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Small angle neutron scattering study of two nonionic surfactants in water micellar solutions

RAJEWSKA ALDONA
Institute of Atomic Energy, 05-400 Swierk-Otwock, Poland
E-mail: aldonar@cyf.gov.pl

Abstract. Two classic nonionic surfactants – $C_{14}E_7$ (heptaethylene glycol monotetradecyl ether) and $C_{10}E_7$ (heptaethylene glycol monodecyl ether) were investigated in heavy water solution for concentration $c = 0.17\%$ (dilute regime) at different temperatures in the range $t = 10$–35°C by small angle neutron scattering (SANS) method. In the case of $C_{14}E_7$ surfactant – for all temperatures at $c = 0.17\%$ there are two axial ellipsoidal micelles with longer axis 15 nm at 10°C and 49.5 nm at 35°C in investigated solutions. For $C_{10}E_7$ surfactant at the same concentration of solution and temperature – two axial ellipsoidal micelles were observed, too. The longer axis is equal to 7.5 nm at 10°C, 9 nm at 20°C and at 35°C this axis is equal to 12 nm. Micelles of $C_{10}E_7$ nonionic surfactant are smaller than those of $C_{14}E_7$ surfactant in the same experimental conditions.

Keywords. Small angle neutron scattering; complex fluids; aggregation of nonionic classic surfactants.

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1. Introduction

It is well-known that surfactants form micelles above the critical micellization concentration (CMC) in aqueous solution. The form and size of micelles is connected with concentration, temperature of water solution, and with structure and size of the molecule of each surfactant. Polyoxyethylene alkyl ethers have the general formula $C_nH_{2n+1}(OCH_2CH_2)_mOH$. They will be referred to as C_nE_m with n indicating the number of carbons in the alkyl chain and m the number of ethylene oxide units in the hydrophilic moiety.

In the dilute regime the C_nE_m+water binary system forms an isotropic phase called the L_1 phase, which consists of micelles formed with the amphiphilic molecules and water. The system exhibits LCST (lower critical solution temperature) behaviour, the micellar solutions are phase-separated into two phases at high temperatures. It is now well established that the micelles grow in size with increasing concentration and rising temperature, in particular, to a greater extent when approaching the phase boundary, assuming a thread-like or worm-like shape.

2. Experimental

2.1 *Materials*

Two nonionic heptaethylene glycol monotetradecyl ether ($C_{14}E_7$) and heptaethylene glycol monodecyl ether ($C_{10}E_7$) were investigated in D_2O (heavy water) solutions by small angle neutron scattering method [1–6]. The micellar solutions were prepared in D_2O (heavy water), since the contrast between the micelles and the solvent in neutron experiments is better with D_2O than with H_2O. The results were calculated with the help of the PCG software 1.01.02 (Austria). The information on size and form of the micelles was obtained from of the experimental data.

Heavy water was purchased in the Prikladnaya Chimia in St. Petersburg, Russia. All surfactant solutions were made using D_2O as a solvent (99.9% deuterated), $C_{14}E_7$ (heptaethylene glycol monotetradecyl ether) (MW = 522.77, CMC = 1.28×10^{-5} M) and $C_{10}E_7$ (heptaethylene glycol monodecyl ether) (MW = 466.66, CMC = 0.96 mM) were obtained from Fluka and were used without further purification.

2.2 *Small angle neutron scattering (SANS) experiment*

All SANS measurements were performed on the time-of-flight spectrometer MURN of the IBR-2 pulsed reactor, JINR, Dubna, Russia and on the SANS diffractometer 'Yellow Submarine' at the Budapest Neutron Center, Budapest, Hungary. The characteristics of these spectrometers were described in detail in [7,8]. Neutrons were used in the wavelength Q range from 8×10^{-3} to 0.4 Å^{-1}. For the measurements, quartz cells of 2 mm thickness were used which were sealed to prevent evaporation during the experiment. Up to 15 such cells were placed in a sample holder, and the temperature within the cells was kept constant in the range of ±0.5°C by means of a thermostat. Conversion of the scattered intensities into absolute differential cross-sections was done by using an internal calibration standard (vanadium). Background scattering was subtracted by comparison with a corresponding pure D_2O sample. The data treatment was done according to the standard procedures [9].

