
STRUCTURE TRANSFORMATIONS IN THE TRIPLE LIQUID SYSTEM TETRADECYLTRIMETHYLAMMONIUM BROMIDE–D₂O–NaBr**L.A. BULAVIN,¹ O.I. IVANKOV,^{1,2} A.KH. ISLAMOV,² A.I. KUKLIN²**¹*Taras Shevchenko National University of Kyiv, Faculty of Physics
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Structure transitions in the triple liquid system tetradecyltrimethylammonium bromide–D₂O–NaBr are studied by the method of small-angle neutron scattering (SANS) in wide ranges of the temperature, pressure, and salt concentration. The phase P – T diagrams of the transition of the colloidal micellar liquid system to a colloidal system of the suspension type through a structural micelles–crystals (precipitates) transition are constructed. It is shown that the addition of the salt does not result in a change of the slope of the line of phase equilibrium between a micellar colloidal system and a suspension with precipitates which is equal to 53 bar/K. It is shown that an increase in the salt concentration causes a shift of the line in the direction of higher temperatures and lower pressures.

1. Introduction

The necessity to study cationic surfactants is related, to the first turn, to their wide use in industry and in various branches of science. In biology, cationic surfactants are widely applied in the separation of DNA (RNA) [1], protection of DNA from enzymatic cleavage, extraction of membrane proteins from cells and plasmids, *etc.* The important role is played by the possibility to stabilize nanoparticles by cationic surfactants, which prevents their agglutination and precipitation. In addition, cationic surfactants are efficient antiseptics. We mention also their catalytic action on the reactions with the participation of polyamides and polycarbonates [2, 3]. The application of surfactants in industry is related, to the first turn, to their use in the production of various detergents [4].

Such wide field of the use of cationic surfactants requires the detailed study of properties of systems formed with the participation of surfactants under various thermodynamic conditions on the molecular level. It is known that cationic surfactants participate in the creation of crystalline structures, the so-called precipitates, in liquid systems at certain values of the pressure, concentration of surfactants, and temperature (lower than the Kraft temperature) [5–7]. In work [7], the authors investigated the transition micelles–precipitates with the participation of cationic surfactants – tetradecyltrimethylammonium bromide C₁₄H₂₉N(CH₃)₃Br (TTAB) within the method of small-angle neutron scattering and the method of Raman spectroscopy. The dependence of the pressure on the temperature on the line of phase equilibrium between a liquid system with micelles and a liquid system with crystallites for the micellar liquid system C₁₄H₂₉N(CH₃)₃Br–D₂O and the triple micellar liquid system C₁₄H₂₉N(CH₃)₃Br–D₂O–NaBr was studied. The purpose of the present work is the study of the influence of the salt concentration on the structural transition micelles–precipitates in the above-mentioned liquid colloid system.

2. Method of Experiments

To realize the posed problem, we choose the diffraction method, namely the method of small-angle scattering of slow neutrons which allows one to trace a change in the structure of a colloid micellar liquid system occurring under the action of the pressure and the temperature. As a micellar liquid system, we took the system TTAB–D₂O

which was earlier studied in [7]. To this micellar system, we add salt NaBr in order to trace the influence of the salt concentration on the structural transition micelles-precipitates.

For the experiments, we prepared the liquid system TTAB-heavy water with a TTAB concentration of 50 mM. To this micellar system, we add the NaBr admixture. As a result, we obtained triple liquid systems TTAB-heavy water-NaBr with NaBr concentrations of 25, 50, 100, 200, and 800 mM.

In order to prepare micellar liquid systems of surfactants, we took dry TTAB of the Sigma-Aldrich Co. (a content of TTAB equals 99%) and D₂O of the Izotop firm (Moscow) (a content of D₂O equals 99.8%).

At the normal pressure, we placed specimens in quartz Hellma cuvettes with a neutron path length of 1 mm or 2 mm. To study of the influence of the pressure, temperature, and concentration of electrolyte admixtures on the structural state of the system under study, the specimens were placed in a thermostatted chamber with high hydrostatic pressure [8]. In this case, the temperature of specimens was maintained with the help of a thermostat of the Lauda firm to within ± 0.1 °C.

The SANS experiments were carried out on a modernized spectrometer YuMO [9] in a two-detector version [10, 11]. The spectrometer is positioned at the IBR-2 pulse reactor of the Joint Institute of Nuclear Research (Dubna, Russia). The available experimentally interval of the wave vectors q was $7 \times 10^{-3} \text{ \AA}^{-1} - 1.4 \times 10^{-1} \text{ \AA}^{-1}$.

