Scattering and Spectroscopic Study on the Hydration and Phase Behavior of Aqueous Alcohol Ethoxylate and Methyl Ester Ethoxylate: Effects of Terminal Groups in Hydrophilic Chains

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ABSTRACT: Using dielectric relaxation spectroscopy (DRS), small-angle X-ray scattering (SAXS), dynamic light scattering (DLS), and viscometry, we have investigated the hydration behavior, static structures, Brownian dynamics, and mechanical properties of aqueous solutions of alcohol ethoxylate (C_{12}E_{15}) and methyl ester ethoxylate (C_{12}MEE), hereafter abbreviated as AE and MEE, respectively, in which we especially focus on the effects of the endcaps of these nonionic surfactants. We find that AE and MEE exhibit fairly different phase behaviors in water: AE produces liquid crystalline phases at \( \omega \) (surfactant weight fraction) > 0.35, whereas MEE retains a liquid phase in an extremely wide concentration range (\( \omega < 0.7 \)) at ambient temperature. The structure factor deduced from SAXS intensities using a generalized indirect Fourier transformation technique and the effective hydration number evaluated from the negative excess bulk water relaxation amplitude revealed by DRS unambiguously demonstrate that hydration water molecules, exhibiting about 4-times-slower collective reorientational dynamics than that of bulk water, contribute to the excluded volume of the micelles. The blocked terminal hydrogen-bond donor/acceptor site of MEE leads to smaller hydration number of MEE than compared to that of AE, and consequently the lower excluded volume of the MEE micelles. The effective micellar volume fraction, \( \phi_{\text{eff}} \), should be defined by incorporating such different hydration effects. Importantly, voluminosity, defined as the micellar volume fraction per unit mass, is clearly a decreasing function of \( \omega \), demonstrating progressive dehydration at a higher \( \omega \). The collective diffusion constants determined by DLS for the AE and MEE micelles show a monotonous increase up to \( \phi_{\text{eff}} \approx 0.5 \), as expected for the hard spheres. Low-shear-rate viscosities follow a Krieger–Dougherty model in the identical micellar packing fraction range. All static, dynamic, and mechanical properties of these micellar solutions can be explained in a consistent and quantitative manner only when the excluded volume of hydration water molecules is properly taken into account.

1. INTRODUCTION

Nonionic surfactants in aqueous media play an important role in diverse industries, such as detergent, food, and cosmetics, and are still of great interest in basic research. Because of hydrophobic driving forces, namely, a solvent-water-mediated tendency of hydrophobic groups to segregate, surfactants form a variety of self-assembled structures, such as micelles, liquid crystals, and vesicles. The knowledge of the structure and dynamics of these solutions not only involves implications for understanding biological systems but may also help formulate functional liquid systems. Poly(oxyethylene) monoalkylethers and alcohol ethoxylates (AEs), often abbreviated as C_{12}E_{j}, have been known as the most representative nonionic surfactants.\(^5\)–\(^8\)

A number of disordered and liquid crystalline (LC) phases are formed in their aqueous solutions.\(^3\)–\(^5\) Phase transition occurs upon changing the composition, temperature, or other external conditions, reflecting a delicate balance between the thermal fluctuations and interacting forces of the surfactant and water molecules.\(^6\)

In this study, we use two kinds of nonionic surfactants. Pentadecaoxyethylene monododecyl ether (C_{12}E_{15}), classified as a conventional C_{12}E_{j}-type surfactant, is also called AE, which possesses –OH as a terminal group in its hydrophilic chain. On the other hand, methoxy poly(oxyethylene) dodecancanoate or methyl ester ethoxylate (C_{12}MEE)\(^9\)–\(^12\) synthesized from natural plant-based oils for high-performance detergents, has a methoxy terminal group (–OCH_{3}). Hereafter, these surfactants are abbreviated as AE and MEE, respectively.
Despite quite similar hydrophobic and hydrophilic chain lengths, different molecular architectures of their endcaps have great influence on their phase behaviors in water. Such different phase behaviors may seem to arise, at least in part, from different hydration efficiencies, thus yielding the biased dynamically cooperative nature of their hydrophilic chains in an aqueous environment. Hanke et al. reported considerably different dielectric behaviors of poly(ethylene glycol) (PEG), HO-\([\text{CH}_2\text{CH}_2\text{O}]_{15}\)-CH_2CH_2-\text{OH}, and poly(ethylene glycol) dimethyl ether (PEGDME), CH_2O-\([\text{CH}_2\text{CH}_2\text{O}]_{15}\)-CH_2CH_2-OCH_3 where \(n\) is the degree of polymerization. PEGs and their aqueous solutions exhibit strong cooperative nature and essentially behave as hydrogen-bond liquids. In contrast, PEGDME and its solutions with low water content show far shorter relaxation times and considerably smaller dielectric constants than those of PEGs and their solutions, indicating far weaker cooperative nature due to the presence of the blocked terminal hydrogen-bond donor/acceptor site.

