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Adsorption of cellulose derivatives on flat gold surfaces and on spherical gold particles

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ABSTRACT

The adsorption of hydroxyethylcellulose (HEC), ethyl(hydroxyethyl)cellulose (EHEC), and their hydrophobically modified counterparts HM-HEC and HM-EHEC has been studied on planar gold and citrate-covered gold surfaces by means of quartz crystal microbalance with dissipation monitoring (QCM-D), and on citrate-covered gold particles with the aid of dynamic light scattering (DLS). The QCM-D results indicate that larger amounts of polymer are adsorbed from aqueous solutions of HM-HEC and HM-EHEC on both substrates than from solutions of their unmodified analogues. The adsorption affinity for all the polymers, except EHEC, is higher on the citrate-covered surfaces than on the bare gold substrate. This indicates that more adsorption sites are activated in the presence of the citrate layer. The experimental adsorption data for all the polymers can be described fairly well by the Langmuir adsorption isotherm. However, at very low polymer concentrations significant deviations from the model are observed. The value of the hydrodynamic thickness of the adsorbed polymer layer (δ_h), determined from DLS, rises with increasing polymer concentration for all the cellulose derivatives; a Langmuir type of isotherm can be used to roughly describe the adsorption behavior. Because of good solvent conditions for HEC the chains extend far out in the bulk at higher concentrations and the value of δ_h is much higher than that of HM-HEC. The adsorption of EHEC and HM-EHEC onto gold particles discloses that the values of δ_h are considerably higher for the hydrophobically modified cellulose derivative, and this finding is compatible with the trend in layer thickness estimated from the QCM-D measurements.

1. Introduction

The adsorption of polymers on solid surfaces is very important for practical purposes in different technological fields such as stabilization of colloidal dispersions, chromatography, development of biocompatible materials, and microelectronics. In materials sciences, it is used to control surface properties such as wetting, hardness, or resistance to aggressive environments.

Depending on the application, two different approaches can be envisaged: either polymer grafting onto the surface by covalent bonds [1] or spontaneous physical adsorption [2]. The latter phenomenon is simpler to implement to implement, because no specific reaction sites are needed. However, the adsorbed polymer layer is easier to remove than a covalently bonded surface, and the adsorption approach puts constraints on the chemical nature and architecture of the polymers, which can be difficult to fulfill.

Chemically dissimilar polymers usually have different affinities for a surface, which leads to preferential adsorption of the polymer with the highest segmental adsorption energy [3–5]. Polymer adsorption can be affected by many parameters such as the solvent power, charge density [6], molecular weight [7], conformation of the chains [3,4,8,9], and hydrophobicity of the polymer [10]. For highly charged polyelectrolytes the repulsion between the segments dominates the adsorption behavior [6]. Adsorption preference with respect to molecular weight occurs when macromolecules that differ only in chain length are adsorbed [7]. The conformation of chains at an interface can also have an impact on the adsorption characteristics of the surface [3,4,8,9]. In this work, we have focused on the effect of polymer hydrophobicity on the adsorption of polymer on flat gold or citrate-covered gold surfaces, and binding of polymer onto citrate-covered gold particles. To elucidate the effect of hydrophobicity on the adsorption features, non-ionic cellulose ethers and their hydrophobic modified analogues have been employed in this study.

Non-ionic cellulose derivatives are of substantial industrial interest as they have found applications as stabilizers in colloidal dispersions [10], additives for improving rheological properties in aqueous solutions [11], as potential drug delivery devices [12–14], and in other areas [15]. An interesting category of amphiphilic

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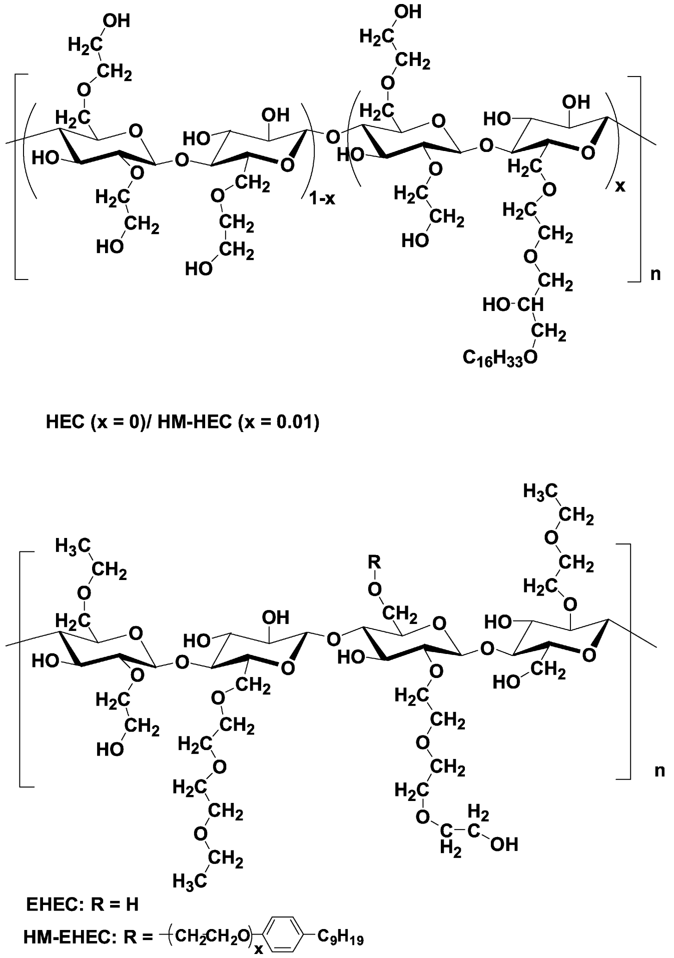

