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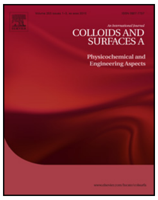

Complexation of polymeric stabilisers in solution and at the silica nanoparticle interface

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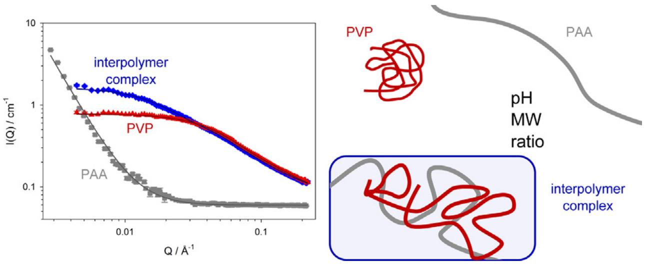
HIGHLIGHTS

- Interpolymer complexes of PVP and NaPA are observed under basic conditions.
- Complexation is observed both in solution and at the surface of silica nanoparticles.
- Addition of NaPA to dispersed silica nanoparticles destabilises the system.
- NaPA removes adsorbed PVP from silica nanoparticles making them colloidally unstable.
- No interpolymer complexation is seen for low molecular weight polymers.

GRAPHICAL ABSTRACT



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ABSTRACT

The weak polyelectrolyte sodium polyacrylate, NaPA, and the neutral poly(vinyl pyrrolidone), PVP, were combined and the effects of complexation both in solution and at the nanoparticle interface were studied under basic pH conditions. Using a combination of SANS and PCS, we demonstrate that attractive interpolymer interactions occur between PVP and NaPA in solution (for polymers with molecular weights equal to 40 K and 60 K respectively); typically, no attractive interactions between PVP and NaPA are reported above a critical pH of 4–5. Polymer interactions in the bulk are observed between the larger molecular weight polymers studied. The mass ratios of polymer also affect the interactions in the bulk, indicating that polymer interactions are influenced by the charges present in the system. The addition of NaPA to a silica dispersion with PVP previously adsorbed to the particles is shown to led to polymer desorption and the destabilisation of the system leading to particle aggregation or even flocculation. SANS data show that the interparticle potential changes from being repulsive with bare silica or PVP-coated silica to attractive on addition of NaPA. The molecular weight of PVP is seen to affect the amount of polymer desorbed, whereas the molecular weight of NaPA had an effect on the aggregation of particles.

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1. Introduction

Both charged and neutral polymers are frequently added to formulations as stabilisers to improve the stability of particles or emulsions. The combination of different polymeric stabilisers within a system, sometimes also with additional surfactants, poses further problems to understanding colloidal stability [1]; the antagonistic interactions between polymers and surfactants are well documented [2–5]. Polymer–polymer and polymer–surfactant complexation can lead to quite complex structures being formed either in the bulk [6] or at the surface [2–4,7], with the surfactant-mediated desorption of the polymeric stabiliser being quite problematic for maintaining colloidal stability.

Sodium polyacrylate, NaPA, has a wide range of commercial and industrial uses. It is an important component in detergents and especially in laundry formulations as it inhibits calcium carbonate precipitation via the formation of a chelating complex [8,9]. A number of studies have focused on the interactions between NaPA and silica nanoparticles leading to diverging findings, i.e. atomic force microscopy by Milling et al. [10] showed that NaPA is depleted for the silica interface whereas Flood et al. [11] observed, using solvent relaxation NMR that NaPA weakly adsorbs onto silica nanoparticles. Zaman et al. [12] found no absorption of NaPA to planar silica surface using attenuated total reflection infrared spectroscopy techniques while Joksimovic et al. [13] showed considerable adsorption of poly(acrylic acid) onto positively charged aminated silica particles that resulted in charge reversal. These observations suggest that repulsive and attractive interactions are occurring between these components and that small differences in the experimental condition might lead to one type of interaction prevailing.

Poly(vinyl pyrrolidone), PVP, is also used in many technical and medical applications. It is used in detergents as a dye-transfer inhibitor, but also helps to prevent redeposition of soils and dyestuff. As a stabiliser for silica and other nanoparticles, PVP has been extensively studied [3–5,14–17]; it is known to adsorb strongly to silica, e.g. adsorbed poly(ethylene oxide)is displaced by the addition of PVP to the system. At low polymer concentration (compared to silica), PVP adopts a flat configuration at the interface, loops and tails form with increasing concentration until the maximum adsorbed amount is reached at ca. 1.0 mg m^{-2} of polymer added. PVP adsorbed at the silica interface complexes with surfactants such as sodium dodecyl sulfate, leading to desorption of PVP from the solid–liquid interface.