Substantial contribution of hydration water to the micellar excluded volume has been vaguely pointed out. However, such cardinality important aspects are still ambiguous and understood in a rather qualitative manner. In a colloidal dispersion of hard spheres (HSs), they interact as a consequence of the excluded volume. Therefore, phase behavior is largely controlled by the volume fraction, \(\phi_{\text{HS}}\). A drastic increase in the viscosity is observed at \(\phi_{\text{HS}} \sim 0.53\). Glass transition eventually occurs when \(\phi_{\text{HS}}\) exceeds \(\phi_{\text{g}} \sim 0.58\), leading to divergence of the viscosity. The interaction between nonionic micelles may be approximated as HS interaction. Despite possible deviation from an ideal HS system, the effective micellar volume fraction, \(\phi_{\text{eff}}\), involving the effects of hydration water should be a crucial parameter that governs phase behavior.

Here, we have thoroughly investigated the phase behavior and the structural, dynamical, and mechanical properties of the AE/water and MEE/water binary systems, employing a series of experimental techniques. Dielectric relaxation spectroscopy (DRS)\(^{13-15,18,21-30}\) can be an eminent tool for investigating liquid-state dynamics, which is in particular sensitive to the cooperative motions in hydrogen-bond liquids, such as water,\(^{21}\) alcohols,\(^{21}\) and their binary mixtures,\(^{23}\) as well as aqueous solutions of amino acids,\(^{24}\) proteins,\(^{25}\) and surfactants.\(^{8,14,15,18}\) A series of dielectric studies on nonionic surfactant systems have shown that DRS provides peerless information about micelle hydration,\(^{8,14,15,18}\) which is practically not accessible by other methods. On the other hand, small-angle X-ray scattering (SAXS)\(^{6,14-18,31-36}\) is a well-established, powerful technique for investigating the structure and interaction of colloidal particles. The generalized indirect Fourier transformation (GIFT) technique,\(^{33}\) developed by Glatter and co-workers as an extended version of the well-established indirect Fourier transformation technique,\(^{34}\) allows us to split scattering intensities into intra- and interparticle interference contributions. Dynamic light scattering (DLS) experiments provide information about the Brownian dynamics of colloidal particles. Thus, we can compare a concentration series of the collective diffusion constants of the present micelles with those of extensively studied HS systems in a disordered phase. The DLS results are reinforced by low-shear-rate viscosity measurements.

2. EXPERIMENTAL SECTION

2.1. Materials. AE and MEE can be obtained through hydrogen reduction from methyl ester and directly from methyl ester in plant-based surfactants,\(^{9-12}\) respectively. We use AE and MEE synthesized by Lion Co. (Tokyo, Japan). All of the syntheses are done according to the previously reported procedures.\(^{9-12}\) In Scheme 1, we depict the molecular structures of AE and MEE.

Scheme 1. Molecular Structures of AE (C_{12}E_{15}) and MEE (C_{12}MEE)

2.2. Phase Behavior. Aqueous solutions of AE and MEE were prepared by adding Millipore (Milli-Q) water to solid samples of AE and MEE and their concentrations were defined by the surfactant weight fraction, \(w\). The samples were sealed into ampules thoroughly mixed using a vortex centrifuge to attain homogeneity and kept at ambient temperature for a couple of weeks for equilibration. We carried out phase identification of the water/AE and water/MEE binary systems for almost the entire concentration range (except for the highest concentration regime of MEE, \(w > 0.96\)) by visual observation using a cross-polarizer.

2.3. DRS. We determined the complex dielectric spectra, \(\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)\), of the aqueous micellar solutions of AE and MEE at 25 °C in the frequency range 0.1 ≤ \(\nu\) (GHz) ≤ 20 with the help of time-domain reflectometry (TDR). The TDR system was based on the Hewlett-Packard instruments HP54121A and HP54120B. All time-domain measurements and conversion of the time-dependent reflected waveforms to the frequency-domain \(\varepsilon^*(\nu)\) spectra were performed according to the previously reported procedure.\(^{23}\) For the quantitative description of the experimental \(\varepsilon^*(\nu)\) spectra, we tested a series of conceivable relaxation models on the basis of superposition of \(n\) Havriliak–Negami\(^{28}\) equations, or their variants, using a nonlinear least-squares fitting procedure.

\[
\varepsilon^*(\nu) = \varepsilon_\infty + \sum_{j=1}^{n} \left( \frac{\Delta \varepsilon_j}{1 + (\nu \tau_j)^{\alpha_j}} \right) 
\]

where the \(j\)th dispersion step (\(j = 1, 2, ..., n\)) is defined by its relaxation time, \(\tau_j\) (\(\tau_j > \tau_{j+1}\)), and amplitude, \(\Delta \varepsilon_j\). \(n\) is the number of the dispersion steps, \(\varepsilon_\infty\) is the infinite frequency permittivity, and \(\alpha_j\) and \(\beta_j\) are the shape parameters representing the asymmetric\(^{29}\) and symmetric shapes\(^{30}\) on a spectrum, respectively.

