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Neutron spin echo studies of the effects of temperature and pressure in a ternary microemulsion

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Abstract. In order to clarify the self-assembling mechanisms in complex fluids involving amphiphiles, we have investigated dynamic features of amphiphilic membranes and droplets at high temperature and at high pressure in a ternary microemulsion, consisting of AOT, water, and *n*-decane. A high-pressure cell for neutron spin echo (NSE) experiments has been improved, and the static and dynamic features of droplets are observed in detail by means of small angle neutron scattering and NSE. It is found that the size fluctuation and the diffusion of droplets are enhanced by increasing temperature, while they are suppressed by increasing pressure.

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Recently, physical aspects of microemulsion systems composed of oil, water, and surfactants have been studied intensively. Amphiphiles decrease interfacial tension of water and oil, and the mixture forms various mesoscopic structures depending on its composition, temperature, and pressure. It has been suggested that the bending modulus κ of amphiphilic monolayers plays an important role in self-assembling mechanisms [1, 2]. Neutron spin echo spectroscopy (NSE) is a decisive technique to clarify the behavior of κ [1–3].

In a semi-dilute water-in-oil droplet system consisting of an ionic surfactant AOT (dioctyl sulfosuccinate sodium salt), water, and *n*-decane, increasing temperature or pressure induces a macroscopic phase separation to a dilute droplet structure and a dense droplet structure [4–6]. In order to clarify the mechanisms of this phase transition, we have investigated dynamic features of monolayers and droplets by means of NSE [7, 8].

In this study, we investigated the temperature or pressure dependences of the semi-dilute droplet system by small angle neutron scattering (SANS) and NSE and compared the effects of temperature with those of pressure. The SANS result indicated that the size fluctuation of droplets is enhanced by temperature. From the NSE measurements, a difference of temperature and pressure effects on the membrane dynamics is emphasized.

1 Experiments

A mixture of 5.4 vol. % of AOT (99% purity, purchased from Sigma Inc.), 4.6 vol. % of D_2O (99.9 at. %-D, purchased from Isotec Inc.), and 90 vol. % of $C_{10}D_{22}$ (99.9 at. %-D, purchased from Isotec Inc.) was used. The composition leads to 10 vol. % of droplets. Because the neutron-scattering lengths of D_2O and $C_{10}D_{22}$ are almost the same, only the AOT layers could be observed (shell contrast).

The SANS experiments were carried out at the SANS-U spectrometer at the C1-2 port in the cold neutron guide hall of JRR-3M JAERI, Tokai, Japan and at KWS1 of FRJ2 in FZ-Jülich, Jülich, Germany.

1.1 Settings for SANS-U

The wavelength of the incident neutron beam was 7.0 Å with a spread of $\delta\lambda/\lambda = 10\%$. The distances from the sample to a two-dimensional position-sensitive detector were 1 m and 4 m. The momentum transfer q ranged over $0.01\ \text{Å}^{-1} \le q \le 0.14\ \text{Å}^{-1}$. The temperature was changed from 23 °C to 80 °C with a step of about 3 °C at ambient pressure. The pressure was changed from 0.1 MPa to 66.5 MPa with a step of about 5 MPa at room temperature.

1.2 Settings for KWS1

The wavelength of the incident neutron beam was 7.0 Å with a spread of $\delta\lambda/\lambda = 20\%$. The distances from the sample to a two-dimensional position-sensitive detector were 2 m and 8 m. The momentum transfer q ranged over $0.006\ \text{Å}^{-1} \le$

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$q \le 0.14\,\text{Å}^{-1}$. The temperature was changed from 13 °C to 25 °C with a step of about 2 °C with increasing pressure from 0.1 MPa to 30 MPa with a step of about 10 MPa.

1.3 Settings for ISSP-NSE

The NSE experiments were performed at the ISSP-NSE spectrometer at the C2-2 port of JRR-3M JAERI, Tokai, Japan. The wavelength of the incident neutron beam was 7.14 Å with a spread of $\delta\lambda/\lambda = 18\%$. The measured momentum transfer q ranged over $0.04\,\text{Å}^{-1} \le q \le 0.13\,\text{Å}^{-1}$ and the Fourier time t over $0.15\,\text{ns} \le t \le 15\,\text{ns}$. The temperature was set at 19, 25, and 35 °C at ambient pressure. The pressure was set at 0.1, 20, and 40 MPa at room temperature.

