



Role of hydration and water coordination in micellization of Pluronic block copolymers

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ARTICLE INFO

Article history:

Received 6 May 2010

Accepted 30 July 2010

Available online 4 August 2010

Keywords:

Pluronics
Raman
ATR FTIR
Water coordination

ABSTRACT

Raman, attenuated total reflectance FTIR, near-infrared spectroscopy, and DFT calculations have been used in a study of aqueous solutions of three tri-block copolymers poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) or PEO-PPO-PEO with commercial names Pluronic PE6200, PE6400 and F68. It is shown that the process of micellization as a response to increased temperature is reflected in the hydroxyl stretching region of infrared and Raman spectra, which contains information both about restructuring of water and changes of polymer chains in polymer/water aggregates. Raman spectra exhibit differences between individual Pluronics even at temperatures below the critical micellization temperature (CMT). According to the attenuated total reflection (ATR) FTIR spectra, the same five water coordination types defined by the number of donated/accepted hydrogen bonds are present in interacting water as in bulk water. It indicates that models considering mixed states of water with different hydrogen bonding environments provide appropriate descriptions of bound water both below and above the CMT. Above the CMT, aggregate hydration increases in the order PE6400 < PE6200 < F68, although that does not fully correspond to the EO/PO ratio, and points to the differences in microstructure of aggregates formed by each copolymer. This study relates nanoscale phenomena (hydrophobic and hydrophilic hydration) with the mesoscale phenomenon of micellization.

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1. Introduction

In self-organizing polymers, the structure of polymer networks, their conformation and macroscopic properties are decided not only by solvent-solvent and polymer-polymer interactions, but also by polymer-solvent interactions [1]. Self-organizing effects at different scales are most likely correlated: gelation of tri-block copolymers (a macroscale effect) is thought to be linked to micellization (a mesoscale effect) and to nanoscale effects (e.g. conformation) [2,3]. Polymer-water interactions and water structure play an important role in kinetics and mechanism of loading of therapeutics and their release in hydrogels [4,5]; mechanical properties of a polymer may change if a small amount of water is adsorbed to it [6]. These interactions may significantly depend on temperature and concentration [7].

Pluronics, tri-block copolymers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), PEO-PPO-PEO, are non-ionic macromolecular surfactants widely used in industry, pharmacy, bioprocessing and separation [8]. At low temperatures and/or concentrations, they exist as unimers in solution, upon increasing the temperature and/or concentration they form micelles [9] and lyotropic liquid crystalline phases. Various tech-

niques were employed to investigate the micellar solutions. It was concluded that micelle formation was driven by the hydrophobic effect and was accompanied by dehydration of the propylene oxide (PO) groups, which form the core of the micelles; the corona of the micelles consists of the still hydrated ethylene oxide (EO) groups. Aggregation and the phase behavior of Pluronics were described by Wanka et al. [10].

There are indications, that properties of water confined to small spaces or interacting with other substances are modified [11–14]. Water interacts with the polymer via van der Waals, hydrogen bonding interactions and hydrophobic hydration [15–18]. In the case of hydrophilic hydration electrostatic solute-water interaction can induce radial orientation of the surrounding water molecules [18,19].

Vibrational (infrared and Raman) spectroscopy is a useful technique for study of the effects of the local environment since the O-H stretching vibrations are correlated to the overall structure of water [20–25]. Water molecules in bulk water as well as in interacting water can display various hydrogen bonding interactions and orientations [26] that can result in several coordination types of water molecules (Fig. 1). Czarnik-Matuszewicz et al. [27] found three spectral components and correlated them with three different configurations of the OH groups: (1) the free OH group at 3580 cm⁻¹; (2) vibration of asymmetrically bonded OH groups with one strong and one broken donor H-bond at 3420 cm⁻¹ and

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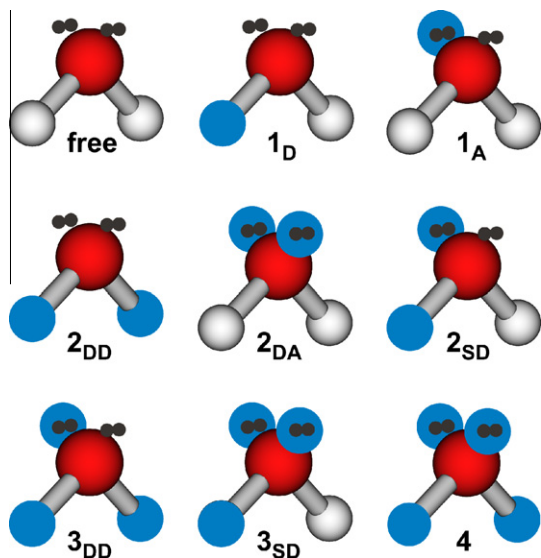


Fig. 1. Coordination properties of water. Blue color indicates a hydrogen atom or an electron pair involved in hydrogen bonding to other molecules, a digit indicates the degree of coordination, the capital letters indicate the following: A – hydrogen acceptor, D – hydrogen donor, SD – single donor, DD – double donor, DA – double acceptor. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(3) tetrahedrally coordinated OH at 3230 cm^{-1} . Lenz and Ojamäe [28] computed infrared spectra for the O–H stretching vibration region of finite water clusters and fitted spectra of liquid water. They found that there were five coordination types present in the liquid water represented by the five distinct vibrational bands: (1) the free water molecules at about 3700 cm^{-1} , (2) the 3_{DD} type around 3550 cm^{-1} , (3) the 4-coordinated type around 3400 cm^{-1} , (4) the 2_{SD} type around 3330 cm^{-1} and (5) the 3_{SD} type around 3200 cm^{-1} . The symmetric stretching vibration of the same five coordination types were identified in a Raman spectrum of water at 290 K and 0.1 MPa pressure by Sun [29].

