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Mechanisms of flocculation with poly(ethylene oxide) and novel cofactors

Roger Gaudreault[a,b,c], Theo G.M. van de Ven[a,b,*], M.A. Whitehead[a]

[a] Department of Chemistry, McGill University, 801 Sherbrooke Street W, Montreal, Que., Canada H3A 2K6
[b] Pulp & Paper Research Centre, McGill University, 3420 University Street, Montreal, Que., Canada H3A 2A7
[c] Cascades Inc., Recherche et Développement, 471 Marie-Victorin Boul., Kingsey Falls, Que., Canada J0A 1B0

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Abstract

Poly(ethylene oxide), a widely used flocculation agent, has its efficiency enhanced by various compounds known as cofactors. The cofactors are known to form an association complex with poly(ethylene oxide) (PEO). The mechanism of interaction of non-ionic poly(ethylene oxide) with the model cofactors tannic acid (TA), corilagin, polystyrene sulfonated sodium salt (PSS-Na) and folic acid (FA), was studied using photometric dispersion analysis (PDA). PEO–corilagin interactions were studied by isothermal titration calorimetry (ITC) and liquid state proton nuclear magnetic resonance (^{1}H NMR). The stability ratios clearly show that TA, corilagin, PSS-Na, FA, PEO, as well as PEO/cofactors, do not flocculate microcrystalline cellulose (MCC) in the absence of salt. Isothermal titration calorimetry shows that PEO and corilagin do not associate at 30 °C in the absence of salt, in agreement with the PDA experiments. The ^{1}H NMR results show no association between PEO and corilagin at room temperature in the absence of salt. The ITC and NMR results agree with gas phase PM3 Semi-Empirical Molecular Orbital Theory calculations which show that PEO/corilagin complexes do not form at room temperature in the absence of salt, because the entropy loss is larger than the enthalpy gain. These findings are surprising, because the complexation of PEO with cofactors is well-documented. The association between PEO and corilagin in the presence of salt (KCl) has been confirmed by ^{1}H NMR. Consequently, salt is needed to induce MCC flocculation. It was found that there are two types of cofactors: those which cluster PEO in solution (clustering cofactors) and those which do not (non-clustering cofactors). The PEO/TA system flocculates MCC nearly instantaneously by the following mechanism: PEO/cofactor association, followed by PEO-clustering, adsorption and bridging. For the non-clustering cofactors, an induction time was clearly observed, and a new mechanism is proposed to explain their flocculation behaviour: surface-induced clustering coupled to association-induced polymer bridging.

Keywords: Clustering; Poly(ethylene oxide) (PEO); Microcrystalline cellulose (MCC); Cofactor; Mechanism of flocculation; Fibre fines; Papermaking

1. Introduction

For environmental and energy saving reasons, the paper industry has drastically reduced its water consumption over the last two decades. Unfortunately, this has led to an increase in dissolved and colloidal substances in process waters, which interfere with the fibre flocculation ability of cationic flocculants. A flocculating agent, which is more effective than charged polymers in highly contaminated closed systems, is the poly(ethylene oxide) (PEO)–cofactor retention aid system. High molecular weight PEO is produced in large quantities and mainly used for flocculation in pulp and paper, mining, water purification and for drag reduction. The formation of a complex between the high molecular weight PEO and cofactor, which is considered necessary to flocculate cellulose fibres, fines and fillers, and to aid retention and drainage, has been described by different mechanisms. These are: polymer network formation [1], complex bridging [2], association-induced polymer bridging and asymmetric polymer bridging [3,4] and temperature-induced flocculation [5]. Recently, using PEO and tyrosine containing water-soluble polypeptide (TCP), Lu [6] extended the complex bridging [2] mechanism, by considering TCP deactivation and PEO

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* Corresponding author. Tel.: +1 514 398 6177; fax: +1 514 398 6256.
E-mail address: theo.vandeven@mcgill.ca (T.G.M. van de Ven).

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saturation. van de Ven and co-workers [7–12] performed extensive research to understand fines flocculation and deposition, induced by PEO–cofactor interactions. These findings are summarized in a recent review [13], which shows association-induced bridging to be the dominant flocculation mechanism. However, many questions remain, especially about the nature of the PEO/cofactor association.

