SAXS and Rheometry Studies of Diglycerol Monolaurate Reverse Micelles in Styrene

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Abstract: We have investigated the structure and rheology of diglycerol monolaurate ($C_{12}G_2$) reverse micelles in styrene using small-angle X-ray scattering (SAXS) and rheometry techniques. The SAXS data have been evaluated by *generalized indirect Fourier transformation* (GIFT) method and further supported by geometrical model fittings. We found that the $C_{12}G_2$ when added into styrene spontaneously self-assemble into ellipsoidal prolate type reverse micelles under ambient conditions. Micelles grew and micellar aggregation number (N_{agg}) increased with the increase in surfactant concentration demonstrating concentration induced one dimensional micellar growth, which was further supported by rheology data; the relative viscosity, η_r , for the $C_{12}G_2$ /styrene mixtures exhibit far steeper concentration dependence behavior than those predicted for a dispersion of spherical particles based on the Krieger–Dougherty relation, due to the elongated micellar structures. On the other hand, a distinct modulation in the shape and size of micelles favoring ellipsoidal prolate-to-sphere type transition was observed upon heating, whose scheme could be attributed to the enhanced penetration tendency of oil into the lipophilic shell of the surfactant at the higher temperatures. As anticipated reverse micelles swelled with water causing two dimensional micellar growth; both the maximum dimension and maximum core radius increase with water.

Key words: diglycerol monolaurate, nonionic surfactant, styrene, reverse micelles, small-angle X-ray scattering (SAXS), rheometry

1 INTRODUCTION

Amphiphilic molecules such as surfactants or polymers undergo spontaneous self-assembly process and shape a variety of structures in water or in oil^{1–3}. They may structure into micelles, liquid crystals, vesicles, and reverse micelles depending on the molecular architecture of surfactant and solvent, composition, and temperature. Just above the critical micelle concentration (*cmc*) surfactant molecules self-assemble into spherical micelle, which grow into cylinder or wormlike (entangled networks) under a certain condition of temperature, composition, or upon addition of salts or cosurfactants^{4–8}. At sufficiently higher concentration, disorder-order transition to liquid crystal phases takes place. Liquid crystals are well known to be good stabilizers of foam^{9, 10} and emulsions¹¹ and are also efficiently used as

template for particle synthesis in materials science research^{12, 13}. In depth knowledge of surfactants self-assembly and the derived structures is therefore a basic requirement in industry from the view point of practical applications.

In the last few years we have been investigating the self-assembly of nonionic amphiphiles in nonaqueous media, in particular, without addition of water, and to optimize the system for free structure control of the reverse micelles. In the studies of phase behavior of conventional monoglycerides (monoglycerol fatty acid esters having different chain length) in different nonpolar oils such as liquid paraffin, squalane, and squalene, we have found that the monoglycerides are insoluble in these oils at all compositions. However, the solid phase could be transformed into an iso-

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Accepted April 18, 2011 (received for review February 28, 2011)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
<http://www.jstage.jst.go.jp/browse/jos/>

tropic single phase reverse micellar solution upon heating. Small-angle X-ray scattering (SAXS) measurements showed the presence of rod-like micelles, whose length decreases with further increase in temperature and an increase in the alkyl chain length of surfactant¹⁴⁾. A similar phase behavior; a solid phase at lower temperatures and reverse micellar solution at higher temperatures, was observed when liquid paraffin, squalane, and squalene are replaced with linear chain alkanes^{15, 16)}. Phase behavior turned out to be very different in diglycerol fatty acid esters in the same set of oils. We found evidences on the formation of various self-assembled structures¹⁷⁾. A swollen lamellar liquid crystal (L_a) phase in the concentrated region followed by a dispersion of reverse vesicles in the dilute region was observed at 25°C. The L_a phase was transformed into a reverse micellar solution phase upon heating. We found that the diglycerol monolaurate, and diglycerol monomyristate would best offer a variety of reverse micellar structures such as globular, prolate, short rods, cylinder and planar depending on the solvent properties, temperature, composition and added water^{18, 19)}. Note that the mono- and diglycerol non-ionic surfactants could structure into reverse micelles only at the elevated temperatures, as a result, their practical applications are limited. Nevertheless, reverse micelles was possible to formulate under ambient conditions with long chain diglycerol polyisostearate and polyglycerol mono-oleate surfactants^{20–22)}. The structure and dynamics of reverse micelles could be tuned playing with surfactant and solvent molecular structure.

