NEUTRON STUDIES OF THE NaBr IMPURITY INFLUENCE ON MICELLE FORMATION IN THE HEAVY WATER–TETRADECYLTRIMETHYLAMMONIUM BROMIDE SYSTEM

L.A. BULAVIN,[1] V.I. GORDELIY,[2,3] O.I. IVANKOV,[1,2] A.KH. ISLAMOV,[2] A.I. KUKLIN[2]

[1]Taras Shevchenko National University of Kyiv, Faculty of Physics
(1, Bld., 2, Academician Glushkov Ave., Kyiv 03022, Ukraine)

[2]I.M. Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research
(6, Joliot-Curie Str., Dubna 141980, Russia)

[3]Institut de Biologie Structurale J.P. Ebel
(41, Jules Horowitz Str., Grenoble F-38027, France)

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Micelle formation in the triple liquid system tetradecyltrimethylammonium bromide–heavy water–NaBr has been studied by means of small-angle neutron scattering (SANS). The rescaled mean-spherical approximation by Hayter–Penfold has been used to treat the small-angle neutron diffraction data on charged micelles. The dependences of the micelle size and aggregation number on the liquid system temperature and NaBr concentration have been found.

1. Introduction

One of the properties of surfactants in a solution is their ability to self-organize, the mechanisms of which have not been studied in full till now. Challenging are the researches of the influence of the temperature and electrolyte concentration in such a liquid system on the micelle structure [1]. In work [2], the light scattering method was used to study the dependence of a variation of micelle dimensions and shapes on the concentration of salt added to the liquid system. The authors showed that, provided the electrolyte concentration was high, micelles became prolate ellipsoids. The next step in studying the behavior of such micellar systems was their research using small-angle neutron scattering [3]. In that work, a possibility for bromine ions to arrange on the micelle surface or for the micelle head group to dehydrate under the electrolyte action, which changes the micelle size, was studied. Our work continues the researches of the micellar systems of cation surfactant tetradecyltrimethylammonium bromide (TTABr). The work aimed at determining the influence of the concentration of an electrolyte added to the liquid system on the micelle parameters within the temperature interval 25–60 °C using the small-angle scattering of thermal neutrons.

2. Experimental Technique

To find the micelle sizes and the aggregation number [1], we used the method of SANS. The corresponding experiments were carried out on a YuMO installation [4] in the two-detector regime [5, 6]. The installation was located at an IBR-2 pulsed reactor of I.M. Frank Laboratory of Neutron Physics (the Joint Institute for Nuclear Research, Dubna, Russia). It allowed the researches to be carried on in the range of transferred wave vectors with absolute values $|\mathbf{q}| = (0.07 \div 5)$ nm^{-1} (or in the range of neutron wavelengths $\lambda = (0.05 \div 0.8)$ nm). It made possible the density heterogeneities in the liquid system under investigation to be measured in the range from 1 to 100 nm. The diagram of YuMO installation for small-angle neutron scattering is presented in Fig. 1. The basic installation components are two-reflector system (*1*), a reactor zone with moderator (*2*), chopper (*3*), first (*4*) and second (*6*) collimators, vacuum pipe (*5*), thermostat (*7*), a cartridge with specimens in thermostatting box (*8*), a table for specimens (*9*), vanadium standards (*10*), ring detectors with central holes (*11* and *12*), and direct beam detector (*14*).

In the YuMO installation, the absolute value of **q**-vector was changed by varying both the wavelength λ and the angle θ. The main change of q occurred due to a variation of the neutron wavelength. The angle was changed by means of two ring He detectors of scattered neutrons. The neutron wavelength was determined by the time-of-flight method [7]. The specimens to study were arranged at a distance of about 18 m from the

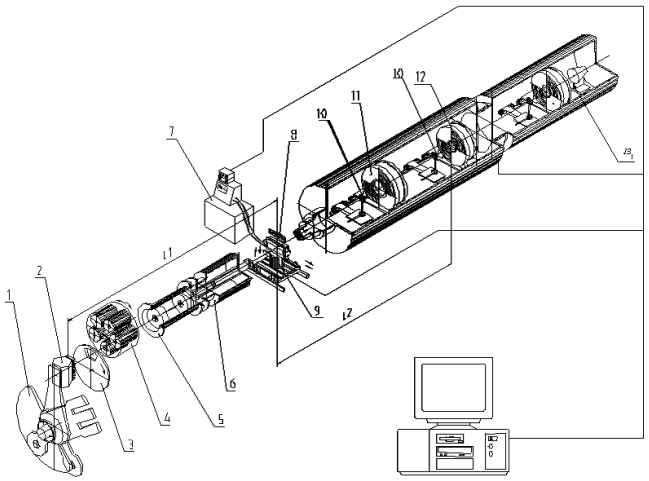

Fig. 1. Diagram of the YuMO installation for small-angle neutron scattering at the IBR-2 reactor of JINR (Dubna, Russia)