2.4. DLS. DLS experiments were carried out using an ALV-5000E DLS system (ALV-Laser Vertriebsgesellschaft, Germany), equipped with single-mode fiber optics and a single-photon detector for detecting the time-dependent scattered intensity, \(I(t)\). A 10 mm cylindrical sample cell was immersed in a temperature-controlled index match bath filled with decalin solvent. Data acquisition was performed with an ALV-5000 multiple tau digital correlator. The wavelength of the light source was 530 nm. All measurements were performed at a total scattering angle of 90°. These experimental conditions correspond to the magnitude of the scattering vector \(q = 0.022\) \(\text{nm}^{-1}\) in aqueous media (refractive index \(n = 1.33\) at 25 °C). The ALV-5000E software package was used to calculate the
time-correlation functions, $g_1(r)$. A series of 30 s measurements and ensemble averaging of typically 10 $g_1(r)$ functions were performed to calculate the collective diffusion constant, $D_C$, of AE and MEE micelles. The diffusion coefficient in the limit of zero particle density, $D_0$, can be related to the hydrodynamic radius, $R_H$, of the particle via the Stokes–Einstein relation

$$D_0 = \frac{k_B T}{6\pi\eta R_H},$$

(2)

where $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\eta$ is the viscosity of the solvent.

2.5. SAXS. SAXS experiments were performed using a SAXSess camera (Anton Paar, Graz, Austria). An X-ray generator with a long fine-focus sealed-glass X-ray tube (GE Inspection Technologies, Germany) was operated at 40 kV and 50 mA. A focusing multilayer optics and a block collimator provided a line-shaped monochromatic primary beam (Cu Kα radiation, $\lambda = 0.154$ nm). Samples filled into a vacuum-tight thin quartz capillary were set in a temperature-controlled sample holder unit. The two-dimensional (2D) scattered intensity was detected by an imaging plate. Transmission calibration was made by referring to an attenuated primary beam at $q = 0$, taking advantage of a semitransparent beam stop. The 2D data were integrated into a one-dimensional scattering curve as a function of the magnitude of the scattering vector, $q = (4\pi/\lambda)\sin(\theta/2)$, where $\theta$ is the total scattering angle. The background scattering contributions from capillary and solvent were corrected. The absolute intensity calibration was done using water as a secondary standard. A model-independent collimation correction procedure (desmearing) was carried out relying on the Lake algorithm.

The scattering intensity, $I(q)$, from a globular particle system can be determined by the product of the form factor, $P(q)$, and the static structure factor, $S(q)$, as $I(q) = nP(q)S(q)$, where $n$ is the particle number density. $P(q)$ is the reciprocal-space coordinate of the pair-distance distribution function, $p(r)$, and they are connected via Fourier transformation as

$$P(q) = 4\pi \int_0^\infty p(r) \sin(qr) \frac{dr}{qr}.$$

(3)

The static structure factor, $S(q)$, embodies a length-scale-dependent density fluctuation and is given by the Fourier transformation of the total correlation function, $g(r) - 1$, as

$$S(q) = 1 + 4\pi \int_0^\infty \left(g(r) - 1\right) \sin(qr) \frac{dr}{qr}.$$

(4)

where $g(r)$ is the pair-correlation function. The SAXS data of the aqueous solutions of AE and MEE are analyzed using the GIFT technique, which allows us to simultaneously determine $P(q)$ and $S(q)$ from the experimental $I(q)$, letting $P(q)$ virtually model-free.

2.6. Low-Shear-Rate Viscosities. We performed rheological measurements to complement the results of SAXS, DRS, and DLS. The low-shear-rate viscosities, $\eta_\infty$, of the aqueous solutions of AE and MEE were measured using an AMVn automated rolling-ball viscometer (Anton Paar, Graz, Austria) at 25 °C. We used five different angles of the moving capillary block ranging from 30 to 70°. The measured viscosities were extrapolated to 0° to obtain zero-shear-rate viscosities.

2.7. Densimetry. Using a high-precision densimeter DMA5000 (Anton Paar, Austria), which is based on a conventional mechanical oscillator method, density measure-ments were carried out on the micellar solutions of AE and MEE at 25 °C. The density data were used for converting the surfactant weight fraction, $\omega$, into mass concentration, $c$ (g mL$^{-1}$), and molar concentration, $c_s$ (mol L$^{-1}$), and for calculating analytical water concentration, $c_w$ (mol L$^{-1}$).

3. RESULTS AND DISCUSSIONS

3.1. Phase Behavior of Aqueous Solutions of AE and MEE. In general, an intricate balance between hydrophobic and hydrophilic interactions and their relative changes depending on water content and temperature govern the phase behavior of nonionic surfactant in water. Figure 1 shows the phase diagrams of the AE/water and MEE/water binary mixtures as a function of temperature $T$ and surfactant weight fraction $w$. $L_1$ denotes an isotropic liquid phase, and $L_I$ and $H_I$ denote discontinuous (micellar) cubic and hexagonal LC phases, respectively. $S$ and $II$ represent solid-present and two-phase regions, respectively. The filled circles indicate the investigated points using SAXS, DRS, DLS, and viscometry. Only SAXS experiments are carried out for the points indicated by filled squares.
3.2. Dielectric Properties of the Aqueous Solutions of AE and MEE. In Figure 2, we present a concentration series of the complex dielectric spectra, \( \varepsilon^*(\nu) \), for aqueous micellar solutions of AE and MEE at 25 °C. As shown in Figure 2, addition of either AE or MEE to water induces a pronounced low-frequency broadening of the \( \varepsilon^*(\nu) \) spectrum, whereas the loss-peak frequency centered at \( \sim 19 \) GHz for water (\( w = 0 \)) is only slowly shifted to the lower frequency side with increasing \( w \) at \( w < 0.3 \). The observed broadening is attributed to the emergence of a new slower process. As a result of the fitting procedure based on eq 1, we find that the superposition of a low-frequency Cole–Cole \(^{30} \) (\( j = 1 \)) and a high-frequency Debye (\( j = 2 \)) relaxation