So far, it was difficult to keep the pressure constant for a long time (about one week for each observation) with our old high-pressure cell made of non-magnetic stainless steel [7, 8]. Therefore, a new high-pressure cell made of non-magnetic stainless steel and inconel was developed with Hikari High-Pressure Machinery Co. Ltd. Because the cell was magnetized slightly and neutron-spin depolarization occurred, we set some correction coils to increase the guiding magnetic field. The improved cell made it possible to keep the pressure unchanged at least for one week and precise data at high pressure could be obtained.

2 Results and discussion

2.1 SANS experiments

Typical SANS spectra $I(q)$ are shown in Fig. 1. The forward-scattering intensity $I(0)$ became larger with increasing temperature and pressure, because of the critical scattering of a concentration fluctuation of droplets [4, 5]. Although the sample was not at the critical composition, $I(0)$ increased when approaching the phase boundary and decreased above it. From such a behavior of $I(0)$, we estimated that the transition temperature at ambient pressure was $T_c = 59$°C and the transition pressure at room temperature was $P_c = 40$ MPa. Thus, the conditions of the NSE measurement were assured to be in one phase region. In order to deduce the mean radius $R_0 = \langle R \rangle$ and the polydispersity index of the droplets p ($p^2 = \langle R^2 \rangle / \langle R \rangle^2 - 1$), we utilized the model proposed by Gradzielski et al. [9, 10] as follows:

$$I(q) = NS(q) \int h(R) F(q, R)\,\mathrm{d}R\,, \tag{1}$$

where N is the number density of the aggregates, R the radius of the droplets, $h(R)$ a Gaussian distribution function for the radii, and $S(q)$ the structure factor, which is assumed to be unity for systems with a low volume fraction of droplets in this q-region. $F(q, R)$ is the form factor of the monodisperse spheres with the shell-contrast condition.

From the pressure-variation experiments, $p = 0.14$ and $R_0 = 32$ Å were obtained independent of pressure. On the other hand, it was found that R_0 decreased from 32 Å to 28 Å and p increased from 0.16 to 0.18 with increasing temperature. This means that the size fluctuation of droplets is enhanced by increasing temperature while it is not affected by increasing pressure.

2.2 NSE experiments

Figure 2 presents the normalized intermediate correlation functions $I(q, t)/I(q, 0)$ at $T = 43$°C, observed by NSE experiments. They were analyzed using a theory proposed by Milner and Safran [11], which was successfully applied by Huang et al. [12] and by Farago et al. [13] to express the dynamics of microemulsion droplets. They could fit the obtained $I(q, t)$ to a single exponential function as follows:

$$I(q, t)/I(q, 0) = \exp\left[-D_{\text{eff}}(q) q^2 t\right]\,, \tag{2}$$

where $D_{\text{eff}}(q)$ is the effective diffusion coefficient. Taking the shape deformation of the droplets into account, $D_{\text{eff}}(q)$ consists of two terms:

$$D_{\text{eff}}(q) = D_{\text{tr}} + D_{\text{def}}(q)\,, \tag{3}$$

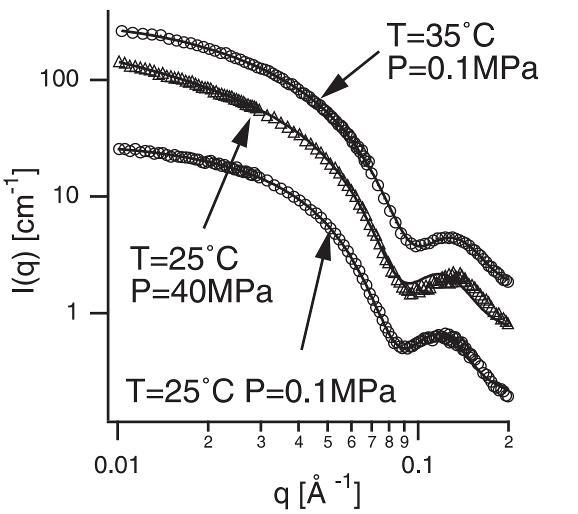

Fig. 1. SANS profiles observed at three conditions. The SANS profile at $T = 25$ °C and $P = 0.1$ MPa is shown in absolute units. Two other curves are shifted by a factor of $80\,\text{cm}^{-1}$