In this contribution, we have studied the self-assembled structure of short chain diglycerol fatty acid esters; diglycerol monolaurate ($C_{12}G_2$) in aromatic organic solvent styrene in the dilute regions directed on the effect of surfactant concentration, temperature, and water addition on the structure of reverse micelles using small-angle X-ray scattering (SAXS). The SAXS data were evaluated by the generalized indirect Fourier transformation (GIFT) method and complemented by geometrical model fittings. Moreover the rheology of reverse micelles at different concentration was also investigated.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Diglycerol monolaurate (designated as $C_{12}G_2$ and purity >91.1%) was a generous gift from the Taiyo Kagaku Co., Ltd., Yokkaichi, Japan. The main impurities are unreacted diglycerol and diglycerol difatty acid esters. The surfactant was used as received. The nonpolar organic solvent styrene with purity >99% was purchased from Tokyo Chemical Industry, Tokyo, Japan. The schematic molecular structures of surfactant and styrene are given in Scheme 1.

Scheme 1 Schematic molecular structures of diglycerol monolaurate ($C_{12}G_2$), and styrene.

2.2 Methods

2.2.1 Isothermal phase behavior in dilute region

Equilibrium phases in the dilute regions (5–25 %) of the binary mixtures of $C_{12}G_2$ /styrene were identified by visual inspection through a crossed-polarizer at 25°C. For this purpose, $C_{12}G_2$ /styrene binary mixtures with surfactant concentration between 5 % and 25 % were prepared in 5 mL clean and dry glass ampoules with the screw cap. Note that the concentration represents wt% of surfactant throughout this paper. The samples were mixed using a dry thermobath and a vortex mixer with repeated centrifugation to achieve homogeneity. The samples were kept in a temperature-controlled water bath at 25°C for 2 h to observe the equilibrium phases. The accuracy of the temperature control was better than $\pm 0.5^\circ\text{C}$. Isotropic solutions were observed in all the systems.

2.2.2 Small-angle X-ray scattering (SAXS)

SAXS measurements were carried out on $C_{12}G_2$ /styrene systems to investigate the effects of surfactant concentration, temperature, and added water on the reverse micellar structure. A SAXSess camera (Anton Paar, Austria) attached to a PW3830 sealed-tube anode X-ray generator (PANalytical, Netherlands) operated at 40 kV and 50 mA and equipped with the Göbel mirror and a block collimator gave a focused monochromatic X-ray beam of Cu- K_α radiation ($\lambda = 0.1542$ nm) with a well-defined line-shape. A thermostated sample holder unit (TCS 120, Anton Paar) allowed us to control the sample temperature over a wide temperature range.

The 2-D scattering pattern was recorded on an imaging-plate (IP) detector (a Cyclone, Perkin Elmer, USA) and integrated into one-dimensional scattered intensities, $I(q)$, as a function of the magnitude of the scattering vector $q = (4\pi/\lambda) \sin(\theta/2)$ using SAXSQuant software (Anton Paar), where θ is the total scattering angle. All measured intensities were semi-automatically calibrated for transmission by normalizing a zero- q attenuated primary intensity to unity, by taking advantage of a semi-transparent beam stop. All $I(q)$ data were corrected for the background scattering from the capillary and the solvents, and the absolute scale calibration was made using water as a secondary standard.

The generalized indirect Fourier transformation (GIFT) method^{23–26)} was used to obtain the real-space pair distance distribution function, $p(r)$, of the reverse micelles. Details on SAXS and GIFT/IFT are given elsewhere^{27–34)}.