\[
\varepsilon^*(\nu) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1 + (i2\pi\nu\tau_1)^{\beta_1}} + \frac{\Delta\varepsilon_2}{1 + i2\pi\nu\tau_2},
\]

gives the best description for the experimental spectra of aqueous AE and MEE at \( w \leq 0.3 \), yielding a consistent set of the fitting parameters. The region of \( w \leq 0.3 \) covers almost the entire micellar phase region of AE. At \( w > 0.35 \), AE forms LC

Figure 2. Concentration series of the complex dielectric spectra of the aqueous AE and MEE solutions in 0.1 ≤ \( \nu \) (GHz) ≤ 20 at 25 °C. \( \varepsilon^*(\nu) \) spectra of AE solutions at \( w = 0.03, 0.10, 0.20, \) and 0.30 and those of MEE solutions at \( w = 0.03, 0.10, 0.20, 0.30, 0.40, \) and 0.45.
phases, whereas aqueous MEE still retains a disordered phase even at \( w = 0.6 \) at ambient temperature. At a high MEE concentration of \( w > 0.35 \), the superposition of two Cole–Cole relaxation processes

\[
\varepsilon^*(\nu) = \varepsilon_\infty + \frac{\Delta \varepsilon_1}{1 + (i2\pi \nu \tau_1)^{\alpha_1}} + \frac{\Delta \varepsilon_2}{1 + (i2\pi \nu \tau_2)^{\alpha_2}}
\]

turns out to be necessary for the description of the \( \varepsilon^*(\nu) \) spectra.

If one carefully observes the spectra shown in Figure 2 and compares with those for aqueous AE and MEE at identical \( w \), one can notice that the aqueous AE shows a broader spectra and a smaller loss-peak value than those of aqueous MEE. Cooperative molecular kinetics in aqueous AE and MEE is characterized by two different time scales \( \tau_1 \) and \( \tau_2 \). Figure 3

![Figure 3](image_url)

shows the relaxation times \( \tau_j \) and amplitudes \( \Delta \varepsilon_j \) of these solutions. The relaxation amplitude of the low-frequency process, \( \Delta \varepsilon_j \), increases with increasing \( w \), whereas that of the high-frequency one, \( \Delta \varepsilon_j \), decreases. At small \( w \), the relaxation time of the high-frequency process, \( \tau_2 \), for both the AE and MEE solutions is close to the Debye relaxation time of pure water \( \tau_2 = 8.3 \text{ ps} \) at \( 25 \text{ °C} \)\(^2\), which only gradually increases with the increase of \( w \) in the region \( w < 0.3 \). The low-frequency process \( (j = 1) \) exhibits about 4-times-longer relaxation time than that of bulk water.

It can be inferred from the above-mentioned behavior that the high-frequency process is assigned to the cooperative rearrangement of the hydrogen-bond network of bulk water. The low-frequency process is attributed to the kinetics of the hydrophilic layer of the micelles, including hydrophilic chains and hydration water. The process is expected to be highly cooperative in the densely packed hydrophilic layer, in which the conformational change of the poly(ethylene oxide) chains and displacement of water molecules are likely to occur in a concerted manner. This may lead to a significantly longer dielectric relaxation time compared to that of bulk water. Note that the low-frequency process cannot be attributed to the rotational diffusion of the whole AE and MEE micelle because \( \tau_1 \) is 3 orders of magnitude shorter than the predicted value referring to the Stokes–Einstein–Debye equation for the micellar radius.

We find that \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) of AE solutions are, respectively, larger and smaller than those of MEE solutions if these quantities are compared at identical \( w \). Such trends of \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) are manifested by a low-frequency broader spectrum and a smaller loss-peak value of the AE solution than those of the MEE solution at identical \( w \). Comparison of the \( \varepsilon^*(\nu) \) spectra of the solutions of AE and MEE at \( w = 0.30 \) is shown in Figure S3, which confirms the different behaviors of \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) for the solutions of AE and MEE displayed in Figure 3A,B.

