

## Carbon Number Study on Self-Assemble Mechanisms in AOT/D<sub>2</sub>O/*n*-alkane Microemulsion Systems

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We performed small angle neutron scattering (SANS) experiments in ternary microemulsion systems, consisting of AOT (dioctyl sulfosuccinate sodium salt), water and 3 kinds of *n*-alkane (hexane, octane and decane). The observed SANS profile was analyzed by two different models; one is a traditional Ginzburg-Landau model and the other is a product of a particle form factor and a structure factor. In the second model, a particle form factor of polydisperse spherical droplets and a structure factor of hard-sphere with the adhesive inter-droplet potential were used. The first model explained the broad peak profile only at low *Q* range and the second did at all the measured *Q* range. From the fitting by the second model, the stickiness parameter was estimated and it increased with increasing the carbon number of *n*-alkane. This result indicates that the interaction between droplets increases with increasing carbon number. This tendency is almost the same as increasing pressure.

KEYWORDS: small angle neutron scattering, complex fluids, microemulsion, interaction

### §1. Introduction

Structural formations in microemulsion systems have been intensively investigated by many researchers because these systems form various self-assembling structures of mesoscopic scale. In AOT (dioctyl sulfosuccinate sodium salt), water and *n*-alkane systems, effects of temperature and salinity have been investigated by Chen *et al.*<sup>1)</sup> With increasing temperature, dissociation of counter ion from AOT molecules is promoted and the repulsion among headgroups increases. Therefore, the spontaneous curvature of the AOT membrane should change. This scenario was confirmed by the salinity experiment, in which the added salt screens the electrostatic interaction and increasing salinity has the opposite effect with increasing temperature.

Eastoe *et al.*<sup>2,3)</sup> have investigated pressure effects on the AOT/D<sub>2</sub>O/*n*-alkane *dilute* droplet systems by means of small angle neutron scattering (SANS) and cloud point method. They showed that the pressure plays the same role on the phase diagram as the temperature in the system including *n*-alkane of the carbon number  $C \geq 6$ . On the other hand, with *n*-alkane of  $C < 6$ , increasing pressure has the same role as decreasing temperature. They concluded that attractive interaction between droplets increased or compatibility of oil and tail of AOT decreased with increasing pressure. However, they could not separate those two factors from their measurement. They also showed that increasing *C* of *n*-alkane plays the same role as increasing pressure, because the density of oil increases in both the cases.

Recently Nagao and Seto<sup>4)</sup> investigated a pressure-induced phase transition from a *dense* droplet structure to a lamellar and a bicontinuous in the AOT/D<sub>2</sub>O/*n*-decane system by means of SANS. They concluded that pressure effects were not just the same as temperature

effects. In case of pressure, the spontaneous curvature should be changed because of the interaction between amphiphile and oil molecules. Seto *et al.*<sup>5)</sup> performed small angle x-ray scattering (SAXS) experiment and analyzed the profiles with the model assuming a polydisperse spherical droplet with adhesive potential. They showed that the radius of the water core of droplets did not change with increasing pressure, on the other hand the radius of corona of droplets decreased and the inter-droplet attractive interaction increased. Therefore, in order to clarify the pressure effects on microemulsion systems, one has to focus on the relations between the tails of amphiphile and oil molecules.

In this paper, we describe SANS results of the AOT/water/*n*-alkane microemulsion systems. Hexane, octane or decane was mixed with the same volume of water and AOT whose volume fraction,  $\phi_s$ , was about 0.2. The SANS data were analyzed in terms of two different models. One is the Teubner and Strey model<sup>6)</sup> and the other is almost the same as the one used by Seto *et al.*<sup>5)</sup> The second model could explain SANS profiles better than the first one. The result indicated that the stickiness parameter increased with increasing *C*. This result is consistent with the result obtained by Eastoe *et al.*<sup>2,3)</sup>

### §2. Experiment

AOT purchased from Sigma was purified with extracting from Benzene in order to remove excess oil and water. 99.9 % purity *n*-alkane (*n*-hexane, *n*-octane and *n*-decane) purchased from Katayama Chemical Co., and 99 % purity D<sub>2</sub>O from Isotec Inc., were used without any treatment.

SANS experiments were performed on the ISSP-owned SANS-U spectrometer at JRR-3M, JAERI, Tokai.<sup>7)</sup> Incident cold neutrons were selected to be 7 Å by a velocity

selector with the resolution of 10 %. The source aperture, 4 m apart from the sample, was 20 mm $\phi$  and the sample aperture was selected to be 3 mm $\phi$ , and the 2 dimensional detector was placed at 2 m behind the sample. The covered momentum transfer,  $Q$ , ranged over  $0.015 \leq Q \leq 0.144 \text{ \AA}^{-1}$ . All the observed 2 dimensional profile were azimuthally averaged and calibrated to the absolute intensity with Lupolen standard.