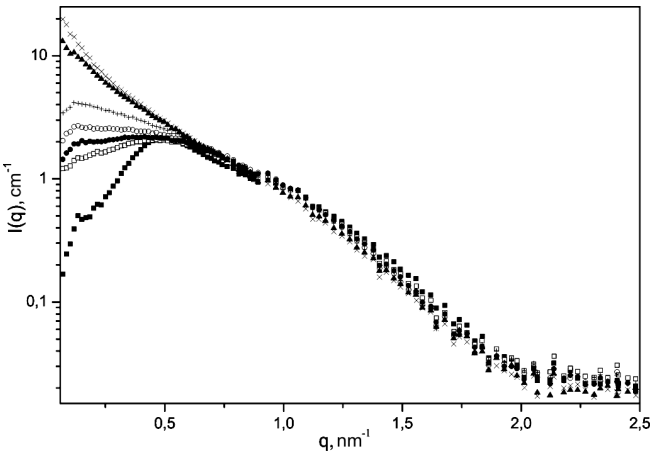

Fig. 2. SANS dependences for the micellar liquid system TTABr–heavy water at a temperature of 40 °C, the TTABr concentration 9.4×10^{-4} m.f., and various NaBr concentrations: 0 (■), 4.6×10^{-4} (□), 9.3×10^{-4} (•), 1.9×10^{-3} (○), 3.7×10^{-3} (+), and 7.6×10^{-3} m.f. (▲)

moderator surface, being imbedded into a special container. A computer-assisted thermostat allowed the temperature in the container to be maintained within the researched temperature interval of 25–60 °C to an accuracy of ±0.01 °C. During measurements, specimens in the neutron beam were changed automatically. The peculiarities of the YuMO installation were central apertures in the scattered-neutron detectors, as well as a vanadium scatterer that was automatically inserted into and removed from the neutron beam and served to calibrate the scattered radiation. The former allowed undesirable effects produced by long-periodic oscillations of reactor power to be avoided, the latter made it possible to obtain the scattering cross-section in absolute units [4]. A direct beam detector was used to measure the transmission of objects under investigation.

A neutron diffraction pattern recorded in such a manner is a dependence of the pulse number produced by registered neutrons in every analyzer channel on the channel number, which corresponds to either the transit time or the wavelength of neutrons. Therefore, the neutron diffraction pattern recorded at the YuMO installation represents a time scan of the diffraction pattern of thermal neutrons scattered by a specimen.

3. Specimen Fabrication

We fabricated a micellar liquid system, namely, a TTABr solution in heavy water with a concentration of 9.2×10^{-4} m.f. (molecular fraction, m.f. $= N_2/(N_1 + N_2)$, where N_1 and N_2 are the numbers of water and surfactant molecules, respectively). NaBr admixtures were added to the studied micellar system to obtain ternary liquid systems heavy water–TTABr–NaBr with concentrations of 4.6×10^{-4}, 9.3×10^{-4}, 1.9×10^{-3}, 3.7×10^{-3}, 7.6×10^{-3}, and 1.6×10^{-2} m.f. To prepare micellar liquid systems of the surfactant, we used dry TTABr produced by Sigma-Aldrich Co. (a TTABr content of 99%) and D_2O produced by Isotope (Moscow) (a D_2O content of 99.8%). The specimens fabricated were placed in a Hellma quartz cuvette across a beam of neutrons with a neutron path length of 1 or 2 mm.

4. Experimental Part

In Fig. 2, we present the SANS curves obtained for the micellar liquid system TTABr–heavy water with a TTABr concentration of 9.2×10^{-4} m.f. at the temperature $t = 40$ °C and with addition of certain NaBr concentrations. The analysis of the curves testifies that the SANS curves in the liquid systems TTABr–heavy water demonstrate a peak which corresponds to the intermicelle interaction or the presence of a certain short-range order in the micelle arrangement in the given liquid system. An addition of NaBr impurities to the TTABr–heavy water system changes the character of the intensity curve substantially, namely, the peak gradually disappears. This testifies to the disappearance of the electrostatic interaction between micelles [3]. Figure 2 shows that, at NaBr concentrations higher than 1.9×10^{-3} m.f., the peak is absent. The subsequent addition of NaBr is accompanied by a growth of the scattering intensity in

the range of small q, which evidences the growth of the size of micellar formations.