2.2.3 Rheological measurements

Steady-shear rheological measurements were performed in a stress-controlled rheometer, ARG2 (TA Instruments), using a cone-plate geometry (diameter 60 mm with a cone angle of 1°) with the plate temperature controlled by a peltier unit, which uses the peltier effect to rapidly and accurately control heating and cooling. All the samples showed Newtonian fluid like behavior; viscosity is independent to shear-rate. Zero-shear viscosity (η_0) was determined by extrapolating the plateau value to zero shear rates.

2.2.4 Densimetry

Densities of oil and reverse micellar solutions were measured at temperatures corresponding to SAXS measurements using a high precision DSA5000 densimeter (Anton Paar, Austria). The DSA5000 instrument is based on the conventional mechanical oscillator method, which measures the natural resonant frequency of a U-shaped glass tube, filled with 1 mL sample. The highly tuned temperature control of the apparatus enables an accuracy of 10 mK in an absolute value.

2.2.5 Measurement of water content

Water content in surfactants and oil was determined by Karl Fisher method using CA-06 Moisture meter (Mitsubishi Chemicals Co., Tokyo, Japan). The results showed that the $C_{12}G_2$ and styrene contain 0.89 and 0.12 % water, respectively.

3 RESULTS AND DISCUSSION

3.1 Isothermal phase behavior of $C_{12}G_2$ /styrene in the dilute region

Phase behavior of $C_{12}G_2$ /styrene system in the dilute regions concentration ranges from 5–25 % were investigated at 25°C . It was found that the $C_{12}G_2$ surfactant forms an isotropic solution of reverse micelles in styrene under ambient conditions. A series of SAXS measurements were carried out in the isotropic solution phase and intrinsic parameters for the structural variation of reverse micelles have been determined. In the following sections, we will discuss the effect of surfactant concentration, temperature, and water on the reverse micelles structure.

3.2 Effect of concentration

In order to investigate the effect of surfactant concentration on the reverse micellar structure, a series of SAXS measurements were carried out on the $C_{12}G_2$ /styrene system in a wide concentration range; 5–25 %, at 25°C . The results obtained from SAXS measurements; the X-ray scattered intensities, $I(q)$, and the corresponding real-space pair-distance distribution function, $p(r)$ deduced by the GIFT method, are presented in Fig. 1.

Formation of reverse micelles can simply be confirmed by the q dependence behavior of $I(q)$ in the scattering curves;

Fig. 1 (a) The X-ray scattered intensities, $I(q)$, of the $C_{12}G_2$ /styrene system at different concentrations; 5, 10, 15, 20, and 25 % on absolute scales at 25°C , (b) the corresponding pair-distance distribution functions, $p(r)$, (c) the normalized $p(r)$ functions by surfactant weight fraction, $p(r)/W_s$, and (d) the static structure factor $S(q)$ curves. The solid and broken lines in panel (a) represent GIFT fit and the calculated form factor for n particles presented in unit volume, $nP(q)$, respectively. The arrows and broken lines in panel (b) and (c) highlight the maximum dimensions, $D_{\max}$, and cross section diameter, $D_{c\max}$, of the micellar core, respectively.

in the absence of aggregates, the $I(q)$ is independent of q in the SAXS regime. The scattering intensity increases throughout the q -range with an increase in surfactant concentration from 5 to 10 % due to an increase in the number density of micelles in the unit scattering volume. With further increase in concentration above 10 wt%, the forward scattering intensity in the low- q regions, $I(q=0)$, tends to suppress causing a weak interaction peak at intermediate q values ($q \sim 1.2 \text{ nm}^{-1}$). The interaction peak grows with further increase in concentration and shifts towards higher- q range; e.g. a significant peak is appeared at $q \sim 1.5 \text{ nm}^{-1}$ for the 25 % $C_{12}G_2$ /styrene system (Fig. 1a). From these scattering behaviors, it can be inferred that the intermicellar interaction increases and the intermicellar distance between the neighboring micelles decreases with an increase in surfactant concentration. Similar results have been observed in other systems^{35, 36}.