Verma et al. [14] studied two Pluronics, F88 ($\text{EO}_{103}\text{-PO}_{39}\text{-EO}_{103}$) and P123 ($\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$), by fluorescence measurements. They showed that solvation and rotational relaxation processes were faster in the F88 micelle and their results also indicated the presence of interconversion between water hydrogen bonded to the polymer and water mechanically entrapped in the micellar region. Carageorghopol and Schlick [30] investigated solutions of two Pluronics, L64 ($\text{EO}_{13}\text{-PO}_{30}\text{-EO}_{13}$) and L62 ($\text{EO}_6\text{-PO}_{34}\text{-EO}_6$), by electron spin resonance spectroscopy. They established that a hydration gradient existed along the EO segments in the different phases, including the micellar phase, in both L64 and L62. Raman spectroscopy was applied by Sekine and Ikeda-Fukazawa [31] to poly-*N,N*-dimethylacrylamide (PDMAA) hydrogel to study the effect of dehydration on the structure of water and the polymer network. Vibrational modes of the polymer and the O–H stretching vibration of water responded to dehydration by frequency shifts.

In this study, Raman spectroscopy, attenuated total reflectance Fourier transform infra-red (ATR FTIR) spectroscopy, NIR spectroscopy, and density functional theory (DFT) calculations have been used to investigate evolution of O–H stretching vibration of water in aqueous solutions of Pluronics with temperature. Polymer–water interactions of three Pluronic macromolecules have been characterized, each macromolecule with the same length of the more hydrophobic PPO block (31 PO units) but varying lengths of the hydrophilic PEO block: PE6200 ($\text{EO}_5\text{-PO}_{31}\text{-EO}_5$), PE6400 ($\text{EO}_{14}\text{-PO}_{31}\text{-EO}_{14}$) and F68 ($\text{EO}_{81}\text{-PO}_{31}\text{-EO}_{81}$). Interaction of water with Pluronic macromolecules is viewed as a sum of the interac-

tions of water with individual subunits (EO or PO), each subunit is considered separately and its hydration is viewed as a small solute hydration [1]. It is also proposed that conceptions based on the mixture models are more appropriate than continuous models for description of water interacting with or bound to polymer [21–25]. Our results do not indicate whether mixture or continuous models are more suitable for the liquid state of pure bulk water.

2. Materials and methods

2.1. Sample preparation

Solutions of Pluronics (obtained as a gift from the BASF company) in water were prepared with concentration of 10 wt.%. Water used was the type LCMS CHROMASOLV produced by Riedel-de-Haen.

2.2. Vibrational spectroscopy

ATR FTIR spectra were collected on a Nicolet Nexus 870 FTIR spectrometer purged with dry air and equipped with a cooled mercury-cadmium-telluride (MCT) detector, KBr beam splitter and horizontal micro-ATR Golden Gate unit (SPECAC). The ATR accessory had a controlled heated top plate and a diamond prism. Before spectral subtraction spectra were processed in the following way: subtraction of the spectrum of empty diamond crystal with water vapor, baseline correction, advanced ATR correction using OMNIC™ software version 7.1a or 8 that include correction for the wavelength-dependent penetration depth and for the absolute shift in band position [32], and baseline correction again. NIR spectra were also collected on a Nicolet Nexus 870 FTIR spectrometer purged with dry air and equipped with a deuterated triglycine sulphate (DTGS) detector and CaF_2 beam splitter. The sample was placed into a home-built temperature cell cooled with water. Ambient-pressure Raman spectra at various temperatures were obtained on a Renishaw In-via Raman micro-spectrometer with Ar^+ ion laser with excitation line at 514.5 nm.

2.3. Data processing

All spectra were processed with OMNIC™ software. At given temperature, vibrational spectra of pure water were subtracted from spectra of Pluronic/water solutions. At no temperature was it possible to achieve complete subtraction of the OH stretching vibration fundamental or overtone band down to the underlying baseline. A maximal subtraction factor was chosen, so that no negative peaks occurred in the O–H bond stretching region between 2800 cm^{-1} and 3750 cm^{-1} (Raman and ATR FTIR) and between 6000 and 7000 cm^{-1} (NIR). Such visualization of the spectral changes – i.e. the incomplete subtraction of a reference spectrum, which yielded a positive difference curve in the region of interest, was used successfully by Kristiansson et al. [33] and by Stangret and co-workers [34–37]. The spectra after the subtraction of a reference water spectrum are described as difference spectra in the following text.

2.4. Quantum chemical calculations

The model calculations were carried out at the density functional theory (DFT) level with the B3LYP functional and the 6-31G(d) and 6-31+G(d,p) basis sets employing the Gaussian 03 program package [38]. In order to verify the reliability of the presented DFT calculations, selected stable structures were re-optimized at the Møller-Plesset (MP2) levels of theory and it was found that the optimized geometries did not differ significantly from the

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