### 3.3. Hydration of AE and MEE Micelles

As shown in Figure 3B, the bulk water amplitude, \( \Delta \varepsilon_2 \), smoothly decreases from 72.4 for pure water with an increase in \( w \). \( \Delta \varepsilon_2 \) is always smaller than expected from the analytical water concentration, \( c_w \), which means that a negative excess polarization fluctuation appears for bulk water relaxation. We evaluate the effective hydration number of the AE and MEE molecules, \( Z_{\text{hyd}} \), using a generalized Cavell equation\(^{26,27} \)

\[
\Delta \varepsilon_2 = \frac{\varepsilon - N_w \mu^2}{2\varepsilon + 1 + k_B T \varepsilon_0 c_w^{\text{app}}}
\]

where \( \varepsilon \) is the static permittivity, \( k_B \) is the Boltzmann constant, \( N_w \) is the Avogadro number, and \( \varepsilon_0 \) is the vacuum permittivity. The squared effective dipole moment, \( \mu^2 \), in eq 7 can be written as

\[
\mu^2 = \frac{g \mu_G^2}{(1 - \alpha \mu_G^2)}
\]

where \( \mu_G \) is the gas-phase dipole moment, \( g_w \) is the dipole–dipole correlation factor, \( \alpha \) is the polarizability, and \( f_w \) is the field factor. Using eq 7, we connect \( \Delta \varepsilon_2 \) to the apparent bulk concentration, \( c_w^{\text{app}} \). Assuming a spherical water molecule having a radius of 0.1425 nm and a polarizability of \( \alpha = 1.607 \times 10^{-40} \text{ C m}^2 \text{ V}^{-1} \), \( c_w^{\text{app}} \) is calculated as a function of surfactant molar concentration \( c_w \). \( c_w(c) \) can be interpreted as the concentration of water molecules that still retain the nature of bulk water in the presence of the surfactant molecules. Then, we define the effective hydration number of the AE or MEE molecule, \( Z_{\text{hyd}} \), by converting the difference between \( c_w^{\text{app}} \) and the analytical water (molar) concentration, \( c_w(c) \), into the corresponding number of water molecules per surfactant molecule

\[
Z_{\text{hyd}} = \frac{c_w(c) - c_w(c)^{\text{app}}}{c_w(c)}
\]

According to eq 9, \( Z_{\text{hyd}} \) gives the number of water molecules that cannot contribute to the bulk water relaxation process due to hydration effects. Figure 4 shows \( Z_{\text{hyd}} \) as a function of \( w \). The hydration number per oxyethylene monomer unit is about 4 at infinite dilution \( (w \rightarrow 0) \), demonstrating that approximately four water molecules are so tightly bound to the hydrophilic chains of the surfactant molecules that they lose the nature of bulk water. The present results for the aqueous solutions of AE and MEE are broadly consistent with the existing set of PEG hydration numbers.\(^8,14,15,18,22 \) For instance, Schrödl et al. performed an extensive dielectric study on aqueous \( C_{12}E_8 \) for both the aqueous micellar and LC phases and obtained about 3.5–4.0 bound water molecules per ethylene glycol monomer unit for micellar solutions.\(^8 \) Two important findings are manifested in Figure 4. \( Z_{\text{hyd}} \) for both the AE and MEE solutions is a decreasing function of \( w \). This demonstrates a progressive dehydration of the micelles at higher \( w \). Systematically greater \( Z_{\text{hyd}} \) values of AE than those of MEE, which can be distinguished within the accuracy of the present DRS...
experiments/analysis, indicate that the hydration ability of AE is higher than that of MEE.

3.4. Static Structures of AE and MEE Micelles. Figure 5 shows concentration-normalized SAXS intensities, $I(q)/c$, of the AE and MEE solutions on an absolute scale, where $c$ is the weight concentration of the surfactants. The experimental $I(q)$ shows a typical feature of core–shell globular particles. As shown in Figure 5C, the forward intensity, $I(q \to 0)/c$, of the AE solutions is a monotonously decreasing function of $w$ in the entire micellar region, whereas that of the MEE solutions exhibits a minimum at $w \approx 0.35$ and then gradually increases at $0.35 < w \leq 0.6$. To extract specific information about the micellar structure (size, shape, and internal core–shell structure) and the micelle–micelle positional correlations, a further quantitative analysis of $I(q)$ is required. The SAXS data for the aqueous solutions of AE and MEE are analyzed using the GIFT technique. We use a polydisperse HS interaction potential and a Percus–Yevick (PY) closure for modeling $S(q)$.

In Figure 6, we show the results of the GIFT analysis of the aqueous solutions of AE and MEE at $w = 0.1$ at $25 \degree C$. We point out that the scattering vector corresponding to the local minimum of $I(q)$, $q_{\text{min}}$, is a function of not only the whole particle size but also the contrast, that is, the electron density fluctuation of the core and shell and their thicknesses. The $p(r)$ values of the AE and MEE micelles are shown in Figure 6B. The maximum diameter, $D_{\text{max}}$, of the AE and MEE micelles is estimated to be about 8.5 nm from the $r$-value at which $p(r)$ goes to 0. The low-$r$ local maximum and minimum in $p(r)$ result essentially from the convolution of the negative and positive electron density fluctuations of the hydrophobic core and hydrophilic shell, respectively.