Similarly to the normal micelles in aqueous systems, the shape, size, and internal structure of reverse micelles depend on the molecular structure of surfactant and oils^{37, 38}. Usually, elongated micelles show growth with concentration. On the other hand, spherical micelles do not grow. For instance, diglycerol monomyristate ($C_{14}G_2$) spheroid

reverse micelle in styrene does not grow with concentration despite a wide variation in concentration 5-30 %³⁹⁾. On the other hand, increase in concentration favors ellipsoid prolate-to-rod transition in the diglycerol monocaprate ($C_{10}G_2$)/styrene system⁴⁰⁾. Judging from the distinct peak in the lower- r side with an extended downward convex shaped tail in the higher- r side of the $p(r)$ curve, the structure of micelles is assumed to possess an ellipsoidal prolate type of geometry in the 5 % $C_{12}G_2$ /styrene system at 25°C^{41, 42)} whose size grew with an increase in surfactant concentration. As can be seen in Fig. 1b, D_{max} increases from ca. 4.4 to 8.5 nm upon an increase in surfactant concentration from 5 to 25 %. Nevertheless, the inflection point after the maximum of $p(r)$ curves, as highlighted by broken line, which roughly estimates the cross section diameter of micellar core, remains essentially constant at ~ 1.70 nm demonstrating that the growth is one dimensional (1-D). The increase of curve height with the weight fraction of surfactant in the normalized $p(r)$ curves further supports the concentration induced 1-D growth (Fig. 1c).

The $S(q)$ curves obtained from the GIFT method (Fig. 1d) reveal the considerable intermicellar interactions mainly at higher concentrations say above 15 %. The $S(q)$ peak position, which measures the mean distance between the neighboring micelles tends to shift towards higher- q regions with concentration inferring the decrease in the micellar distance at higher concentrations. Note that the actual structure factor peaks may differ from what is predicted for mono-dispersed hard spheres, for which the extrapolated $S(q)$ to zero q , $S(q=0)$, value reflects the osmotic compressibility of the system and is determined by the packing fraction of hard spheres⁴³⁾. We found that the $S(q=0)$ decreases with the increase in surfactant concentration illustrating that the osmotic compressibility as well as packing fraction of reverse micellar solutions may be explained in a quantitative manner if excluded volume of surfactant is taken into account.

In addition to the GIFT method, we have also performed geometrical model fittings and additional information such as micellar aggregation number (N_{agg}) has been determined. The calculation was done based on the method reported elsewhere^{44, 45)}. Densities of 5, 10, 15, 20, and 25 % $C_{12}G_2$ /styrene systems at 25°C were 0.906214, 0.913804, 0.921394, 0.927838, and 0.934715 g/cm³, respectively. These values gave electron density fluctuation of 99.04, 132.33, 142.95, 140.99, 141.39 e/nm³, respectively. Based on the shape of the total $p(r)$ function, we chose an ellipsoidal prolate model in the model fittings and in addition to the short and long axes of an ellipsoid prolate, a and b , volume of geometrical model was possible to determine by fittings, which when divided by volume of hydrophilic core (obtained from density measurements) gives N_{agg} .

The results obtained from model fittings along with the results obtained from the GIFT method are presented in

Fig. 2 (a) Model fitting (solid lines) to the experimental scattering intensities (symbols) with GIFT fit (dashed lines) at different surfactant concentrations; 5, 10, 15, 20, and 25 % on absolute scales, and (b) comparisons of $p(r)$ curves obtained from GIFT method (symbols) and model fittings (solid lines). The arrows in panel (b) indicate the maximum diameter of the reverse micellar core, D_{max} . The data were fitted considering a homogeneous ellipsoidal prolate model.

Fig. 2. We noted that an ellipsoidal prolate model is able to explain the shape and size of the resulting $p(r)$ with a notable deviation in the high- q regime of the experimental $I(q)$ functions (Fig. 2a). The absence of the theoretically predicted minima in the high- q part of the experimental $I(q)$ could be attributed to the polydispersity in size and/or small electron density fluctuations inside the micellar core^{41, 42)}. The geometrical parameters obtained from model fittings well support the results deduced from the GIFT method. Namely, micellar size and N_{agg} increase with the increase in surfactant concentration.

