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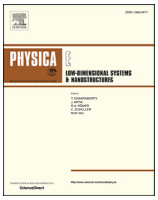

The state equation of aggregation behaviours for Poly(oxyethylene)-Poly(oxypropylene)-Poly(oxyethylene) tri-block copolymers in aqueous solution

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ABSTRACT

In this work, the aggregation equation is developed to describe the aggregation number of copolymer molecules and micellar diameters from experimental data. Based on the regression parameters in the aggregation equation, it is concluded that the PO parts are beneficial to enlarge the micellar size and the EO parts suppress the formation of the micelles. By fitting the parameters with the EO and PO number, the aggregation equation was proposed to predict the aggregation behaviours of tri-block copolymers having EO units between 26 and 212, and with PO number between 30 and 70. By applying the equation to aqueous solution with salt additives, it can be extended to evaluate the impacts of the additives on the micelle formation.

1. Introduction

Since the discovery of MCM-41 and SBA-15 [1,2], controllable soft-template approach has become a powerful methodology to synthesize nano-materials with different morphologies, including nanowires, membranes and particles, in order to fulfil their promising applications in the areas of gas separation, catalysts and sensors [3–7]. Directing-agents for the molecular imprinting can be classified into cationic, anionic, and non-ionic surfactants, where the non-ionic type is available in an abundance of chemical structures and widely used in the industries due to their attractive characteristics, such as low price, non-toxicity and biodegradability [8,9]. Compared with the conventional types of surfactants, the non-ionic amphiphilic block copolymers (and surfactants) could provide larger pore sizes, thicker walls and superior hydrothermal stabilities [3].

Thus there has been extensive research to explore their aggregation behaviours and phase diagrams [10–14] in aqueous solutions, including the critical micellization concentration (CMC) and the critical micellar temperature (CMT), which provides bottom-up instruction for the fabrication of nanoporous materials [15–17]. And modelling method has become a powerful tool to investigate such complex systems [18,19] or conditions [20–22], a wide range of applications related to complicated subjects became tractable. It is known that Poly(oxyethylene)-Poly(oxypropylene)-Poly(oxyethylene) (PEO-PPO-PEO) tri-block co-polymers can behave in many ways like normal hydrocarbon surfactant except some peculiar behaviours in aqueous solution. For the concentration below the CMT, both PEO and PPO blocks are hydrated, where the copolymer molecules remain in the form of unimers, so the material is completely soluble. When the concentration increases to the CMT, the PPO blocks become more hydrophobic as the water molecules are dehydrated. In order to form spherical micelles, the PPO blocks serve as the core (providing large pores) and the PEO blocks would form the shell contacting with water, termed as corona (providing small pores).

As the temperature further increases, more tri-block copolymer molecules are dragged into the micelle, so both PPO and PEO blocks begin to expel water molecules until the PEO blocks become too insoluble and phase separation occurs at the cloud point (CP). It was experimentally demonstrated that a water concentration gradient from the core to the corona generally occurs [23,24]. The possible thermodynamic reason is that the hydrophobicity of PPO is dramatically weakened by the oxygen atoms, as the transfer energy for a PO group from the aqueous medium to the micellar core is in the range of about 0.2–0.3 kT, which is much lower than the value provided for a CH_2 group (1.2 kT) in the hydrocarbon

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surfactant [10]. The behaviours of block copolymers between the CMT and CP can be used as directing-agents to synthesize a large variety of meso-porous materials with different meso-structures including cubic, hexagonal, and lamellar with different pore sizes [25,26].

On the other side, although extensive research has been conducted to investigate the thermodynamic characteristic (phase diagrams) of surfactants and their applications as templates, the relationship between the micellar diameters and the molecular aggregation number in the aqueous (or other solvent) condition has not been established yet. This is critical to fundamentally understand the aggregation behaviours of the surfactants and their applications in the sol-gel process for synthesizing different meso-porous materials. There is no equation of state that could be applicable to predict the impact of additives on the behaviour of surfactants in the aqueous medium. Hereby, the current work aims to explore the relationship between the molecular numbers and micellar hydrodynamic diameters for the PEO-PPO-PEO tri-block copolymers based on the data from literatures [10,24,27–30] by different technologies, including light scattering (LS) and small-angle neutron scattering (SANS). The parameter analysis in proposed equation could also be used to evaluate the impact of small additive (e.g., ions) on the aggregation behaviours of the surfactants.

2. Aggregation equation

Due to the hydrophobic interaction in aqueous medium, surfactants aggregate together and form spherical micelles with the hydrophobic parts in the core and hydrophilic parts in the corona. So the spherical micelle can be analogue to the adsorption of copolymer molecules on the water surface, where the micelle diameter is correlated with molecule numbers, which could be achieved by increasing the temperature (c.f. Fig. 1).