2.3 *SANS data analysis*

The intensity of scattered radiation as a function of the magnitude of the scattering vector q is represented for monodisperse particles by [10]

$$I(q) = nP(q)S(q),$$

where $q = 4\pi/\lambda \sin(\theta/2)$, λ is the wavelength of radiation, θ is the scatterring angle, and n is the number density of particles, $P(q)$ is the particle form factor and contains the effect of particle size, shape and scattering power on scattered intensity,

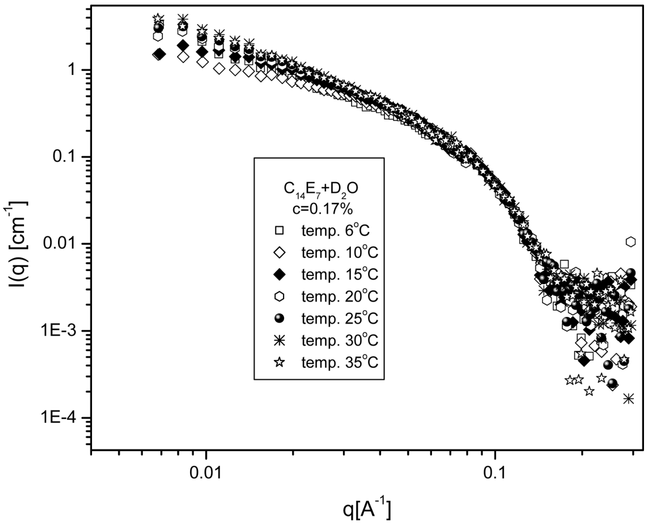

Figure 1. Intensity of neutron scattering vs. scattering vector for $C_{14}E_7+D_2O$ solution at concentration $c = 0.17\%$ for temperatures 6, 10, 15, 20, 25, 30 and 35°C.

$S(q)$ is the structure factor which accounts for interparticle interactions, $S(q) \to 1$ when there are no interacting particles or in the limit of a very dilute solution. The micelle shape determination for the experimental results was achieved using the generalized indirect Fourier transformation (GIFT) method [11]. The conventional Fourier transformation of $I(q)$ involves the integral

$$p(r) = \frac{1}{2\pi^2} \int I(q) qr \sin(qr) \mathrm{d}q$$

which yields the pair distance distribution function $p(r)$, where r is the distance in real space. The point, at which the $p(r)$ falls to zero, is indicative of the particle maximum dimension.

3. Results and discussion

Few scattering curves of $C_{14}E_7+D_2O$ as a function of temperature for concentration $c = 0.17\%$ (dilute regime) is shown in figure 1 and for $C_{10}E_7+D_2O$ is shown in figure 2. Interparticle interactions can be neglected at this low concentration.

Figure 3 shows the distance distribution function as determined by the indirect Fourier transformation (IFT) method for $C_{14}E_7+D_2O$ solutions ($c = 0.17\%$) for temperatures 10, 20 and 35°C and figure 4 shows the distance distribution function for $C_{10}E_7+D_2O$ solutions ($c = 0.17\%$) for the same temperatures. The IFT is only applicable to very dilute systems where particle interactions can be neglected.

In the case of $C_{14}E_7$ surfactant – for all temperatures at $c = 0.17\%$ there are two axial ellipsoidal micelles in the investigated solutions, with longer axis 15 nm