The structure parameters obtained from model fittings supplied in Table 1 shows that short axes, a , of ellipsoidal prolate changes in a narrow range ca. 1.40 to 1.60 nm, whereas, long axes, b , increases from ca. 2.20 to 4.25 nm with the increase in concentration from 5-25 %. Similarly N_{agg} increases from ca. 36 to 75 representing concentration

Table 1 Effect of surfactant concentration on the geometrical parameters, short axis (a), and long axis (b) of ellipsoid prolate, radius of gyration (R_g), and aggregation number (N_{agg}) obtained from the results of model fittings for the $C_{12}G_2$ /styrene systems at 25°C:

Surfactant concentration (wt%)	Short axis (a)/nm	Long axis (b)/nm	Radius of gyration (R_g)/nm	Aggregation Number (N_{agg})
5	1.40	2.20	1.27	36
10	1.64	2.65	1.42	49
15	1.70	3.20	1.59	55
20	1.60	3.50	1.70	62
25	1.60	4.25	2.07	75

induced 1-D micellar growth.

The concentration induced micellar growth is assumed to be driven by entropy effect. Free energy of a surfactant molecule is expected to be higher in spherical micelles than in rod-like or disk like micelles. The larger the magnitude of the free energy difference, the steeper is the increase of the micellar size with an increase in surfactant concentration. With increasing surfactant concentration above cmc, the repulsive intermicellar forces come into play and work perpendicular to the interface. Therefore any decrease in the intermicellar distance with increase in concentration, increases the free energy of the system. To compensate the excess free energy and to maintain an intermicellar distance as large as possible the spherical micelles must grow axially or two dimensionally.

Coming to the internal structure of micelles, we have estimated the cross section diameter of micellar core in the range of ca. 1.6–1.8 nm from the inflection point in the $p(r)$ curves. To quantify this estimation, we used the indirect Fourier transformation (IFT) method and the cross-sectional pair-distance distribution function, $p_c(r)$, could be obtained from the experimental $I(q)$. The radial electron density distribution profile, $\Delta\rho_c(r)$ could further be obtained with the deconvolution of the $p_c(r)$. Figure 3 shows $p_c(r)$ and $\Delta\rho_c(r)$ for the $C_{12}G_2$ /styrene system at different surfactant concentrations. The $p_c(r)$ functions represent typical homogeneous aggregates with the maximum cross section diameter, $D_{c\max}$, ca. 1.50 nm at all concentrations. The positive electron density profiles in Fig. 3b show the electron rich hydrophilic reverse micellar core. The maximum core radius (R_c) estimated from the $\Delta\rho_c(r)$ profile, ca. 0.745 nm seems to be surprisingly smaller than the extended chain length of the twice the glycerol moiety as one glycerol molecule accounts ca. 0.4–0.5 nm. This unusual phenomenon could not be explained unless we assume the partial solubility of water with styrene.

Rheological measurements have been performed to complement the results derived from the SAXS measurements. Figure 4a shows the measured viscosity, η , of the $C_{12}G_2$ /

Fig. 3 (a) The cross-sectional pair-distance distribution function, $p_c(r)$, of the $C_{10}G_2$ /styrene systems at different surfactant concentrations, and (b) the resulting cross-sectional radial electron density profile, $\Delta\rho_c(r)$, calculated with the deconvolution procedure of $p_c(r)$ using program DECON.

Fig. 4 (a) Viscosity against shear rate curve for the $C_{12}G_2$ /styrene system at 25°C at different surfactant concentrations (5–25%) as obtained from steady-shear rheological measurements, and (b) the relative viscosity, η_r , for the same concentration series. η_r is compared to predicted values for a suspension of spherical particles referring to a Krieger–Dougherty relation (Eq.(1))

styrene systems against shear rate at different concentrations. We observed that all the samples behave as a Newtonian fluid; viscosity is independent of applied shear rate, persists over a wider concentration range. The geometry of dispersed particles in suspension should have a crucial role on the rheological properties of colloidal dispersions. Relative viscosity for a suspension of spherical particles can be compared to the Krieger–Dougherty relation⁴⁶⁾,

$$\eta_r(\phi) = [1 - (\phi/\phi_{\max})]^{-k_E\phi_{\max}} \quad (1)$$

where η_r is relative viscosity, ϕ is particle volume fraction, $\phi_{\max}$ is maximum packing fraction of spheres in disordered state ($= 0.63$), and k_E is Einstein constant ($= 2.5$).