5. Experimental Results

The neutron scattering intensity in the liquid system under study can be written down as follows:

$$I = n\langle F^2(q)\rangle S(q), \tag{1}$$

where n is the particle concentration, and $F(q)$ is a formfactor that describes the intensity of neutron scattering by a single micelle:

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

Here, ρ and ρ_s are the densities of scattering length for a micelle and the solution, respectively. In formula (1), $S(q)$ describes the interaction between micelles and corresponds to a certain distribution of micelle centers of masses in space. For the structure factor $S(q)$, we have [8]

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

where $g(r)$ is the pair correlation function, and V is the volume per one micelle. In our case, this volume is approximately equal to 550 Å^3 [9].

In the absence of interaction between micelles, $S(q) = 1$, so that experimental data can be approximated taking only the formfactor into account.

Provided that micelles formed in the liquid system can be approximated as ellipsoids of rotation with semiaxes a, a, and νa, the expression for the formfactor reads [10]

$$P(q) = \int_0^1 \Phi^2[qa\sqrt{1 + x^2(v^2 - 1)}]dx, \tag{4}$$

where $\Phi(t) = 3(\sin(t) - t\cos(t))/t^3$.

If a micelle is a cylinder of radius R and height H, the formfactor looks like

$$P(q) = 4\int_0^1 \frac{J_1^2(qR\sqrt{1 - x^2})}{(qR\sqrt{1 - x^2})^2} Z^2(\frac{qHx}{2})dx, \tag{5}$$

where $Z(t) = \sin(t)/t$.

The interaction between micelles makes it necessary to consider the structure factor. To find it, it is necessary to solve the Ornstein–Zernike equation. In work [13], the authors proposed a method for determining the structure factor, the rescaled mean-spherical approximation (RMSA). Let us write down the Ornstein–Zernike equation:

$$h(r) = c(r) + nd^3\int h(|\mathbf{r} - \mathbf{r}'|)c(\mathbf{r})d^3\mathbf{r}, \tag{6}$$

where, according to the RMSA, the boundary conditions are given by the system of equations

$$\begin{cases} c(r) = -\beta V_c(r), & r > d, \\ g(r) = 0, & r < d, \end{cases} \tag{7}$$

In this formula, $V_c(r)$ is the Coulomb repulsion potential between two charged spherical particles which is given by the expression

$$V_c(r) = \pi\varepsilon\varepsilon_0 d^2\psi_0^2\exp[-\kappa(r - d)]/r, r > d, \tag{8}$$

where d is the micelle diameter, r the distance between ions, ε_0 the dielectric permittivity of vacuum, ε the dielectric constant of the medium, κ the inverse Debye screening length, and

$$\psi_0 = \frac{z}{\varepsilon\varepsilon_0\langle d\rangle(2 + \kappa\langle d\rangle)} \tag{9}$$

is the surface potential of a micelle with charge z.

To approximate the SANS data obtained by us for ternary micellar systems TTABr–heavy water–NaBr, we used two computer programs: the Fitter program [11] which does not make allowance for the interaction between micelles (Fig. 3), and the FISH program [12] (Fig. 4) which takes such an interaction into account using the RMSA. Those programs were applied to obtain information on micelle parameters in the following way: we used the FISH program for concentrations lower that 1.9×10^{-3} m.f. and the Fitter program for higher ones. Figures 3 and 4 demonstrate that the model curve describes the experimental data well. The micelle parameters obtained by treating the experimental data are quoted in Table, where $a = b$ and c are the semiaxes of the ellipsoid of rotation, and N_{agg} is the number of surfactant monomers in a micelle, i.e. the aggregation number.

The analysis of the tabulated data shows that the micelle dimensions and the aggregation number decrease, as the temperature of the liquid system heavy water–TTABr grows. At the same time, the addition of salt brings about the growth of micelle dimensions and an increase of the aggregation number.