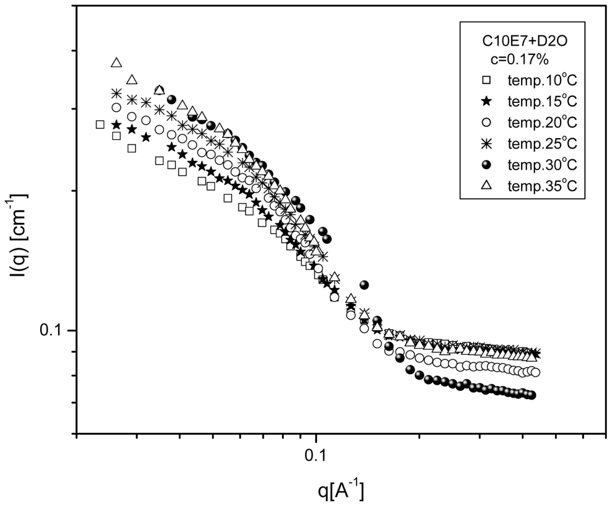

Figure 2. Intensity of neutron scattering vs. scattering vector for $C_{10}E_7$+D_2O solution at concentration $c = 0.17\%$ for temperatures 10, 15, 20, 25, 30 and 35°C.

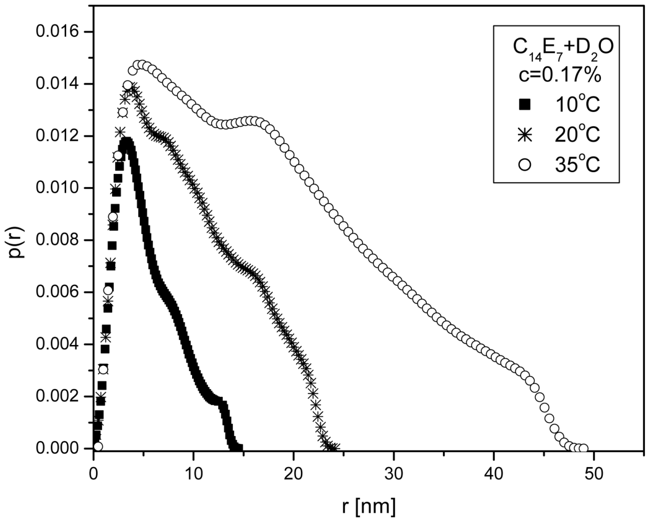

Figure 3. The distance distribution function as determined by the IFT method for $C_{14}E_7$+D_2O solutions at concentration $c = 0.17\%$ for temperatures 10, 20 and 35°C.

at 10°C and 49.5 nm at 35°C. For $C_{10}E_7$ surfactant at the same concentration of solution and temperature – two axial ellipsoidal micelles were observed, too. The longer axis is equal to 7.5 nm at 10°C, 9 nm at 20°C and at 35°C this axis is equal to 12 nm. Micelles of $C_{10}E_7$ nonionic surfactant are smaller than those of $C_{14}E_7$ surfactant in the same experimental conditions.

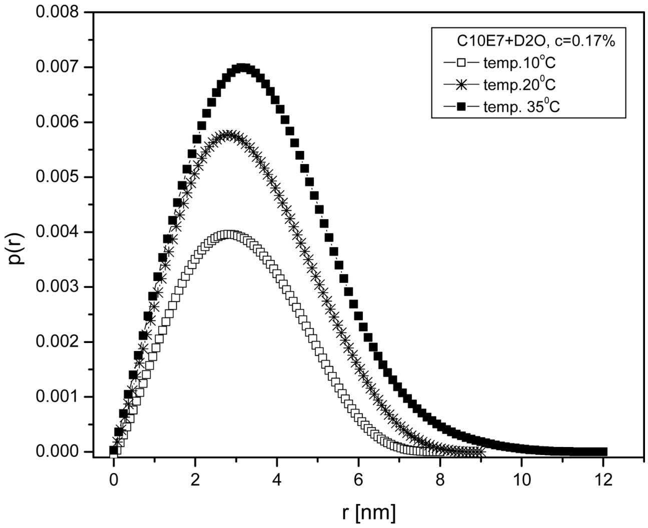

Figure 4. The distance distribution function as determined by the IFT method for $C_{10}E_7$+D_2O solutions at concentration $c = 0.17\%$ for temperatures 10, 20 and 35°C.

4. Conclusions

Two investigated nonionic classic surfactants are from the same homologous series with different carbon number in alkyl chain. That is why the size of micelles change at the same concentration of surfactants in heavy water solution. It was observed that the temperature influences the size of micelles too. For these two investigated surfactants, the size of micelles increases with increase of temperature and concentration.

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