As shown in Fig. 4b, the relative viscosity, η_r , for the $C_{12}G_2$ /styrene mixtures exhibit far steeper concentration dependence behavior than those predicted for a dispersion of spherical particles based on the Krieger–Dougherty relation, due to the elongated micellar structures. The monotonous growth of the η_r with concentration well supports the concentration induced 1-D micellar growth as confirmed by the SAXS.

3.3 Effect of temperature

Figure 5 shows temperature effect on the reverse micellar structure; the $I(q)$, corresponding $p(r)$, and $S(q)$ curves for the 10 % $C_{12}G_2$ /styrene system at different temperatures 25, 50, and 75°C are presented. The scattering behavior is modified with increase in temperature. The decreasing tendency of the low- q scattering intensity with the increase in temperature from 25 to 75°C shows the shortening of reverse micelles and can best be seen in the $p(r)$ curves as shown in Fig. 5b. The maximum size of the reverse micellar core, $D_{\max}$, is decreased from ca. 5.2 to 3.4 nm; micelles shrunk by ~ 35 %.

It is interesting to note that $S(q=0)$ value increases and structure factor peak tends to move towards right with increase in temperature (Fig. 5c). It seems that both the

Fig. 5 Effect of temperature on the reverse micellar structures of the 10 % $C_{12}G_2$ /styrene system as obtained by SAXS; (a) The X-ray scattering intensities, $I(q)$, in absolute scales at different temperatures 25, 50, and 75°C, (b) the corresponding real-space $p(r)$ functions, (c) static structure factor curves. The solid and broken lines in panel (a) represent GIFT fit and the calculated form factor for n particles in unit volume $nP(q)$, respectively. Arrows in panel (b) highlight the maximum core diameters, $D_{\max}$.

osmotic compressibility of the system and intermicellar distance of the neighboring micelles increase upon heating. This might be caused by the dehydration of surfactant headgroup and/or enhanced solubility of water with styrene at higher temperatures. Here again we have tested the consistency of GIFT method by performing geometrical model fittings. Densities of 10 % $C_{12}G_2$ /styrene systems were 0.913804, 0.881562, and 0.85369 g/cm³ at 25, 50, and 75°C, respectively. These values gave electron density fluctuation of 132.33, 152.84, and 146.31 el/nm³ at 25, 50, and 75°C, respectively. **Figure 6** shows the results obtained from GIFT method and model fittings. Among tested models only a homogeneous ellipsoidal prolate could fit the data.

From the results of model fittings, we have calculated the geometrical parameters and presented in **Table 2**, which shows that the geometrical parameters, short axis (a), and long axis (b) of ellipsoid prolate, radius of gyration (R_g), and aggregation number (N_{agg}) of 10 % $C_{12}G_2$ /styrene reverse micelle decrease with the rise of temperature.

Temperature induced microstructure transition in non-aqueous media could be explained in terms of enhanced penetration of solvents in the surfactant, higher lipophilicity of the surfactant, and dehydration of surfactant's headgroup. The penetration increases the c_{pp} of the surfactant and, hence, aggregates with a more negative curvature are likely to form. Moreover, at higher temperatures the effec-

Fig. 6 (a) Experimental $I(q)$ (symbols), model fitting (full lines), and GIFT fit (dashed lines) in absolute scales at different temperatures 25, 50, and 75°C, and (b) comparison of the experimental $p(r)$ derived with GIFT (symbols) and those obtained from model fitting (solid lines). The data were fitted using a model of a homogeneous prolate ellipsoid. Arrows in panel (b) highlight the maximum diameter of the micellar cores, $D_{\max}$.