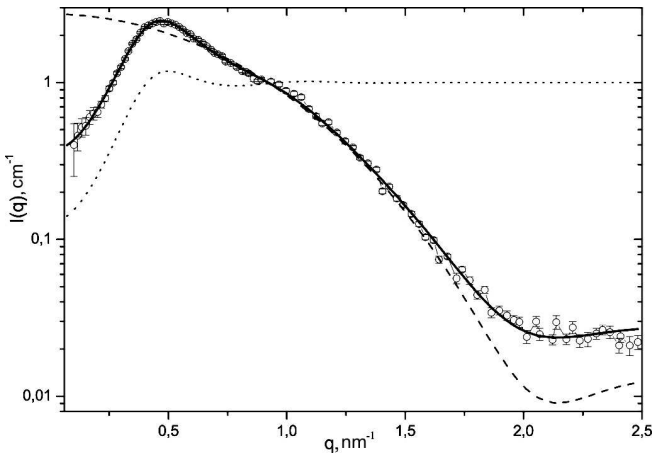

Fig. 3. Approximation of SANS data for the ternary liquid system TTABr–heavy water–NaBr using the FISH computer code (taking the interaction between micelles into account). The TTABr concentration is 9.4×10^{-4} m.f., the NaBr concentration is 0 m.f.: experiment (circles), resulting theoretical curve (solid curve), theoretical formfactor (dotted curve), theoretical structure factor (dashed curve)

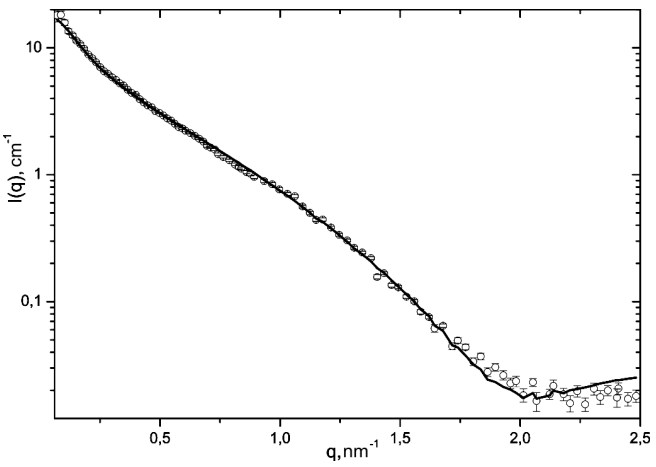

Fig. 4. Approximation of SANS data for the ternary liquid system TTABr–heavy water–NaBr taking no interaction between micelles into account. The TTABr concentration is 9.4×10^{-4} m.f., the NaBr concentration is 0.016 m.f.: experiment (circles), resulting theoretical curve (solid curve)

Micelle parameters for the ternary liquid system TTABr–heavy water–NaBr. The TTABr concentration is 9.4 × 10^{-4} m.f

X_{NaBr},	25 °C			
10^{-4} m.f.	$a = b$,Å	c,Å	N_{agg}	χ^2
0	19.9	30.22	95	2.115
4.6	20.45	34.24	113	2.33
9.3	20.58	36.4	120	2.52
19	21.16	37.82	133	2.38
37	18.92	79.50	324	2.95
76	19.21	152.8	642	3.45
		40°C		
0	19.34	27.67	83	2.09
4.6	19.88	30.69	96	2.07
9.3	20.00	31.84	101	2.07
19	20.2	32.14	103	4.95
37	20.4	41.74	137	3.35
76	18.62	90.55	370	2.04
		60°C		
0	18.57	25.42	70	2.132
4.6	19.05	27.99	81	2.11
9.3	19.26	28.57	85	2.37
19	19.54	31.15	92	1.77
37	19.5	32.18	95	2.05
76	19.52	45.48	134	5.05

6. Conclusions

The method of small-angle neutron scattering was applied to study the influence of salt on the micelle formation in the liquid system heavy water–tetradecyltrimethylammonium bromide–NaBr in the temperature interval 25–60 °C. The addition of salt to the liquid system heavy water–TTABr has been shown to result in the growth of micelle dimensions and the aggregation number.

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НЕЙТРОННІ ДОСЛІДЖЕННЯ ВПЛИВУ ДОМІШОК NaBr НА МІЦЕЛОУТВОРЕННЯ В СИСТЕМІ ВАЖКА ВОДА–ТЕТРАДЕЦИЛТРИМЕТИЛАМОНІЙ БРОМІД

Л.А. Булавін, В.І. Горделій, О.І. Іваньков, А.Х. Ісламов, А.І. Куклін

Р е з ю м е

Методом малокутового розсіяння нейтронів досліджено формування міцел в потрійних рідинних системах тетрадецилтриметиламоній бромід–важка вода–NaBr. Дані про малокутову дифракцію нейтронів на заряджених міцелах було оброблено у наближенні моделі перемасштабованої середньосферичної апроксимації Хайтера–Пенфольда. Визначено залежність розмірів міцел та числа агрегації від температури рідинної системи та концентрації NaBr.