coordinates $\ln A$ from $(\gamma g \delta)^2 t_d$. At temperatures below the cloud point, diffusion decays are linear, and the echo signal decays down to 1–2 decimal orders. At temperatures above the cloud point, diffusion decays become nonlinear.

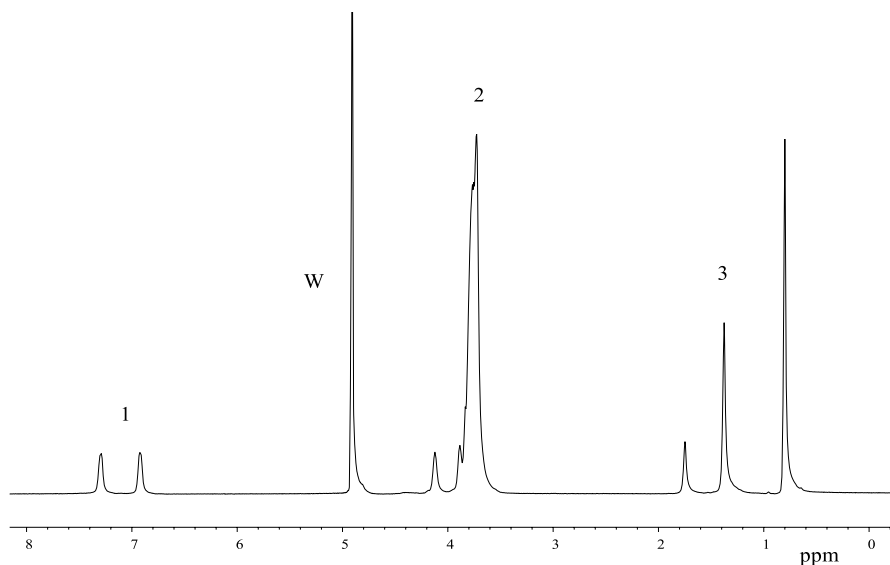


Fig. 2 ^1H NMR (400 MHz) spectrum of Triton X-100 in D_2O , $C = 1$ wt%, $T = 298$ K: 1—group of lines of phenylene protons, 2—group of lines of oxyethylene protons, 3—group of lines of alkyl protons, W—residual proton line of deuterated water

This means the absence of the micelle's polydispersity at temperatures below the cloud point and its appearance at cloud point temperatures. With the increase of temperature, the polydispersity of destruction of aggregates by thermal motion and the rate of curvature of diffusion decays increase.

Dynamic Light Scattering. The sizes of micelles in $\text{H}_2\text{O} + \text{D}_2\text{O}$ solutions of Triton X-100 were also measured by DLS using Zetasizer Nano-ZS (Malvern Instruments, Ltd., Malvern, U.K.). A He–Ne laser with $\lambda = 632.8$ nm was used. The Dynamic Light Scattering (also known as PCS—Photon Correlation Spectroscopy) method [25] is based on the measurement of temporal fluctuations of light scattered by particles (micelles, aggregates) with sizes of 0.6 nm to 6 μm performing Brownian motion in a micellar solution. The relationship between the size of a particle and its speed due to Brownian motion is defined in the Stokes–Einstein equation. Solutions for DLS measurements were subjected to fine filtration to remove microscopic impurities. The measurements were performed in disposable sizing cuvettes. At each temperature, the sample was equilibrated for 10 min prior to measurement. Thereafter, three consecutive measurements were performed at 1-min intervals to ensure that the system had reached a steady state. The DLS data were analyzed by the cumulant method. The particle diameter values obtained from the size distribution by volume presented in the results are the average of three replicates.

Cloud point. The cloud point of an aqueous solution of Triton X-100 was determined visually. The sample was slowly heated (~ 5 $^\circ\text{C}/\text{min}$) with stirring until cloudy, then the samples were gradually cooled (~ 0.5 $^\circ\text{C}/\text{min}$). The cloud point was taken to be the temperature at which the slowly cooled solution became transparent