We registered the curves of small-angle neutron scattering at various pressures, temperatures, and concentrations of the NaBr admixture in the indicated system with regard for its diagram of state. As is known [4], one of the main characteristics of the diagrams of state of liquid systems with surfactants is the Kraft line, on which the structural transition in a colloid liquid system, namely the transition of the colloids of micelles into the colloids of crystallites, occurs.

To determine the influence of the salt admixture in the liquid system with cationic surfactants on parameters of such structural transition, we investigated the small-angle neutron scattering in the interval of thermodynamical parameters which includes the Kraft line.

The experiment was performed as follows: a specimen was heated to a temperature higher than the Kraft temperature, and then the temperature was decreased. In this case, we registered the scattering pattern with an exposure of 10 min. If no variations in the neutron scattering curve happened during 20 min, then the temperature was decreased further.

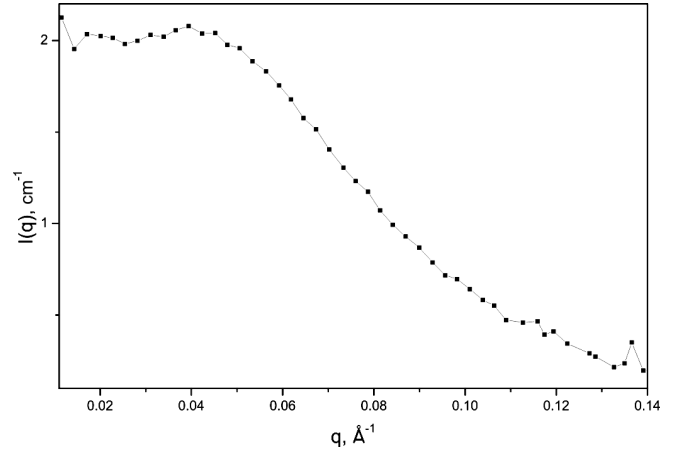


Fig. 1. Intensity of small-angle neutron scattering at the pressure $P = 320$ bar when the temperature is higher than the Kraft one, $T = 16$ °C. The concentration of TTAB is 50 mM. The concentration of NaBr equals 50 mM

3. Results and Discussion

On the first stage, we studied inhomogeneities in the liquid system with the help of SANS in the case where the system is in the micellar state.

In Fig. 1, we present the curves of small-angle neutron scattering for the liquid micellar system with cationic surfactants and the NaBr admixture. As seen in Fig. 1, we observe a peak at $q \sim 0.044 \text{ \AA}^{-1}$ which corresponds to the interaction between charged micelles.

Indeed, the neutron scattering intensity in the liquid system under study can be written in the form

$$I = n \langle |F^2(q)| \rangle S(q), \quad (1)$$

where n is the concentration of particles, and $F(q)$ is the form-factor corresponding to the intensity of neutron scattering by a single micelle:

$$F^2(q) = \left[\int (\rho - \rho_s) \exp(i\mathbf{q}\mathbf{r}) d^3\mathbf{r} \right]^2, \quad (2)$$

where ρ and ρ_s are, respectively, the scattering length densities of micelles and the solution. In formula (1), $S(q)$ describes the interaction between micelles and corresponds to a certain distribution of the centers of masses of micelles in space. Just this structural factor is the cause for the formation of such a peak. The structural factor $S(q)$ can be given in the form [12]

$$S(q) = 1 + V^{-1} \left[\int (g(\mathbf{r}) - 1) \exp(i\mathbf{q}\mathbf{r}) d^3\mathbf{r} \right], \quad (3)$$

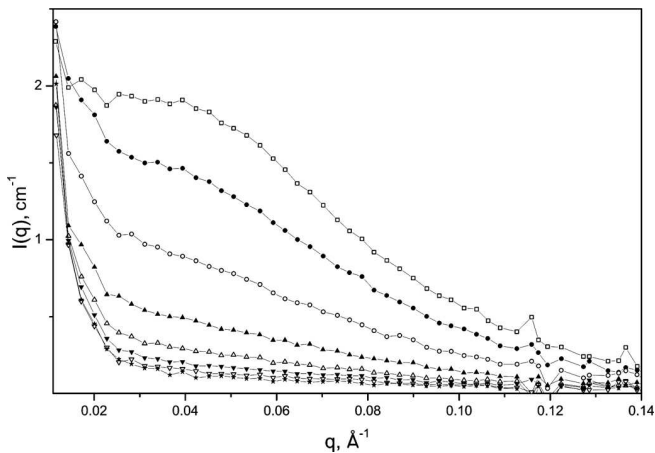


Fig. 2. Intensity of small-angle neutron scattering reflecting the kinetics of the structural transformation micelles-precipitates at the steady pressure $P=320$ bar at the passage across the Kraft line. $T=14$ °C. The concentration of TTAB is 50 mM, and the concentration of NaBr is 50 mM