Table 2 Effect of temperature on the geometrical parameters, short axis (a), and long axis (b) of ellipsoid prolate, radius of gyration (R_g), and aggregation number (N_{agg}) obtained from the results of model fittings for the 10 % $C_{12}G_2$ /styrene reverse micelles:

System	Short axis (a)/nm	Long axis (b)/nm	Radius of gyration (R_g)/nm	Aggregation Number (N_{agg})
25°C	1.64	2.65	1.42	49
50°C	1.60	2.05	1.24	40
75°C	1.12	1.55	0.99	25

tive hydrophobic volume of the surfactant chain increases by increasing the kink states in the chain. Under this condition, increasing temperature dehydrates the surfactants head group and increases the c_{pp} .

3.4 Effect of water

Reverse micelles have been regarded as a good candidate for the encapsulation of water or water soluble materials as they tend to be soluble in the reverse micellar core⁴⁷. Investigations have shown that water modulates reverse micellar geometry producing bigger micelles^{48–53}. As expected addition of traces water induced a notable difference in the present system. **Figure 7** shows SAXS results for the 10% $C_{12}G_2$ /styrene system without and with 0.36% water as typical example.

As can be seen in **Fig. 7a**, scattering behavior modified in water added system; the low- q scattering intensity ($I(q=0)$) increases significantly and $I(q)$ curve in the cross section region ($1.6 \leq q \leq 3.2 \text{ nm}^{-1}$) shifts towards the lower- q side upon addition of 0.36% water. This is a clear demonstra-

Fig. 7 (a) The X-ray scattering intensities $I(q)$ of the 10 % $C_{12}G_2$ /styrene systems without and with 0.36 % water obtained on absolute scales at 25°C, and (b) the corresponding $p(r)$ curves. Solid and broken lines in panel (a) represent GIFT fit and the calculated form factor for n particles existing in unit volume, $nP(q)$, respectively. The arrows and broken lines in panel (b) indicate the maximum dimension of the reverse micellar core, $D_{\max}$, and maximum cross section diameter, $D_{c \max}$.

tion of the water-induced simultaneous changes in maximum dimension and the cross section structure of $C_{12}G_2$ -based reverse micelles (2-D micellar growth). Note that the inflection point after the maximum of $p(r)$ and the $D_{\max}$ as indicated by broken lines and arrows in Fig. 7b, increase with upon incorporation of water into the system. This result well supports the results derived from our previous studies of water effect on reverse micellar structure. Namely, water favors 2-D micellar growth and form a water pool at the micellar core.

4 CONCLUSIONS

We have investigated the structure and rheology of diglycerol monolaurate ($C_{12}G_2$) nonionic surfactant reverse micelles in aromatic organic solvent styrene in the dilute regions (5–25 %) under ambient conditions. Effects of surfactant concentration, temperature, and water on the geometry of reverse micelles have systematically been studied. Real-space structural information so called pair distance distribution function, $p(r)$, was determined by the generalized indirect Fourier transformation (GIFT) evaluation of small-angle X-ray scattering (SAXS) data and very well supported by the geometrical model fittings. We found that the $C_{12}G_2$ surfactant spontaneously self-assembles into ellipsoidal prolate type of reverse micelles in styrene without external water addition under ambient conditions. The maximum dimension of micelle and the aggregation number, N_{agg} , increase with the increase in surfactant concentration from 5 to 25 %; however, the cross section diameter remains apparently the same, indicating the concentration induced 1-D micellar growth, which is well supported by rheology data; the relative viscosity, η_r ,

for the $C_{12}G_2$ /styrene mixtures exhibit far steeper concentration dependence behavior than those predicted for a dispersion of spherical particles based on the Krieger-Dougherty relation, due to the elongated micellar structures. On the other hand, an opposite effect was observed with the rise of temperature; micelles shrunk and N_{agg} decreased with increase in temperature. Reverse micelles swelled with water causing a 2-D micellar growth; the maximum dimension and cross section diameter of the micellar core increase with water

ACKNOWLEDGEMENT

RGS thanks Japan Society for the Promotion of Science (JSPS) for the post-doctoral fellowship for foreign researcher. LKS thanks International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS) and WPI Center for Materials Nanoarchitectonics (MANA) for financial support.

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