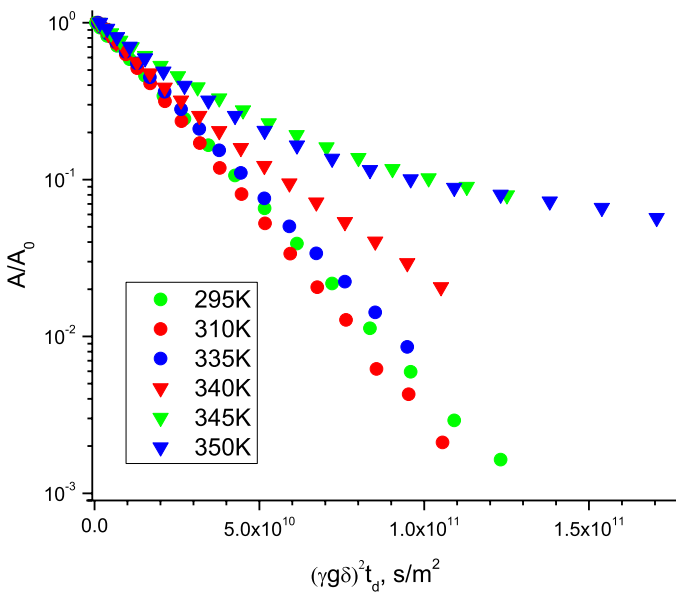


Fig. 3 Diffusion decays of the spin echo signal of oxyethylene protons of Triton X-100 in aqueous ($\text{H}_2\text{O} + \text{D}_2\text{O}$) solutions at 295, 312, 340 K—red, green, blue circle, 345, 351, 356 K—red, green, blue triangle, respectively

(disappearance of turbidity). To improve the reliability of these experiments, the process was repeated at least three times. The cloud point of Triton X-100 in aqueous solutions shows little dependence on the composition of the aqueous mixture. The cloud points of 1 wt.% solutions of Triton X-100 in ordinary and heavy water are 66 and 64 °C, respectively, and vary linearly with the composition of the mixture.

3 Results and Discussion

Self-diffusion coefficients and radii of micelles and aggregates. The temperature dependence of the self-diffusion coefficients of Triton X-100 at a concentration of $C=1$ wt% in a solution of ordinary and heavy water at a volume ratio of $H_2O:D_2O$ in the mixture equal to 0.51:0.49 are shown in Fig. 4.

The temperature dependence of D of Triton X-100 molecules has an anomalous form with characteristic features. In the temperature range of 295 K—310 K, there is an increase in the D of Triton X-100 with temperature. With a further increase in temperature to a cloud point of 338 K and above, D anomalously decreases. At temperatures above the cloud point, the diffusion decay becomes non-monoexponential (Fig. 3), and can be represented as a sum of two exponentials with different weighting coefficients. The relative fraction of the slow component with a lower D sharply decreases with temperature and amounts to 65% at 345 K and 15% at 356 K, respectively, with the fraction of the fast component having a higher increase in D .

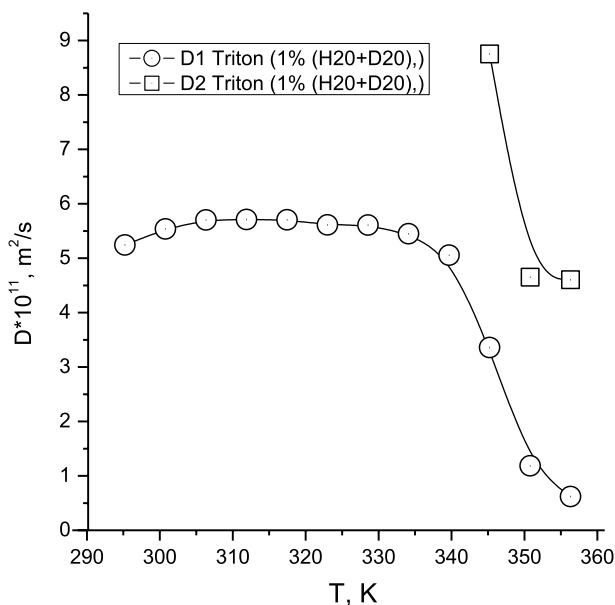


Fig. 4 Self-diffusion coefficients of micelles (circles) and dehydrated aggregates (squares) of Triton X-100 in aqueous (H_2O+D_2O) solutions at $C=1$ wt%

At the same time, there is the usual dependence of the D of water molecules in Arrhenius coordinates with characteristic deviations from linearity at high temperatures without any anomalies (Fig. 5). The value of the activation energy of diffusion of water molecules is:

$$E_D = -\frac{\Delta \ln D}{\Delta(1/RT)} \quad (2)$$

where R is the gas constant. E_D is 18.2 kJ/mol in the temperature range of 20–60 °C, which, within the measurement error, is in good agreement with the values of 17.6 kJ/mol and 18.8 kJ/mol, respectively, obtained by the method of labeled atoms [26] in ordinary and heavy water for the temperature range 15–45 °C.

