Small-angle neutron-scattering study of concentrated nonionic-amphiphile solutions

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Abstract: The structure of aqueous solutions of two polyoxyethylene non-ionic amphiphiles, $C_{10}E_5$ and $C_8E_4$, is studied by small-angle neutron-scattering along isothermal paths crossing the isotropic single-phase region from 0% to 100% amphiphile volume fractions. The scattered intensity $I(k)$ shows a peak at a value $k_m$, which grows monotonically as the amphiphile volume fraction $\Phi$ increases. The interpretation of the scattering data leads to the following conclusion: as $\Phi$ increases the micellar structure becomes less and less sharp, but some orientational correlations between neighboring amphiphile molecules are preserved even in the pure amphiphile phase.

Key words: Non-ionic micelles; neutron scattering

Introduction

Aqueous solutions of non-ionic polyoxyethylene amphiphiles, whose chemical formula is $C_{i}H_{2i+1}(OCH_{2}CH_{2})_{j}OH$ or $C_{i}E_{j}$ for short, have been the subject of many studies [1-3]. If we consider, for instance, $C_{10}E_5$ solutions, whose phase diagram is given in [4], we see that above the mesophase regions and below the cloud-point curve it is possible to follow a continuous path that crosses the isotropic single-phase region from 0 to 100% volume fraction. It is known that above the critical micelle concentration $C_{10}E_5$ forms globular micelles. It is not known, however, up to what amphiphile concentration the system can still be described as a water-continuous dispersion of amphiphile aggregates and how the system evolves towards the pure liquid amphiphile phase. In order to obtain some understanding of the structure of concentrated $C_{i}E_{j}$ solutions, we have undertaken a small-angle neutron-scattering investigation along isothermal paths that do not hit mesophase regions. In the first preliminary article [5], we reported data on $C_{12}E_8$ solutions at 60°C. Here, we present results obtained with $C_{10}E_5$ and $C_8E_4$ solutions. Our data show that the three systems present a very similar evolution of the structure as function of the volume fraction $\Phi$, with characteristic sizes scaling roughly as the monomer length. The interpretation of the scattering data leads to the following conclusion: as $\Phi$ increases the micellar structure becomes less and less sharp, but some orientational correlations between neighboring amphiphile molecules are preserved even in the pure amphiphile phase.

Experimental

Non-ionic amphiphiles were obtained from Nikko Chemical, Japan, and were used without further purification. The solvent was $D_2O$, except for a few data taken with a mixed $D_2O-H_2O$ solvent. The phase diagram of $C_8E_4$ in $H_2O$ [6] shows a cloud-point curve with a minimum at 40°C and no liquid crystalline phases above 0°C. The phase diagram of $C_{10}E_4$ in $H_2O$ [4] shows a cloud-point curve with a minimum at about 45°C and liquid crystalline regions in the range of amphiphile volume fractions between 50 and 85% with temperature between 0 and 20°C. We have not studied the phase...
diagrams in \( \text{D}_2\text{O} \) but the available data \([7, 8]\) indicate that the position of the \( L_t - H_t \) boundary in \( \text{D}_2\text{O} \) is similar to that found in \( \text{H}_2\text{O} \). Furthermore, as explained below, the data taken with the mixed solvent indicate that the shape of \( I(k) \) is independent of the \( \text{D}_2\text{O} - \text{H}_2\text{O} \) ratio.

The neutron-scattering measurements were performed at the Institut Laue-Langevin (Grenoble, France) on the D17 instrument. The data were taken at an incident wavelength 1.0 nm (wavelength spread \( \Delta \lambda / \lambda \) of about 10\%) with a detector-to-sample distance of 80 cm. The detector was placed off-axis with respect to the incoming beam in order to span a wider range of scattering angles. The quartz sample cells had a path-length of 1 mm. The cell temperature was controlled by a thermostat to within 0.1\%. Measurements were performed in the range of amphiphile volume fractions \( \Phi = 0.3 - 1 \) at temperatures 25, 27, and 35\(^\circ\)C for \( \text{C}_{10}\text{E}_5 \) solutions and at 27\(^\circ\)C for \( \text{C}_6\text{E}_4 \) solutions. In the case of \( \text{C}_6\text{E}_4 \) at the volume fractions 0.61 and 0.86, we have performed measurements with the mixed solvent \( \text{H}_2\text{O}-\text{D}_2\text{O} \) by varying the weight fraction of \( \text{H}_2\text{O} \) in the range 0–0.85. We have verified that a single-phase isotropic solution was present in all the investigated situations. We have also measured the scattered intensity and the transmission of a reference cell filled with \( \text{H}_2\text{O} \).

All the measured intensities are converted to absolute units \((\text{cm}^{-1})\) by using the formula \([9]\):

\[
I(k) = \frac{I_s(k)/I_H(k)}{(1 - T_H)/(4\pi s T_s)},
\]

where \( I_s(k) \) and \( I_H(k) \) are the intensities scattered, respectively, by the sample and by the \( \text{H}_2\text{O} \) cell; \( s \) is the thickness of the sample cell; and \( T_s \) \((T_H)\) is the transmission of the sample \((\text{H}_2\text{O})\) cell. We have subtracted from \( I(k) \) the background contributions due to the cell itself as well as the incoherent scattering caused by \( \text{H} \) nuclei present in the amphiphile and \( \text{D} \) nuclei present in the solvent. The incoherent contribution was calculated as \( \Phi I_p + (1 - \Phi)I_D \), where \( I_p \) is the intensity scattered by the pure surfactant and \( I_D \) is that scattered by \( \text{D}_2\text{O} \). Both \( I_p \) and \( I_D \) are found to be approximately \( k \)-independent.

Figures 1–3 show the background-subtracted scattered intensity \( I(k) \) at various values of \( \Phi \) for \( \text{C}_{10}\text{E}_5 \) solutions at 35\(^\circ\)C. \( I(k) \) presents a well-defined peak at a value \( k_m \). We see that \( k_m \) grows monotonically as \( \Phi \) increases. In order to check whether the height and position of the peak depends on the distance from mesophase boundaries, we have studied \( \text{C}_{10}\text{E}_5 \) solutions at a lower temperature \((27\,^\circ\text{C})\), which is closer to the mesophase boundaries. The results are very similar to those obtained at 35\(^\circ\)C, with \( k_m \) slightly shifted to larger values. We performed a measurement below the transition temperature with the sample at \( \Phi = 0.68 \): the position of the peak of \( I(k) \) shows very small changes by going from the isotropic to the liquid-crystalline phase.

Fig. 1. Scattered intensity \( I(k) \) vs \( k \) for three different \( \text{C}_{10}\text{E}_5 \) volume fractions: \( \Phi = 0.32 \) (■); 0.46 (●); 0.68 (▲)

Fig. 2. Scattered intensity \( I(k) \) vs \( k \) for two different \( \text{C}_{10}\text{E}_5 \) volume fractions: \( \Phi = 0.63 \) (●); 0.75 (▲)

Fig. 3. Scattered intensity \( I(k) \) vs \( k \) for two different \( \text{C}_{10}\text{E}_5 \) volume fractions: \( \Phi = 0.86 \) (▲); 0.91 (●). The full lines represent the fit with the model developed in [15] for block-copolymer melts.