The different shapes of $p(r)$ for the AE and MEE micelles can be explained in terms of different internal electron density distributions. In Figure 6C, we show the electron density profiles, $\Delta \rho(r)$, of the AE and MEE micelles deconvoluted from their $p(r)$ functions. The $\Delta \rho(r)$ profiles reveal that in addition to the core radii of about 1.6 nm for AE and a slightly lower value for MEE and the maximum radii of 4.2 nm of the micelles, MEE shows higher $\Delta \rho(r)$ values around $r \approx 2$ nm, which is likely to be due to the higher electron density of the ester group in MEE than that of the ether group in AE.

Figure 7 shows the surfactant concentration dependence of $S(q)$ as obtained by SAXS. The extrapolated structure factor to zero scattering vector, $S(q \to 0)$, is proportional to the osmotic potential and a Percus–Yevick (PY) closure for modeling $S(q)$. We use a polydisperse HS interaction potential and a Percus–Yevick (PY) closure for modeling $S(q)$.

Figure 6. GIFT analysis of the SAXS intensities of aqueous solutions of AE and MEE. (A) SAXS intensities, $I(q)$, at $w = 0.1$ at $25 \degree C$. The black solid and colored dotted curves in the lower panel of (A) represent GIFT fit to $I(q)$ curves and the calculated form factor, $nP(q)$, respectively. In the upper panel of (A), the deduced static structure factors, $S(q)$, are shown. (B) Pair-distance distribution functions, $p(r)$, and (C) electron density profiles, $\Delta \rho(r)$, of the AE and MEE micelles.
compressibility of the system. For a monodisperse HS, \( S(q \to 0) \) is simply determined by the packing fraction of the HS, \( \phi_{\text{HS}}^{\text{eff}} \). Using densimetry, the partial specific volumes of AE and MEE in water are estimated to be 0.915 and 0.907 cm³ g⁻¹ at 25 °C, respectively. The investigated concentration ranges of 0 ≤ \( w \) ≤ 0.30 for aqueous AE and 0 ≤ \( w \) ≤ 0.60 for aqueous MEE correspond to the surfactant volume fractions of 0 ≤ \( \phi_{\text{AE}}^{\text{dens}} \) ≤ 0.282 and 0 ≤ \( \phi_{\text{MEE}}^{\text{dens}} \) ≤ 0.575, respectively. Note that \( \phi_{\text{dens}}^{\text{eff}} \) is rather close to \( w \). On the other hand, \( \phi_{\text{DRS}}^{\text{eff}} \) is defined as

\[
\phi_{\text{DRS}}^{\text{eff}} = \left(1 - \frac{c_w(c_w)^{\text{app}}}{c_w(0)}\right)
\]

where \( c(c_w)^{\text{app}} \) is the apparent water concentration determined from the bulk water relaxation amplitude. According to its definition, \( \phi_{\text{DRS}}^{\text{eff}} \) explicitly involves the volumes occupied by the surfactant molecules and hydration (slow) water molecules detected by DRS, whereas \( \phi_{\text{dens}}^{\text{eff}} \) accounts for the surfactant volume only.

In Figure 7, we compare the zero-\( q \) limit structure factor, \( S(q \to 0)^{\text{SAXS}} \), deduced from the SAXS intensities to that predicted for HS fluid having effective volume fractions \( \phi_{\text{HS}}^{\text{app}} \) and \( \phi_{\text{DRS}}^{\text{app}} \). According to the Carnahan–Starling equation, the extrapolated structure factor to zero scattering vector for an HS fluid, \( S(q \to 0)^{\text{HS}} \), as a function of the volume fraction of HS, \( \phi_{\text{HS}}^{\text{app}} \), is given by

\[
S(q \to 0)^{\text{HS}} = \frac{(1 - \phi_{\text{HS}}^{\text{app}})^4}{(1 + 2\phi_{\text{HS}}^{\text{app}})^2 + \phi_{\text{HS}}^{\text{app}}(1 - \phi_{\text{HS}}^{\text{app}})}
\]

Importantly, we find that \( \phi_{\text{DRS}}^{\text{app}} \) is very close to \( \phi_{\text{DRS}}^{\text{app}} \) for both the AE and MEE solutions except for a highly concentrated region of \( w > 0.45 \) for MEE. Analogously, \( S(q \to 0)^{\text{SAXS}} \) deduced from SAXS intensities coincides well with \( S(q \to 0)^{\text{DRS}} \) calculated using eq 11 by substituting \( \phi_{\text{DRS}}^{\text{app}} \) for \( \phi_{\text{app}}^{\text{app}} \). In contrast, \( \phi_{\text{dens}}^{\text{app}} \) is considerably smaller than \( \phi_{\text{app}}^{\text{app}} \). Accordingly, \( S(q \to 0)^{\text{SAXS}} \) predicted from \( \phi_{\text{dens}}^{\text{app}} \) and eq 11 is far greater than \( S(q \to 0)^{\text{SAXS}} \). This means that when the excluded volume of the hydration water molecules is neglected, the osmotic compressibility and the micellar packing fraction are significantly over- and underestimated, respectively. These findings unambiguously demonstrate that \( S(q \to 0) \) and \( \phi_{\text{app}}^{\text{app}} \) of the AE and MEE solutions are explained in a quantitative manner when the excluded volume of both the surfactant and hydration water molecules are involved.