### §3. Results and Discussion

We have analyzed the SANS profiles of *n*-decane<sup>4,8)</sup> using the theory proposed by Teubner and Strey.<sup>6)</sup> Their model assumed an alternating distribution of water and oil domains, and the correlation decays exponentially with distance. The scattering function is given by,

$$I(Q) = \frac{A}{(k^2 + \xi^{-2})^2 + 2(\xi^{-2} - k^2)^2 Q^2 + Q^4}. \quad (3.1)$$

Here,  $k$  and  $\xi$  are the characteristic wave number and correlation length of water and oil domains. The mean repeat distance of water domains,  $d$ , is expressed as  $d = 2\pi/k$ . This model can explain only the limited region of  $0.014 \leq Q \leq 0.07 \text{ \AA}^{-1}$ . The obtained fit parameters are summarized in Table I. With increasing  $C$ ,  $\xi$  decreased and  $d$  did not change. The disorder parameter,<sup>9)</sup> determined by  $1/k\xi$  and means the polydispersity of water domains, increased with increasing  $C$ .

In order to explain the SANS profiles for wider  $Q$  range, we introduced another model which is a product of a particle form factor,  $P(Q)$ , and a structure factor,  $S(Q)$ . Kotlarchyk and Chen<sup>10)</sup> introduced  $P(Q)$  for the polydisperse droplet system with Schultz size distribution,

$$P(Q) = 8\pi^2 (\Delta\rho)^2 R_0^6 (Z+1)^{-6} \alpha^{Z+7} G(Q), \quad (3.2)$$

and

$$\begin{aligned} G(Q) &= \alpha^{-(Z+1)} - (4 + \alpha^2)^{-\frac{Z+1}{2}} \cos[(Z+1) \tan^{-1} \frac{2}{\alpha}] \\ &+ (Z+2)(Z+1) \{ \alpha^{-(Z+3)} + (4 + \alpha^2)^{-\frac{Z+3}{2}} \\ &\times \cos[(Z+3) \tan^{-1} \frac{2}{\alpha}] \} - 2(Z+1) \\ &\times (4 + \alpha^2)^{-\frac{Z+2}{2}} \sin[(Z+2) \tan^{-1} \frac{2}{\alpha}]. \end{aligned} \quad (3.3)$$

Here,  $\Delta\rho$  is the neutron scattering amplitude differences between water and oil,  $R_0$  the radius of core of water droplet,  $Z$  the width parameter of the polydisperse droplets, and  $\alpha = (Z+1)/QR_0$ . The hard-sphere and the short-range attractive potential of droplet-droplet interaction are known to be appropriate for the water-in-oil droplet structure of the AOT systems. For  $S(Q)$ , the model given by Liu, Chen and Huang<sup>11)</sup> was used, in

Table I. Obtained fit parameters to the TS model.<sup>6)</sup>

	$d[\text{\AA}]$	$\xi[\text{\AA}]$	$1/k\xi$
hexane	$128.2 \pm 0.4$	$81.0 \pm 1.5$	$0.252 \pm 0.005$
octane	$127.7 \pm 0.3$	$65.5 \pm 0.6$	$0.311 \pm 0.004$
decane	$131.0 \pm 0.4$	$51.8 \pm 0.6$	$0.402 \pm 0.005$

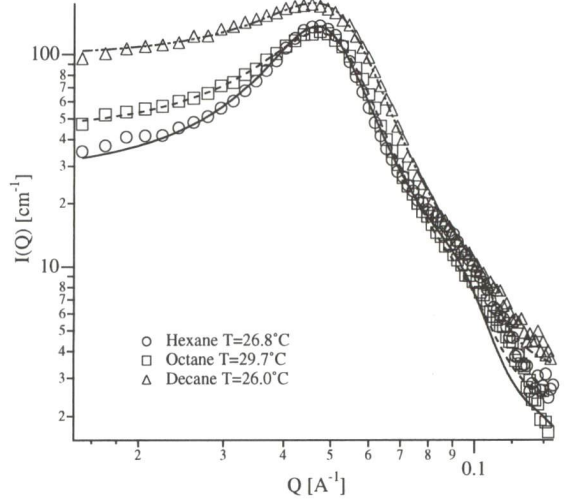


Fig.1. Obtained SANS profiles in AOT/D<sub>2</sub>O/C<sub>6</sub>H<sub>14</sub>(circles), C<sub>8</sub>H<sub>18</sub>(squares) and C<sub>10</sub>H<sub>22</sub>(triangles). The temperature conditions were 26.8, 29.7 and 26.0°C, respectively. Lines are fitting result to the model consists of  $P(Q)$  for spherical particle form factor with Schultz distribution<sup>10)</sup> and  $S(Q)$  for hard sphere adhesive potential.<sup>11)</sup>

