



Solubilization of lignin in copolymer micelles in aqueous solution



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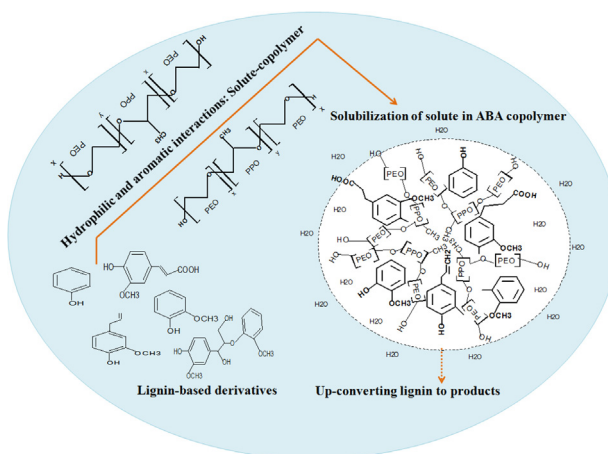
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HIGHLIGHTS

- A block copolymer, Pluronic® F-68, was used to solubilize lignin in aqueous solution.
- The solubilization resulted in upfield chemical shifts of blocks proton resonances.
- The significant chemical shifts showed lignin is incorporated into copolymer micelles.
- Lignin aliphatic oxygenated functional groups manipulate micelle-lignin aggregate structure.
- Aromatic/conjugated groups manipulate micelle-lignin aggregate structure.

GRAPHICAL ABSTRACT



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ABSTRACT

The solubilization of lignin in self-aggregating triblock amphiphilic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) in aqueous solution has been studied utilizing liquid-state proton nuclear magnetic resonance spectroscopy (¹H NMR) and diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY NMR). Our hypothesis for copolymer micelle incorporation of lignin species includes a “hydrophilic-aromatic interaction model”, in which lignin derivatives with amphiphilic characteristics, known to be abundant in the effluent from pulp mill and pretreatment of various lignocellulosic materials, have an affinity for these micelles, and tend to form relatively organized structures within them. Here we show how the chemical/structural features of lignin units and small molecule lignin models determine their solubilization behavior in the micelles. It was found that a buildup of concentration series of lignin and lignin-based model compounds guaiacol, eugenol, phenol, guaiacylglycerol-beta-guaiacyl ether, ferulic acid in Pluronic® F68-deuterium oxide solution results in significant upfield chemical shifts of PEO-(CH₂-CH₂) and PPO-(CH₂) proton resonances, and at a critical guest concentration (CGC), dramatic upfield shifts due to gross structural transitions in the micelles. We present evidence that copolymer micelle-lignin interactions depend on both chemical functional group characteristics of solute (i.e., polarity, H-bonding ability) and π-π interactions between aromatic/conjugated groups. Our results demonstrate how the loci of incorporated solute in the block copolymer micelles are affected by these features.

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1. Introduction

Block copolymers comprise more than one type of block. Usually, the properties of the blocks within the copolymer are quite different from one another and this results in spontaneous self assembly in aqueous solution [1]. One of the key determinants of block copolymers, hydrophilic-lipophilic balance (HLB), predicts the formation of aggregates at the critical micelle concentration (CMC) in aqueous media. Such aggregates or micelles may have spherical, cylindrical, rod-shaped or lamellar shapes [2]. In polar solvents such as water, the hydrophobic blocks are incorporated in the core and the hydrophilic blocks, along with water, form the shell. Due to the polarity gradient present in micelles, the aggregates are able to accommodate hydrophobic substances and thus enhance the solubility of these materials, which are normally relatively insoluble substances in aqueous solutions [3,4].

Solubilization phenomena in aqueous and nonaqueous solutions of conventional low molecular weight surfactants have been extensively investigated theoretically [1,5] and experimentally [6,7]. However, block copolymers have shown remarkable potential compared to conventional low molecular weight surfactants because of their micellization ability in a variety of solvents [8]. Block copolymers are utilized in diverse applications, such as delivery of drugs, as scavengers for pollutants, as chemical extraction aids in separation processes, and for micellar catalysis [9–11]. Block copolymer architecture (ABA, BAB, ABC, AB, BA), hydrophobic-lipophilic balance (HLB), and discrete block molecular weights can significantly influence their solubilization capacity [12]. Many low molecular weight solubilizates (guest/solute), including aromatic solvents benzene, toluene, naphthalene, pyrene, and anthracene, have been investigated in block copolymers [7,13]. To harness the benefit of block copolymer solubilization phenomena, it is necessary to understand how the extent of solubilization can be affected by the structural properties of the solubilize and the block copolymer.