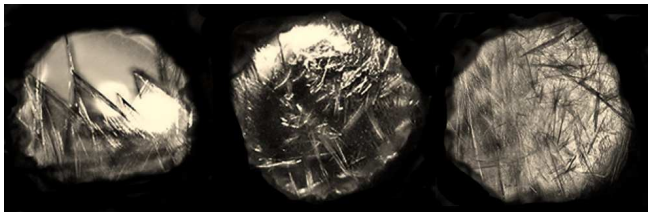


Fig. 3. Photos of the micelles-precipitates transition which are obtained with a chamber with high hydrostatic pressure for visual observations

where $g(r)$ is the pair correlation function, and V is a volume per micelle.

On the second stage of execution of the experiment, we changed the thermodynamical parameters P and T so that the system passed the Kraft equilibrium line. We observed how micelles in such colloid system are transformed into crystallites.

In Fig. 2, we show the curves of small-angle neutron scattering at once after a decrease in the temperature for the following time intervals after the start of the decrease in the temperature: (\square) – $t=30$ min, (\bullet) – $t=60$ min, (\circ) – $t=90$ min, (\blacktriangle) – $t=120$ min, (\triangle) – $t=150$ min, (\blacktriangledown) – $t=180$ min, (∇) – $t=210$ min, (\star) – $t=240$ min. It is seen from Fig. 2 that the kinetics of formation of the solid phase is manifested in the change in the curves of small-angle scattering. The peak at $q \sim 0.044$ Å $^{-1}$ disappears in the course of the time; but, in this case, the neutron scattering intensity in the region of small q increases.

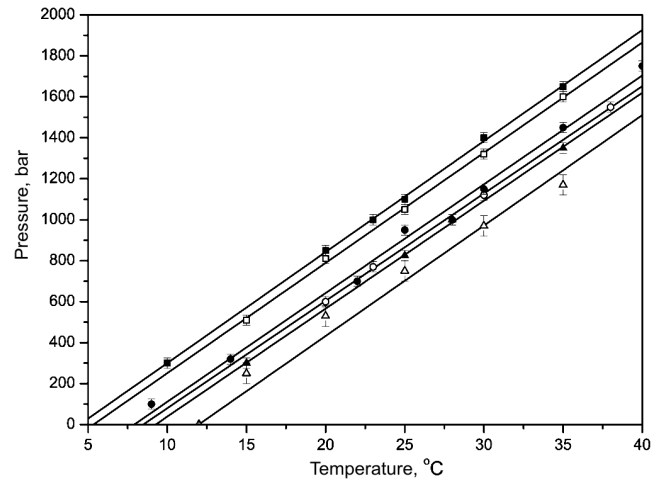


Fig. 4. Dependence of the pressure on the temperature on the Kraft line of phase equilibrium for the triple liquid system TTAB-D₂O-NaBr for various contents C_{NaBr} , mM: \blacksquare – 0; \square – 25; \bullet – 50; \circ – 100; \blacktriangle – 200; \triangle – 800. The concentration of TTAB equals 50 mM

The process of structural transition in the liquid system (in other words, the micelles-precipitates transition) was also observed visually. For this purpose, we used a high-pressure chamber for visual observations. In Fig. 3, we give the photos showing the micelles-precipitates transition. The chamber window diameter is about 1 cm, and the distance between windows equals 1 mm. At the beginning of the process of crystallization, the precipitates sink on the chamber bottom, but their sizes did not allow us to see them visually. In the course of the time, the crystalline structures with significant sizes are formed. They are shown in the photo (see Fig. 3). Therefore, with the help of a chamber, we can obtain the information only about the presence or absence of the process of crystallization, rather than about its kinetics. For example, we see a formed crystal which occupies a half of the chamber window area in the left photo. In the middle and right photos, the crystal is already in contact with the whole surface of a chamber window.

On the basis of the obtained data on small-angle neutron scattering, we constructed the curves showing the dependences of the pressure on the temperature on the line of a phase equilibrium between the micellar system and a suspension (Fig. 4). As seen from Fig. 4, the slopes of the lines of phase equilibrium are the same and are about 53 bar/K.