Molecular Mechanics [14,15] has been used to study the PEO/cofactor hydrogen bond (R–OH···O) interactions between the phenolic hydroxyl group and the PEO ether oxygen. Interactions between poly(vinyl phenol) (PVPh) and PEO were studied by Zhang et al. [16] with ^{13}C solid-state nuclear magnetic resonance (NMR). For the water-soluble ionic cofactor poly(vinyl phenol-co-potassium styrene sulfonate) (PVPh-co-KSS)/PEO complex ^{1}H NMR data show hydrogen bonding and other interactions [17]. Poly(sodium naphthalene sulfonate) (SNS), a known commercial cofactor [9], does not have hydroxyl groups, which excludes hydrogen bonding. Goto et al. [18] speculated that the surface charge of the cofactor and the density of phenolic hydroxyl groups in a given cofactor were important to flocculate colloids. Lu et al. [6,19] found that water-soluble polypeptides with high contents of tyrosine (phenolic moieties), form complexes with high molecular weight PEO in 0.01 M Tris buffer and 1 mM $CaCl_2$. Lu et al. [19] emphasized the importance of the phenolic group in polypeptide/PEO complex formation. The minimum molecular weight of 1:1 poly(tyrosine-glutamic acid), required to bind to a high molecular weight PEO in the presence of salt, is between 1.1 and 36 kDa [19].

Molecular Mechanics and PM3 Semi-Empirical Molecular Orbital Theory have been used to study the cofactors used in papermaking [20]. Recently, these methods were applied to the complexation of the PEO with these cofactors, and showed that PEO/cofactor complexes do not form at room temperature [21].

In this paper, this prediction is verified. The presence of salt is needed to cause the complexation and the flocculation of particles.

Microcrystalline cellulose (MCC) particles, which have been used previously in papermaking studies [1,22–26], were used as a model for fibre fines. For cofactors, corilagin (β-1-*O*-galloyl-3,6-(*R*)-hexahydroxydiphenoyl-D-glucose) [20,27] and tannic acid (TA) [27], which both contain phenolic OH (Fig. 1), were used as models. The phenolic OH groups are characteristic of some of the papermaking phenolic cofactors. Corilagin has been experimentally [28–30] and theoretically [20,21] studied. The molecular structure of TA, was reported by Covington [31] and Verzele et al. [32]. Two other model cofactors, polystyrene sulfonated sodium salt (PSS-Na) [33,34] and folic acid (FA) [35], which do not have phenolic hydroxyl groups (Fig. 1), were also tried as potential PEO cofactors. Interestingly, folic acid was reported as a free radical scavenger [36], and is currently used to control filamentous bulking in over 100 municipal and industrial wastewater plants in Europe and United States [37]. The common characteristics of all these model cofactors are that they have aromatic rings and are negatively charged. The molecular structure of corilagin in Fig. 1c does not show a charge, but streaming potential experiment showed it to be negative, indicating that, like TA, some molecules probably carry carboxylic groups, which are partially dissociated or possibly coming from the impurities. The concentration of these groups was too low to be detected by ^{13}C NMR. It is also possible that some phenolic groups are deprotonated.

In this work, photometric dispersion analysis (PDA), isothermal titration calorimetry (ITC) and nuclear magnetic resonance spectroscopy (^{1}H NMR) are used to study the interactions in the PEO/cofactor complexes and PEO/cofactors with MCC. Corilagin and folic acid are studied experimentally, for the first time, as PEO cofactors for fibre fines flocculation.

2. Methods

2.1. Materials

2.1.1. Corilagin

Corilagin (β-1-*O*-galloyl-3,6-(*R*)-hexahydroxydiphenoyl-D-glucose), with molecular formula $C_{27}H_{22}O_{18}$ and molecular weight of 634.08 g mol^{-1}, was obtained from Aapin Chemicals Limited (UK). The material, C.A.S. 23094-69-1, is natural in origin, with purity 95%. The pH of a 5 ppm corilagin solution is 5.0.

2.1.2. Tannic acid

Tannic acid with molecular formula $C_{76}H_{52}O_{46}$ and molecular weight of 1701.18 g mol^{-1} was obtained from Fisher. The material, C.A.S. 1401-55-4, contained 0.0007% heavy metal (as Pb) and 5.8% water. Two TA solutions were prepared: 50 and 500 ppm having a pH of 3.7 and 3.1, respectively.

2.1.3. Polystyrene sulfonated sodium salt

Certified grades of polystyrene sulfonated sodium salt, with weight-average molecular weights M_w = 17,500 g mol^{-1} (Cat No. 16250, Lot No. 423820) and 35,000 g mol^{-1} (Cat No. 16251, Lot No. 414063) were used, and the ratio of weight-average to the number-average molecular weight was $M_w/M_n = 1.10$. The samples were provided by Polysciences Inc., Warrington, PA, USA. The pH of a 500 ppm PSS-Na solution is 3.8. According to the supplier, the degree of sulfonation is 100%.

2.1.4. Folic acid

Powder grade folic acid (pteroylglutamic acid), prepared by Takeda Chemical Industries Ltd., Osaka, Japan, was provided by Brentag Canada Inc., Lachine, Que., Canada. The molecular formula of folic acid is $C_{19}H_{19}N_7O_6$ and its molecular weight is 441.40 g mol^{-1}. The pH of a 500 ppm FA solution is 4.5.