Fig. 1. Schematic illustration of the chemical structures of HEC, HM-HEC, EHEC, and HM-EHEC.

polymer systems are those that undergo phase transitions in response to external stimuli such as temperature and pH [16], wherein, for example, their solubility decreases as an effect of increased temperature, causing macroscopic phase separation at sufficiently high temperatures [17]. Thermoresponsive polymers such as ethyl(hydroxyethyl)cellulose (EHEC) have been widely investigated for drug delivery purposes, separations, and diagnostics applications [16]. Moreover, by modifying this type of polymer so that its hydrophobicity is enhanced, an increase in viscosity can be observed [18,19] as a result of more intense intermolecular associations. Hydroxyethylcellulose (HEC), on the other hand, is essentially a hydrophilic polymer and this cellulose derivative displays rather weak thermoresponsive properties. It has been established in previous papers that a large amount of EHEC is adsorbed onto polystyrene latex particles [20–22]. If we take into account that the EHEC polymer contains hydrophobic microdomains in addition to regions of hydrophilic nature, one would expect the adsorption behavior to be altered when surfaces of different hydrophobicity are employed and the polymer is exposed to further hydrophobic modification. The EHEC polymer involved in this study was modified by grafting branched nonylphenol groups onto the polymer backbone in a ratio of 1.7 mol%, thus producing a hydrophobically modified ethyl(hydroxyethyl)cellulose (HM-EHEC) that still is water-soluble [23]. In addition to these polymers, the hydrophilic hydroxyethylcellulose (HEC) and its hydrophobic analogue (HM-HEC), modified with glycidyl hexadecyl ether, have been studied. The chemical structures of all studied polymers are displayed in Fig. 1.

Earlier studies [24–28] on the adsorption of cellulose derivatives by means of ellipsometry and surface force experiments show that both the adsorbed amount and the conformation of the adsorbed polymers are sensitive to temperature changes and hydrophobicity of the surface. In both case it was found that hydrophobic interactions between the polymer and the surface constitute the main driving force for adsorption. One of the major drawbacks of ellipsometry and surface force techniques is that ellipsometry does not give detailed information about the conformation of the adsorbed polymers and the surface force method does not provide the adsorbed amount of polymer. One of the major drawbacks of ellipsometry and surface forcetechniques, is that ellipsometry does not give detailed information on the conformation of the adsorbed polymers and surface force does not give adsorb amount.

In this investigation, the quartz crystal microbalance technique with dissipation monitoring (QCM-D) technique has been employed in order to obtain additional information about the adsorption properties of cellulose derivatives at hydrophobic surfaces and the effect of polymer concentration. In the studies mentioned above, changing the temperature altered the hydrophobicity of the systems, whereas in the present work a more straightforward approach is employed where the effect of hydrophobicity is disclosed by comparing the adsorption features of cellulose derivatives and their hydrophobically modified counterparts.

The adsorption characteristics of HEC, HM-HEC, EHEC, and HM-EHEC on flat gold and citrate-covered gold surfaces have been monitored with the aid of the quartz crystal microbalance with dissipation monitoring (QCM-D) technique. In addition, dynamic light scattering (DLS) was utilized to probe the hydrodynamic layer thickness of adsorbed cellulose derivatives on citrate-covered gold nanoparticles (GNP). Analyses performed with QCM-D provide an excellent tool for in situ studies of molecular adsorption at solid planar surfaces. Available information about systems subjected to this type of analyses includes reversibility of adsorption, adsorption kinetics and surface coverage, as well as layer structure/conformation information, all within the same simple experimental setup [29]. DLS is a well-established technique to monitor the hydrodynamic thickness of the adsorbed polymer layer onto nanoparticles in solution [30]. The spatial extension of an adsorbed layer can be determined by DLS via the hydrodynamic radius of particles with and without the adsorbed layer. DLS is routinely used to characterize layer thickness, with a noticeable sensitivity to long tails due to their influence on hydrodynamics. Adsorption protocols applied in this study involved aqueous solutions of HEC, HM-HEC, EHEC and HM-EHEC on gold-coated quartz crystals, citrate-buffered solutions of the above-mentioned polymers onto flat gold surfaces and on GNP. The aim of this work is to elucidate the effects of polymer structure and hydrophobicity on the adsorption features on planar and curved surfaces.

2. Materials and methods

2.1. Materials

In the present work, a HEC sample with the commercial name Natrosol 250 GR (Lot. No. A-0382) acquired from Hercules, Aqualon Division, was used as the hydrophilic polymer and served as the precursor for the synthesis of the hydrophobically modified analogue (HM-HEC). The degree of substitution of hydroxyethyl groups per repeating anhydroglucose unit for HEC was 2.5 (given by the manufacturer), and the weight-average molecular weight was determined to be $M_w = 400{,}000$ by intensity light scattering [31]. The hydrophobically modified analogue was synthesized according to a standard procedure [32], and the fine points of the synthesis as well as the details of the characterization of this sample