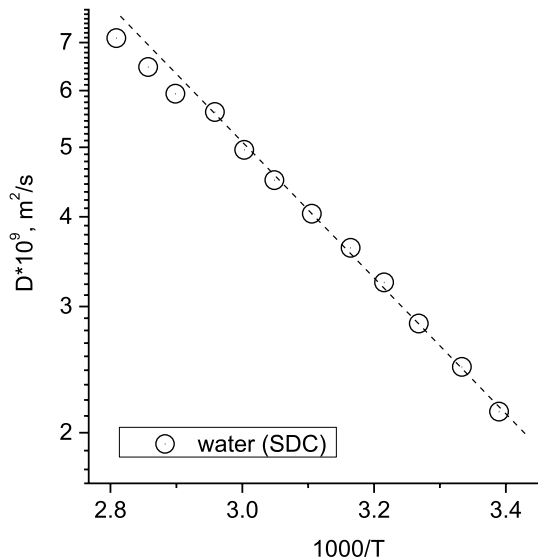
Obviously, the observed anomalies in the temperature dependence of D of Triton X-100 molecules are associated with structural rearrangements of the micellar solution, namely, with changes in the particle sizes formed by surfactant molecules. To determine the size of these particles, we use the Stokes–Einstein relation [27]:

$$D = \frac{kT}{6\pi\eta R}, \quad (3)$$

where k is the Boltzmann constant, η is the solvent dynamic viscosity and R is the hydrodynamic radius of the particle.

Relation (3), obtained for the motion of a spherical particle in a continuous medium, is often used to describe the motion of liquid molecules. Its application to describe the translational motion of micelles or surfactant aggregates is appropriate,

Fig. 5 Self-diffusion coefficients of water molecules in aqueous ($\text{H}_2\text{O} + \text{D}_2\text{O}$) solutions of Triton X-100 ($C = 1$ wt%) according to NMR results. In the temperature range 20–60 °C (dashed line) the diffusion activation energy is 18.2 kJ/mol



since the sizes of these objects significantly exceed the sizes of water molecules and, therefore, the solvent can be considered a continuous medium. In this case, corrections are introduced that take into account the nature of the interaction of solvent molecules with a diffusing particle [28, 29], or the microviscosity parameter [30], corrections for the interaction of diffusing particles with each other [31].

The radii of micelles or dehydrated aggregates obtained on the basis of the Stokes–Einstein relation, assuming the spherical shape of the diffusing particles, are the effective hydrodynamic radii. The viscosity values of the solvent required for the calculations, that is, the viscosity of a mixture of ordinary and heavy water, were determined by interpolation of the viscosity values of H₂O and D₂O [19] at the corresponding temperatures; we did not perform special additional viscosity measurements. In calculating the radii of micelles or aggregates using relation (3), the correction [31] was taken into account, which makes it possible to find the diffusivity under the condition of infinite dilution:

$$D_0 = \frac{D}{1 - 2\phi}, \quad (4)$$

where D is the measured diffusion coefficient, ϕ is volume concentration of micelles (aggregates) in the solution.

Figure 6 shows the effective hydrodynamic radii of particles calculated from NMR diffusometry data, micelles and dehydrated aggregates formed by Triton X-100 molecules, at temperatures both below and above the cloud point, as well as the results of DLS measurements.

According to NMR and DLS data, the micelle radii at a temperature of 295 K are equal to ≈ 3.5 nm. With increasing temperature, the sizes of the micelles and the dehydrated aggregates that appear when approaching the cloud point temperature increase, and the effective hydrodynamic radii of dehydrated aggregates at the cloud point temperature are equal to ≈ 10 nm. With a further increase in temperature, an increase in the size of dehydrated aggregates is observed. According to both NMR and DLS data, aggregates are simultaneously destroyed by thermal motion at high temperatures; objects with radii of ≈ 7 – 15 nm are found in the system, the relative proportion of which increases with temperature.