It follows from Fig. 4 that the addition of the salt admixture into the micellar liquid system TTAB-D₂O

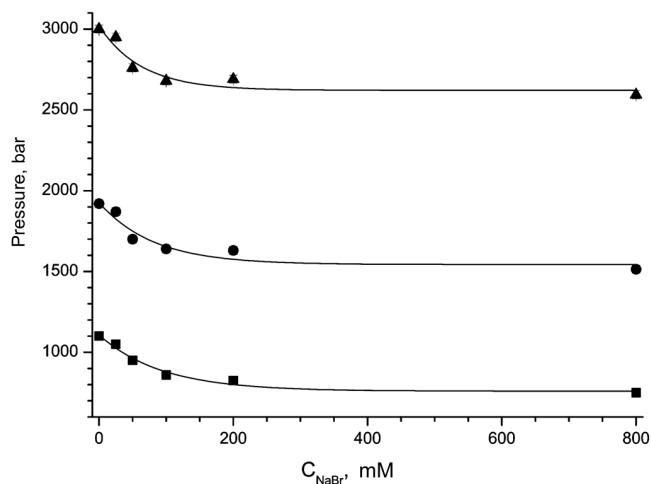


Fig. 5. Dependence of the pressure of the phase transition at a constant temperature on the NaBr admixture concentration in the liquid system. The concentration of TTAB equals 50 mM. ■ – 25 °C, ● – 40 °C, ▲ – 60 °C

causes a shift of the line of phase equilibrium between the liquid system and the solid to the region of higher temperatures and less pressures.

We now analyze the dependence of the pressure of the phase transition on the concentration of NaBr in the liquid system at various temperatures on the Kraft line of phase equilibrium. To this end, we approximated the experimental data on the temperature dependence of the pressure on the line of equilibrium for five values of the NaBr concentration in the liquid system in the studied temperature interval by straight lines. Then, for temperatures of 25 °C, 40 °C, and 60 °C, we constructed the dependence of the pressure of the structural transition on the salt concentration and give it in Fig. 5. It follows from the figure that, at low concentrations of NaBr in the system, the realization of the phase transition requires much higher pressure than that at high concentrations. For example, at a temperature of 25 °C, the ratio of such pressures is ~ 1.5 . This is related, first of all, to the sizes of micelles: at high concentrations of surfactants, the strongly elongated cylindrical micelles are formed [13], and the creation of large aggregates requires a less energy. Figure 5 indicates that we can trace, on the phase equilibrium line, the asymptotic behavior of the dependence of the pressure on the NaBr admixture concentration in the system for the three given temperatures.

4. Conclusions

Within the method of small-angle neutron scattering, we have studied the structural transformations micelles–precipitates in the micellar liquid system TTAB-heavy water in a wide interval of temperatures and pressures at various concentrations of NaBr in the system. We constructed the lines of phase equilibrium for two colloid systems. In one of the systems, the colloid is micelles which are formed by molecules of surfactants. In the second system, the colloid consists of crystallites (precipitates) which appeared in the liquid system under the action of the pressure due to the structural transition. It is shown that the addition of the NaBr admixture does not influence the slope of the line of phase equilibrium which is equal to 53 bar/K. We have found the asymptotic dependence of the behavior of the pressure of the structural transition on the salt concentration. It is shown that the addition of the salt into the micellar liquid system causes a shift of the line of the structural transition micelles–precipitates to higher temperatures and less pressures.

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СТРУКТУРНІ ПЕРЕТВОРЕННЯ В ПОТРІЙНІЙ РІДИННІЙ СИСТЕМІ ТЕТРАДЕЦИЛТРИМЕТИЛАМОНІЙ БРОМІД–D₂O–NaBr

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Резюме

За допомогою малокутового розсіяння нейтронів (МКРН) досліджено структурні переходи в потрійній рідинній системі тетрадецилтриметиламоній бромід–D₂O–NaBr у широкому ді-

апазоні температур, тисків і концентрацій солі. Побудовано фазові P – T діаграми переходу колоїдної міцелярної рідинної системи в колоїдну систему типу суспензія за рахунок структурного переходу міцели–кристаліти (преципітати). Показано, що додавання солі не веде до зміни нахилу лінії фазової рівноваги міцелярна колоїдна система–суспензія з преципітатами, який дорівнює 53 бар/К. Показано, що підвищення концентрації солі викликає зсув вказаної лінії фазової рівноваги в бік більших температур та менших тисків.