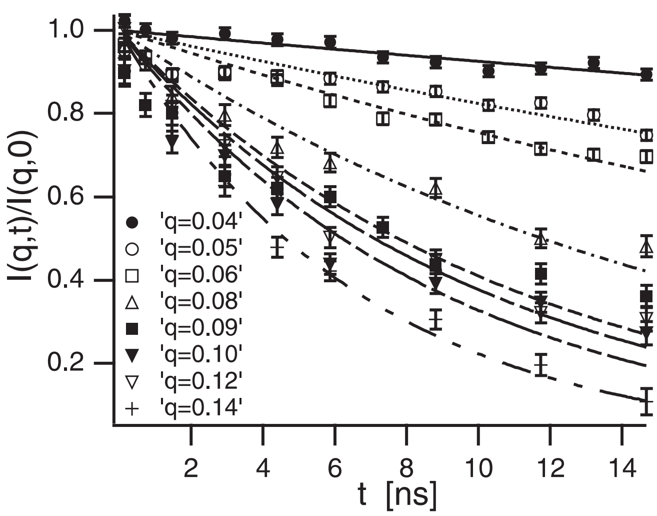

Fig. 2. Intermediate correlation functions obtained from the NSE experiments at $T = 43$ °C, $P = 0.1$ MPa for different q's. *Lines* are the fitting results according to (2)

where D_{tr} is the translational diffusion coefficient independent of q and $D_{def}(q)$ is the diffusion coefficient concerning the shape deformation. The second term is given as [12, 13]:

$$D_{def}(q) = \frac{5\lambda_2 f_2(qR_0)\langle|a_2|^2\rangle}{q^2[4\pi\,[j_0(qR_0)]^2 + 5f_2(qR_0)\langle|a_2|^2\rangle]}\,,$$
$$f_2(qR_0) = 5\,[4j_2(qR_0) - qR_0 j_3(qR_0)]^2\,. \tag{4}$$

Here, j_n is the nth spherical Bessel function, λ_2 the damping frequency of the droplet deformation of the $n = 2$ mode, and $\langle|a_2|^2\rangle$ the mean-square amplitude of the $n = 2$ mode. Mainly, the $n = 2$ mode can be observed in the time window of the ISSP-NSE spectrometer, and the modes of $n \neq 2$ are out of the dynamic range of the spectrometer.

Figure 3 shows the effective diffusion coefficient D_{eff} obtained from the fitting results according to (2). D_{eff} becomes smaller by decreasing temperature or increasing pressure. Hence, the diffusion of droplets is enhanced by increasing temperature while it is suppressed by increasing pressure. The bending modulus κ could be deduced using Milner and Safran's theory [11, 14]. It was also found that κ increased with increasing pressure while it decreased with increasing temperature. These results are consistent with our previous results that amphiphilic monolayers become rigid with increasing pressure while they become flexible with increasing temperature [7, 8, 15, 16]. It has been found that the effects of temperature on the dynamics of droplets are opposite to those of pressure, although the apparent phase separation induced by temperature is similar to that induced by pressure.

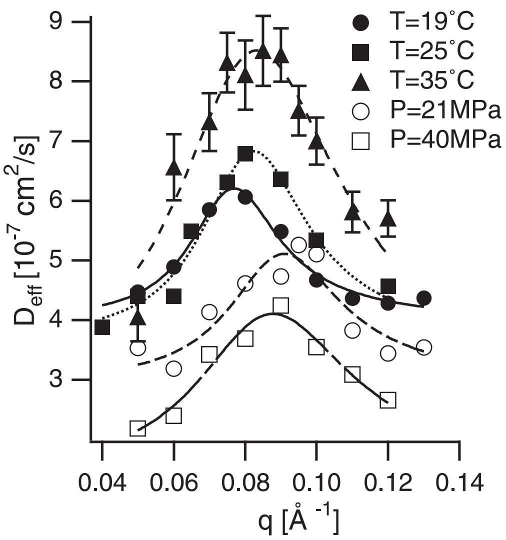

Fig. 3. D_{eff} obtained from NSE data at various conditions. *Lines* are fitting results to (3) and (4). With increasing temperature, D_{eff} becomes larger, whereas it becomes smaller with increasing pressure

3 Conclusion

We performed SANS and NSE experiments on a ternary microemulsion droplet system in order to investigate its static and dynamic features. By improving the high-pressure cell for NSE experiments, we could obtain the pressure dependence of the droplet dynamics. It has been found that the effects of temperature on the dynamics of the droplets are opposite to those of pressure, although the apparent structures of the phases induced by temperature are similar to those induced by pressure. The size fluctuation and the diffusion of the droplets are suppressed by increasing pressure, while they are enhanced by increasing temperature.

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