Aggregation number. The effective hydrodynamic radii of micelles (up to the cloud point) and dehydrated aggregates (after the cloud point) make it possible to calculate the average N_{agg} aggregation number, that is, the number of surfactant molecules that form a separate kinetic unit, micelle or a dehydrated aggregate. The calculation can be performed, for example, by comparing the volumes of these objects with the volumes of individual Triton X-100 molecules. The volume of an individual Triton X-100 molecule, v , calculated by the atomic increment method [27, 32] is 0.607 nm³. The volumes of micelles or aggregates can be related to their effective hydrodynamic radii R , then:

$$N_{agg} = f \cdot \frac{\frac{4}{3}\pi R^3}{v}, \quad (5)$$

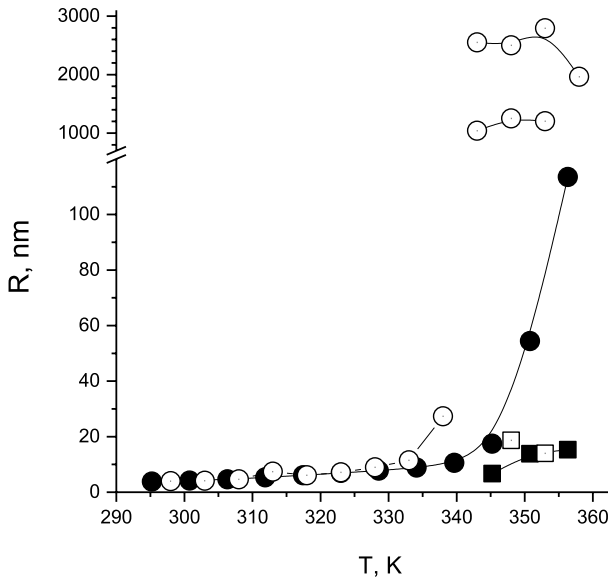


Fig. 6 Temperature dependence of the radii of micelles and aggregates of dehydrated molecules and micelles of Triton X-100 in aqueous ($\text{H}_2\text{O} + \text{D}_2\text{O}$) solutions at concentration $C = 1$ wt%: closed circles are the NMR result; open circles are the DLS data. Closed and open squares are radii of particles formed because of the destruction of aggregates by the thermal motion

where f is the packing factor, that is, the fraction of the volume of a micelle or aggregate occupied by surfactant molecules. Let's take $f = 0.524$, which corresponds to a simple cubic lattice. Calculations show that at $T = 295$ K, the aggregation number $N_{agg} \approx 200$; at the cloud point, $N_{agg} \approx 5000$; and with a further increase in temperature and enlargement of dehydrated associates, the aggregation number sharply increases and reaches values of $\approx 10^9 - 10^{10}$.

4 Conclusions

The mixture of ordinary and heavy water was used to exclude the effects of sedimentation and study the evolution of Triton X-100 micelles and aggregates from room temperature to the cloud point and well above the cloud point by means of NMR diffusometry and dynamic light scattering methods.

According to the NMR data, the diffusivity of Triton X-100 changes abnormally with temperature. Below the cloud point, the self-diffusion coefficient of Triton X-100 micelles decreases with increasing temperature, and above the cloud point, it is characterized by two values. The anomalous decrease in D of Triton X-100 with increasing temperature is explained by an increase in the size of the micelles, and when approaching the cloud point temperature, by an increase in the size of dehydrated aggregates. At temperatures above the cloud point, the destruction of dehydrated aggregates occurs.

Calculations of the radii of the micelles and aggregates from the results of NMR diffusometry using the Stokes–Einstein relation and DLS results are in good agreement with each other. The kinetic units formed by surfactant molecules increase in size with increasing temperature up to the cloud point, changing from micelles to dehydrated aggregates. At temperatures above the cloud point, an increase in the size of dehydrated aggregates is observed; according to the DLS data, associates with sizes on the order of $\approx 10^3$ nm are formed. According to both NMR and DLS data, objects with radii of ≈ 7 –15 nm are found in the system at high temperatures, the relative proportion of which increases with temperature, indicating there are processes of aggregate destruction by thermal motion.

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Author Contributions V.P.A. performed the main experimental work and prepared a draft of the manuscript. R.V.A. performed some NMR diffusion experiments. N.A.K. prepared systems of the study and figures. E.V.P. did the overall design of the study. A.F. did overall supervision and final corrections of the manuscript.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Conflict of Interests The authors declare no competing interests.

Ethical Approval Not applicable.

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