Hydrophobic and hydrophilic interactions between the solubilize and the blocks that form the core and shell of micelles control the scope of solubilization. For instance, the solubilization of galates in polymeric micelles has been studied by Heins et al. [14]. Using electron spin resonance spectroscopy (ESR) and nuclear magnetic resonance spectroscopy (NMR), the authors reported that the locations of antioxidant gallates in micelles are dependent on their hydrophobicity. Also, aromatic molecules were found to be solubilized preferentially compared to aliphatic hydrocarbons in A-B-A type block copolymers [5]. Furthermore, experimental results for hydrocarbon solutes in polyethylene oxide (PEO)-polypropylene oxide (PPO) block copolymers demonstrated large solubilization capacities and high selectivity for aromatic over aliphatic solutes in block copolymer micelles, compared to conventional low molecular weight surfactant micelles [13]. The molecular volume of the solutes can also influence the amount of solubilization in micelles. It has been observed that solutes with larger size are solubilized in smaller number [15]. However, given identical molecular volumes, the polarity of the compounds controls the selectivity of solubilization [7,16]. It was noted that the solubility of benzene in polar and non-polar blocks of PEO/PPO was significantly larger compared to *n*-hexane in the entire composition of the block copolymer [7]. Lignin, with its combination of aromatic and aliphatic hydrocarbons, having polar functional groups, aliphatic bridges and a variety of oxygenated moieties, can show a unique solubilization pattern in aqueous dispersions of block copolymer micelles. Lignin is often described as a random polymer of three mono-lignols, *p*-coumaryl (H), coniferyl (guiacyl, G) and sinapyl (S) alcohols [17].

In this study, lignin is obtained from black effluent produced by the sequential ozone and soaking aqueous ammonia pretreatment of wheat straw, and was previously characterized as

partially-depolymerized fragments of H-G-S with S/G ratio of 0.35 and average molecular weight of 750 (g/mol) [18]. Lignin is partially decomposed during pretreatment (Scheme 1a), and removed from the biomass composition as smaller, soluble fragments through the use of a water washing process which produces a black effluent (Scheme 1b1) [18]. To date, the main lignin utilization pathway has been to concentrate the black effluent by evaporation and burn the residual sludgy lignin to supply energy to the pulping plant and biorefinery. Increasingly, however, lignin is being considered as a renewable source of value-added aromatic compounds and fuels [19,20]. Significant economic barriers to use of this feedstock arise from the cost of chemical plant equipment needed for various chemical processing steps, and also the cost of chemicals, particularly solvents. Considering the amphiphilic character of lignin (Scheme 1b2), we propose to use the solubilization ability of a commercially available non-ionic, amphiphilic tri-block copolymer, polyethylene oxide- polypropylene oxide- polyethylene oxide (under the trade name of Pluronic® F-68) (Scheme 1c1) toward lignin derivatives to concentrate lignin in the aqueous environment of pulping and pretreatment effluents, greatly reducing costs, and opening possibilities for selective chemistries [21]. Also, five phenolic aromatic model compounds, phenol, eugenol, guaiacol, ferulic acid and guaiacylglycerol-*beta*-guaiacyl ether (dimer) are employed in order to assist us in studying the solubilization behavior of lignin in micellar system. The uses of block copolymers (i.e., Pluronic® F-68) in solubilizing aromatic and aliphatic molecules in various applications were reported previously; however, the solubilization of lignin in the block copolymer has not yet been studied.

In the present work, we have studied the solubilization behaviors and interactions of lignin and model compounds with Pluronic® F-68 in aqueous ammonia solutions (black effluent) using nuclear magnetic resonance spectroscopy (NMR) and diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY-NMR).

Nuclear magnetic resonance spectroscopy (NMR) has been used extensively to characterize the structure, reactions and degradation processes of woody biomass [22]. Most lignin analyses by NMR are done by dissolving lignin from a particular source, treated or untreated, in deuterated dimethyl sulfoxide (d_6 -DMSO) and performing a suite of experiments, including 1D ^1H and ^{13}C NMR experiments, 2-D correlation experiments, particularly HMQC, HSQC and HMBC, and/or by solid state NMR of extracted and dried lignin samples [23]. Lignin's low solubility in most solvents has been a major hindrance in the structural characterization of lignin polymers. Furthermore, the randomly composed structure of lignin from its three major sub-unit classes (S, G and H subunits) provides no regular structure that can be fully characterized by any method. Much effort has been made to refine NMR methods of structural analysis for lignins as a class of compounds because of the great interest in these natural substances by plant biochemists, agronomists, materials scientists, lignin producers, end users for various lignin-derived products, and the sustainable biofuels industry [24]. We have used these methods extensively to investigate lignin structure and pathways of decomposition and reformation for many avenues of lignin modification, including processes of nature [25], e.g. degradation of wheat straw by *Phanerochaete chrysosporium* [26] and hardwood lignin by the Western Poplar Clearwing Borer, *Paranthrene robiniae* (Hy. Edwards), [27] as well as lignin digestion in every digestive organ of termites, [28,29] and more recently, chemical processes, such as heterogeneous catalytic hydrodeoxygenation of biomass-derived lignin to aromatic hydrocarbons, [30] aqueous ammonia pretreatment of wheat straw, [31] and physical processes including pyrolysis of corn stover [32] and water-only flow-through pretreatment of *Miscanthus* [33].

The knowledge obtained on the solubilization of the lignin in the copolymer micelle will aid to establish processes to convert the lignin into value-added products such as the antioxidant guaiacol,

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