Further insights into micellar hydration are obtained from voluminosity, \( v = \phi_{\text{app}}^{\text{app}}/c_w \), defined as the volume fraction per unit mass. Voluminosity is an important basic property for examining interactions between hydrating colloidal particles. Recently, Foffi et al. have shown that the packing volume of \( \alpha \)-crystallin in solution, \( v = 1.7 \text{ mL g}^{-1} \), which is considerably larger than that of a typical globular protein, \( v = 0.7 \text{ mL g}^{-1} \), reflects its open, multisubunit structure, and well explains the HS-like nature of \( \alpha \)-crystallin. Figure 8 compares the...
voluminosities, \( \nu^{SAXS} = \phi^{SAXS}/c \) and \( \nu^{DRS} = \phi^{DRS}/c \) of the AE and MEE micelles. The smaller \( \nu \) of MEE again indicates its lower hydration efficiency and the smaller excluded volume compared to those of AE. We emphasize that for both the AE and MEE solutions, \( \nu \) is clearly a decreasing function of \( w \), demonstrating a progressive dehydration of the micelles at higher \( w \). \( \nu^{SAXS} \) of MEE becomes smaller than unity at \( w > 0.50 \), where \( S(q \to 0)^{SAXS} \) gradually increases. This seems to reflect a weak attraction between the micelles. Alternatively, judging from the fact that at \( w > 0.6 \), the hexagonal phase appears at lower temperature (\( T < 17^\circ C \)), this may be related to partial elongation of the micellar structure from sphere or spheroid to rodlike geometry, where the HS model for \( S(q) \) is beyond its application limit while \( \nu^{DRS} \) for MEE converges to unity at highest \( w \).

### 3.5. Effects of Hydration Water on the Collective Diffusion and Low-Shear-Rate Viscosity of the AE and MEE Micelles

To further examine the effects of hydration water and its influence on the packing fraction of the micelles, we measure the collective diffusion coefficient of the micelles, \( D_C \), and (relative) low-shear-rate viscosities, \( \eta/\eta_0 \), of the AE and MEE solutions at 25 °C. We compare these dynamical and mechanical properties to those of an HS fluid. In Figures 9 and 10, we show, respectively, the concentration dependence of \( D_C \) and \( \eta/\eta_0 \) for the aqueous solutions of AE and MEE as a function of the different effective volume fractions \( \phi_{\text{dense}} \), \( \phi_{\text{SAXS}} \), and \( \phi_{\text{DRS}} \), where \( \phi_{\text{dense}} \), \( \phi_{\text{SAXS}} \), and \( \phi_{\text{DRS}} \) are determined from densimetry, SAXS, and DRS, respectively, and \( \phi_{\text{eff}} = \nu_{\text{eff}} \), assuming concentration-independent voluminosity, \( \nu_0 \) where \( \nu_0 = 1.9 \) mL g\(^{-1} \) for AE and \( \nu_0 = 1.5 \) mL g\(^{-1} \) for MEE. The solid line shows the empirically predicted behavior of the HS, \( D(\phi)/D_0 = 1 + 1.56\phi \). The dotted line represents the glass transition point of the HS, \( \phi_{\text{g}} \) \( \approx \) 0.58.

For an HS fluid, \( D_C(\phi_{\text{HS}}) \) is an increasing function of the packing fraction, \( \phi_{\text{HS}} \) which is empirically expressed as

\[
D_C(\phi_{\text{HS}}) = D_0(1 + 1.56\phi_{\text{HS}})
\]

where \( D_0 \) is the diffusion coefficient in the limit of zero particle density. Extrapolating the concentration-dependent \( D_C \) data to \( w \to 0 \), \( D_0 \) is estimated to be \( 6.6 \times 10^{-11} \) m\(^2\) s\(^{-1} \) for AE and \( 6.7 \times 10^{-11} \) m\(^2\) s\(^{-1} \) for MEE, corresponding to \( R_H \approx 3.7 \) nm, which is similar to \( D_{\text{max}}/2 \approx 4 \) nm in \( p(r) \) as determined by SAXS.

The KD equation is often used to model the low-shear-rate viscosity of an HS fluid

\[
\frac{\eta(\phi_{\text{HS}})}{\eta_0} = \left( 1 - \frac{\phi_{\text{HS}}}{\phi_m} \right)^{-[\eta]_0}
\]

where \( \phi_{\text{HS}} \) is the particle volume fraction, \([\eta]_0 \) is the intrinsic viscosity, and \( \phi_m \) is the volume fraction at which \( \eta/\eta_0 \) diverges. When \( \phi_{\text{HS}} \to 0 \), a KD equation is reduced to an Einstein
Correspondingly, the AE and MEE solutions, obeying the HS prediction (eq 13) are equivalent to the linear approximation, with practically equivalent to the linear approximation, scaling factor \( \phi_{cv} \) which far exceed the glass transition point of HS, the Brownian dynamics and the low-shear-rate viscosity of the micelles when \( \phi_{dmn} \) is used as a micellar volume fraction.