which the pairwise interparticle interaction potential was determined as,

$$\frac{V(r)}{k_B T} = \begin{cases} +\infty & : 0 < r < R_i, \\ \Omega & : R_i < r < R, \\ 0 & : R < r, \end{cases} \quad (3.4)$$

where  $k_B$  is the Boltzmann's constant,  $T$  the absolute temperature and  $\epsilon \equiv (R - R_i)/R_i$  the fractional surface thickness. The analytical form of the  $S(Q)$  was described in Ref. 11. Following the Baxter's expression,<sup>12)</sup>

$$1/\tau = 12\epsilon \exp(-\Omega), \quad (3.5)$$

is a dimensionless parameter indicating the degree of stickiness between hard-sphere droplets. The fit parameters in this  $S(Q)$  are the concentration of hard sphere particles  $\phi$ , adhesive potential  $\Omega$ , the fractional surface thickness  $\epsilon$ , and a hard sphere diameter  $R_h$ , which is almost the same as twice of the radius of droplet including the tail of amphiphile molecules. The fitting results were shown in Fig. 1.

This model was successfully used by Seto *et al.*<sup>5)</sup> for SAXS data in the decane case. The differences between SANS and SAXS are a scattering length distribution of each ingredient and the instrumental resolution. In order to check the smearing effects in SANS spectrum, we convoluted the theoretical prediction of the resolution function to be Gaussian with the spread of 12 %. The result indicated that the smearing effects mainly affected the fit value of  $\epsilon$ . This effect results in  $1/\tau_s$ , which is  $1/\tau$  after the convolution is considered, to be decreased about 17 %. The carbon number dependence of  $1/\tau$  and of the other parameters, however, did not change after the resolution was taken into account.

In Fig. 2,  $P(Q)$  and  $S(Q)$  calculated with the fit parameters obtained are shown. The parameters are summarized in Table II. Note that some parameters were



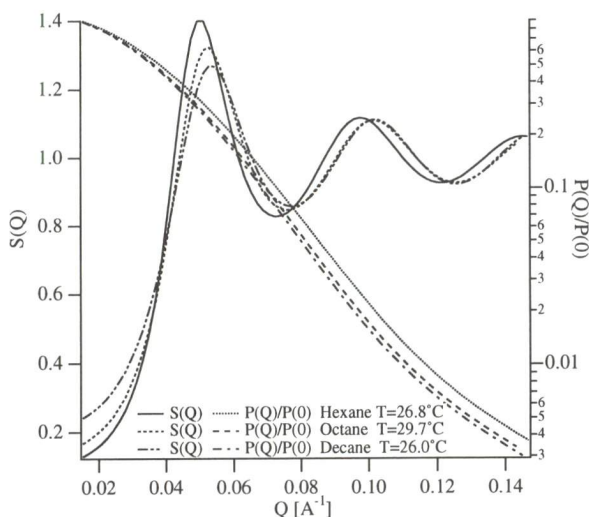


Fig. 2. Calculated structure factor  $S(Q)$  and the normalized form factor  $P(Q)/P(0)$ .

fixed for simplicity,  $Z=10$ ,  $\epsilon = 0.02$  and  $\phi = 0.4$ . In the present model, the relation  $R_h \sim 2(R_0 + \delta)$  should be satisfied, naturally, where  $\delta$  means the length of amphiphile molecule and was estimated to be  $13.7 \text{ \AA}$  for AOT.<sup>4)</sup> In the present analysis, however, obtained  $R_0 \sim 32 \text{ \AA}$  was smaller than  $R_h/2 - \delta \sim 55 \text{ \AA}$ . This is due to the large error bar of the estimated  $P(Q)$ . Note that, the  $R_0$  measured in the dilute droplet system with the same composition of water to AOT molar ratio, we confirmed  $R_0 \sim 55 \text{ \AA}$  in the decane case.<sup>13)</sup> In the present paper we focused our attention on the observed  $S(Q)$ . The obtained  $R_h$  is qualitatively the same meaning as  $d$  obtained by the TS model as described by Seto *et al.*<sup>5)</sup>