Therefore, the relationship between the molecular number (*n*) and the spherical micelle surface area (*S*) with the diameter (*D*) can be mathematically drawn as follows:

$$S = \pi D^2 \tag{1}$$

$$n = \frac{S}{a_0} \tag{2}$$

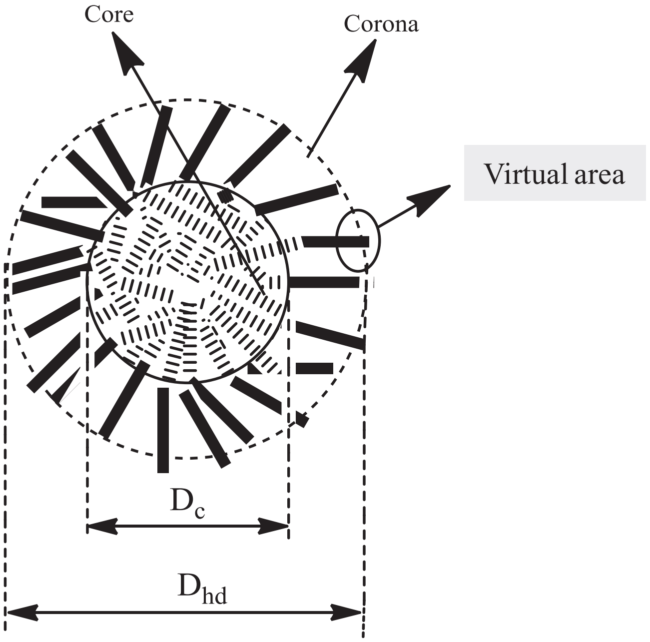

Fig. 1. The schematic drawing of micelle structure and the virtual area occupied by each molecule tail. D_c corresponds to core diameter consisted by hydrophobic parts of the surfactants, D_{hd} is hydrodynamic diameter consisted by hydrophobic and hydrophilic parts.

where a_0 is the virtual occupied area (c.f. Fig. 1) per molecule for the PEO-PPO-PEO copolymers. Based on the above equations, we have:

$$n = \frac{\pi D^2}{a_0} \tag{3}$$

a_0 changes with micelle diameter, number, and temperature as well as the interactions of copolymers with water; thus, a_0 could be expressed as:

$$a_0 = g(T, D, n, k) \tag{4}$$

where *k* is a constant related to the intra-copolymer interaction in the water due to different geometrical orientations. Therefore, smaller *k* represents weaker steric resistance in the micelle, which leads to a higher molecular numbers in the micelle. The copolymer unimer is more dissolvable for smaller value of *k*. Although the tri-block copolymers investigated in this work have similar structural formula, the geometrical orientations of the molecules in the solution are unknown. Therefore the space resistance cannot be deduced only by the size of the molecules.

Virtual area is defined as the area occupied by the hydrophilic part (corona) on the surface of the hydrodynamic micelle, including the cross-section area of the molecule and part of the micelle surface. Since *D*, *n* and *T* are inter-depended with each other within the micelle system, the above Eq. (4) can be changed into the following:

$$a_0 = f(k, D) \tag{5}$$

The boundary conditions are:

$$D = 0(n = 0), a_0 = 0 \tag{6}$$

$$D = D_m(n \to \infty), a_0 = e_0 \tag{7}$$

where D_m is the maximum diameter of the micelle when the aggregation number is infinite, e_0 is the smallest virtual occupied area and identical to the molecular cross section area. Thus, the empirical formula for a_0 could be deduced as:

$$a_0 = k \times D^\alpha \times (\mathrm{Dm} - D)^\beta + D^\alpha \left(\mathrm{Dm} - D + \frac{1}{\mathrm{Dm}^{\alpha/\beta}}\right)^\beta e_0 \tag{8}$$

where α and β are the regression parameters by least minimum square method (LMSM).

The molecular cross-sectional area is far less than the micellar surface area, the maximum cross-section area of the copolymer molecule can be approximately calculated by:

$$d_0 = 2 \times (L_{\mathrm{C-H}} + L_{\mathrm{C-O}}) \tag{9}$$

where d_0 is the theoretical limited cross-section diameter, and $L_{\mathrm{C\text{-}H}}$ is the bond length for carbon and hydrogen atoms (0.107 nm), $L_{\mathrm{C\text{-}O}}$ is the bond length for carbon and oxygen atoms (0.143 nm). The maximum value of d_0 is around 0.50 nm, which is 7 times smaller compared to the smallest experimental micelle diameter (3.4 nm). Thus, the area of the theoretical limited cross-section area will be 49 times smaller compared to the smallest experimental micelle area.

Given the chemical bond can be twisted and flipped, the actual ratio of cross-section area *versus* micelle area is even smaller, so it is reasonable to neglect the cross-section area of the copolymers in the later model derivation. Based on the above arguments and combining Eqs. (3) and (9), it can be derived that:

$$n = \frac{\pi D^2}{k D^\alpha \times (\mathrm{Dm} - D)^\beta} \tag{10}$$

Applying the experimental data, the parameters in Eq. (10) could be obtained. It is rather interesting to find out that, α ≈ 1, β ≈ 1 for the copolymers in the literatures [10,24,27–30] during the regression.

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