It has been known that the concentration dependence of \( D_c \) for a series of nonionic surfactant solutions is underestimated if the surfactant volume fraction, \( \phi_{v} \) or surfactant weight fraction, \( w_\text{s} \), is simply used for \( \phi_{HS} \). In previous literature data, a simple linear relation \( \phi_{eff} = kw_\text{s} \) with an arbitrarily chosen scaling factor \( k \) was assumed. \( k \approx 2.1 \) was obtained for the aqueous solutions of the triblock copolymer poly(ethylene oxide)--poly(propylene oxide)--poly(ethylene oxide) (PPO). A larger \( k \) value of about 4 was reported for poly(oxyethylene-23) dodecylether, \( C_{12}E_{23} \) (Brij 35). Figure 9B shows \( D_c \) as function of \( \phi_{w} \) with \( v_0 = 1.9 \) for AE and \( v_0 = 1.5 \) mL g\(^{-1}\) for MEE. The assumption of constant voluminosity (CV) is practically equivalent to the linear approximation, \( \phi_{eff} = kw_\text{s} \), neglecting the upward convex feature of \( \phi_{SAXS} \) and \( \phi_{DRS} \) shown in Figure 7D. Nevertheless, the CV assumption gives a good fit to the experimental \( D_c \) up to \( \phi_{w} \approx 0.4 \). However, if the relation \( \phi_{w} / c = 1.5 \) mL g\(^{-1}\) for MEE is extended to the highest investigated concentration of \( w = 0.6 \), the corresponding packing fraction approaches \( \phi_{w} \approx 1.1. \eta/\eta_0 \) versus \( \phi_{w} \) shown in Figure 10B gives \( \phi_{w} = 0.72 \) for AE and \( \phi_{w} = 0.77 \) for MEE, which far exceed the glass transition point of HS, \( \phi_{HS} \approx 0.58 \). These findings strongly indicate that \( \phi_{w} \) overestimates the micellar packing fraction, especially at high \( w \).

As for the AE/water system, the micellar cubic (I\(_1\)) phase is produced at \( \phi_{eff} > 0.5 \). In contrast, the MEE/water system retains a liquid state and shows an abrupt decrease of \( \eta/\eta_0 \) at \( w > 0.5 \), avoiding the singularity at the maximum volume fraction, \( \phi_{w} \) predicted by classical models. At the same time, \( D_c \) for MEE solutions decreases at \( w > 0.5 \), where a clear deviation from the HS prediction is manifested. We infer that such a marked behavior of MEE is linked with the weaker hydration capability and the less-cooperative nature of the molecular kinetics in its hydrophilic layer, which is due to the presence of blocked H-bond acceptor and donor sites in its endcap (–OCH\(_3\)).

4. CONCLUSION

We have investigated the static structures, Brownian dynamics, and mechanical properties of the aqueous solutions of AE and MEE, in particular focusing on the hydration effects. The different endcap architectures of these nonionic surfactants, –OH and –OCH\(_3\), result in considerably different phase behaviors of AE and MEE in water. At ambient temperature, AE forms LC phases in the region of \( w > 0.35 \), whereas MEE retains a disordered phase in a far wider concentration range up to \( w \approx 0.7 \). By combining SAXS with DRS, we have convincingly shown that the hydration water molecules of the surfactants serve as a constituent of the micellar hydrophilic shell and thus contribute to the excluded volume of the micelles. \( S(q) \) deduced from SAXS intensities indicates that the osmotic compressibilities of both the AE and MEE solutions are markedly lower than those predicted from the actual surfactant volume and the Carnahan–Starling equation. The effective hydration number of AE and MEE revealed by DRS accounts for the excess osmotic compressibility and the corresponding effective micellar volume fraction, \( \phi_{eff} \), evaluated by SAXS. A blocked terminal hydrogen-bond donor/acceptor site of MEE leads to smaller hydration number of MEE than that of AE and the lower excluded volume of the MEE micelles. The voluminosity of both AE and MEE micelles turns out to be a decreasing function of \( w \), which provides evidence for a progressive dehydration of the surfactant molecules at higher \( w \). The collective diffusion constants of the AE and MEE micelles measured by DLS show a linear increase up to \( \phi_{eff} \approx 0.5 \) as expected for the HSs. The low-shear-rate viscosities of the micellar solutions are also well explained within the framework of the HS, obeying a KD model in the identical packing fraction range. The data demonstrate that the static structures, Brownian dynamics, and mechanical properties of the micellar solutions can be fully understood by incorporating the hydration effects and the resulting concentration-dependent voluminosity of the micelles.

## ASSOCIATED CONTENT

### Supporting Information

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SAXS intensities of the LC phases for the water/AE system at 25 °C and the water/MEE system at 5 °C; a temperature series of SAXS intensities for the water/MEE systems at \( w = 0.35, 0.40, 0.45, 0.50, \) and 0.65; comparison of the complex dielectric spectra of the aqueous solutions of AE and MEE at \( w = 0.30 \) at 25 °C (PDF).
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Notes
The authors declare no competing financial interest.

**REFERENCES**