With increasing  $C$ , the adhesive potential parameter between droplets decreased and, therefore, the stickiness between droplets increased. This fact might imply that the tail-tail attractive interaction increases with increasing carbon number of  $n$ -alkane. This result was almost the same with the case of applying pressure.<sup>5)</sup> The inter-droplet attractive potential considered here is very short-range one (several  $\text{\AA}$ ), and it might be promoted by the overlap of the tails of AOT. The origin of the increase of the tail-tail attractive interaction with increasing  $C$  is not yet clear, however, the compatibility change of tail of AOT and oil molecules with changing  $C$  is one possible reason as Eastoe *et al.*<sup>2,3)</sup> suggested before. In the dense droplet system, the tail of AOT molecules overlapped with the ones of neighboring droplets, and with the oil molecules existing around the tails. This interaction between the tail of AOT should not be changed when  $C$  is changed, however, that of the tail and oil should be changed with changing  $C$ . The short chain alkane can penetrate more into the tails of AOT comparing with longer chain alkane. When the compatibility of the tail and oil becomes worse with increasing  $C$ , the tail-tail miscibility becomes better than the tail-oil miscibility. In that case, effective tail-tail attraction will be increased.

Table II. Obtained fit parameters to the model with the assumption of  $P(Q)$  and  $S(Q)$ . The observed value of  $1/\tau_s$ , after considering the smearing effects, is also shown in the last column.

	$R_0[\text{\AA}]$	$\Omega[kT]$	$R_h[\text{\AA}]$	$1/\tau$	$1/\tau_s$
hexane	$30.6 \pm 0.3$	$-0.42 \pm 0.02$	$136.6 \pm 0.4$	$0.36 \pm 0.02$	0.29
octane	$32.0 \pm 0.2$	$-0.67 \pm 0.01$	$134.0 \pm 0.3$	$0.47 \pm 0.01$	0.39
decane	$32.6 \pm 0.4$	$-0.91 \pm 0.02$	$136.1 \pm 1.0$	$0.60 \pm 0.01$	0.52

Our previous pressure variation experiments<sup>4,5,8)</sup> indicated that the  $1/k\xi$  increased and  $\Omega$  decreased with increasing pressure. In the present  $C$  variation experiment, the same tendency was observed with increasing  $C$ . Therefore, we can conclude that the increasing pressure and increasing  $C$  play the same role for the structural formation in these microemulsion systems.

#### §4. Conclusion

We performed SANS experiments in order to clarify the alkane chain length dependence of the inter-droplet interaction. In order to estimate the stickiness parameter, we considered the instrumental resolution of 12 % and the estimated values of parameters were consistent with the result obtained by SAXS.<sup>5)</sup> With increasing the chain length of  $n$ -alkane, the interaction between droplets increased. This tendency was almost the same as the case of applying pressure.

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- 1) S. H. Chen, S. L. Chang and R. Strey: J. Chem. Phys. **93** (1990) 1907.
- 2) J. Eastoe, B. H. Robinson and D. C. Steytler: J. Chem. Soc. Faraday Trans. **86** (1990) 511.
- 3) J. Eastoe, W. K. Young, B. H. Robinson and D. C. Steytler: J. Chem. Soc. Faraday Trans. **86** (1990) 2883.
- 4) M. Nagao and H. Seto: Phys. Rev. E **59** (1999) 3169.
- 5) H. Seto, D. Okuhara, Y. Kawabata, T. Takeda, M. Nagao, J. Suzuki, H. Kamikubo and Y. Amemiya: J. Chem. Phys. **112** (2000) 10608.
- 6) M. Teubner and R. Strey: J. Chem. Phys. **87** (1987) 3195.
- 7) Y. Itoh, M. Imai and S. Takahashi: Physica B **213&214** (1995) 889.
- 8) M. Nagao, H. Seto, Y. Kawabata and T. Takeda: J. Appl. Cryst. **33** (2000) 653.
- 9) S. H. Chen, S. L. Chang, R. Strey, J. Samseth and K. Mortensen: J. Phys. Chem. **95** (1991) 7427.
- 10) M. Kotlarchyk and S. H. Chen: J. Chem. Phys. **79** (1983) 2461.
- 11) Y. C. Liu, S. H. Chen and J. S. Huang: Phys. Rev. E **54** (1996) 16981.
- 12) R. J. Baxter: J. Chem. Phys. **49** (1968) 2770.
- 13) Y. Kawabata, M. Nagao and H. Seto: unpublished.