Both PVP and PAA are often used in concert in formulation, and gaining a better understanding of potential synergistic or antagonistic interactions between these polymers in the bulk and at the nanoparticle interface is thus of great interest. Although these polymers are extensively used together for applications in neutral or basic pH, their interactions have mostly been studied in acidic media. PVP and PAA form hydrogen bonded interpolymer complexes, IPCs, at low pH and it is these structures that have been studied to date. While IPCs have been extensively studied for 60 years, they still generate a lot of interest due to their potential applications in various disciplines, e.g. drug delivery, vaccine formulation, and colloidal stabilisers [18–20].

The formation of hydrogen bonded IPCs between a poly(carboxylic acid) and a nonionic polymer, both being water soluble, has been widely studied and a wealth of literature is available on the subject [21–25]. These complexes are pH dependent and the determination of the critical pH, pH_{crit}, for the formation of IPC makes it possible to quantify the ability for polymer pairs to complex. It is now well established that the concentration of the polymers, their molecular weight, their hydrophobicity, the functional groups present in the nonionic polymer and the concentration of salts in solution are parameters that affect pH_{crit}. The IPC formation from PVP and PAA is one of the most studied systems for it has one of the highest pH_{crit} known for a hydrogen bonded IPC composed of homopolymers [26,27].

An extensive range of techniques has been used to study IPCs, turbidimetry being the most popular technique to determine pH_{crit} of these systems as formation of large aggregates is thought to be a criterion for complexation [28,29,27,19]. Nurkeeva et al. [27] investigated the PAA/PVP system (in stoichiometric composition), and found that increasing polymer concentration and/or polymer molecular weight increased pH_{crit} of the complexes, but that increasing the salt concentration had the opposite effect. A study of PAA/PVP and PVP copolymers [30] demonstrated a shift in pH_{crit} to a higher value with more hydrophobic copolymers.

The onset of hydrogen bonding interactions is generally determined by optical techniques which identify the flocculation of the complexes rather than the onset of complexation [21]. In a recent study of PAA/PVP complex formation, Henke et al. [31] differentiated between a complex formed of at least one PVP and one PAA molecule and aggregates formed from the merging of several IPC particles. They used a combination of techniques to determine the factors affecting the onset of complexation and aggregation and the structure of the particles formed. Static and dynamic light scattering were used to study the change in apparent hydrodynamic radius and radius of gyration as the pH was varied. The PVP–PAA mixtures were shown to have smaller radii than PVP at pH below pH_{crit}, above which aggregation (large increase in radii) occurred. These weaker polymer interactions leading to small hydrogen bonded IPCs have rarely been studied, although small interactions may have a large effect in complex formulations. It is also important to understand the interactions of these polymers at higher pH and their effect on particulates in the solution as numerous formulations involve mixtures of polymers and particles.

In this study, interpolymer interactions between PVP and NaPA and the effects of the molecular weights and mass ratios of the polymers have been studied by small-angle neutron scattering, SANS, in pH 8.0 aqueous solutions. This pH is significantly higher than pH_{crit} previously reported for the PVP/PAA system ($pH_{crit} = 4.85$ for 2 wt% PVP/PAA mixed in equimolar ratio [27]). The effects of these interactions on the system stability and interfacial interactions were studied on systems containing silica nanoparticles using a combination of PCS and SANS. The use of these complimentary methods demonstrated that adding NaPA to a silica dispersion with PVP previously adsorbed to the particles led to some polymer desorption. This results in the destabilisation of the system, aggregation of some of the silica particles and, in the case of large molecular weight polymers, flocculation.

2. Experimental

2.1. Materials

The colloidal silica used was Bindzil 30/220 kindly provided by EKA Chemicals. It has an average particle diameter of 180 A (equivalent to a surface area of 190 $m^2 g^{-1}$) and is supplied already dispersed in water. PVP 40 K was obtained from Polysciences, PVP 10 K was obtained from Sigma–Aldrich; both polymers have a large dispersity (ca. 3). NaPA 3.8 K and 60 K were obtained from Polymer Source (dispersity <1.1). Samples were prepared from stock solutions made up using Milli-Q water and D_2O. D_2O (99.94% D) was supplied by Goss Scientific. The samples were prepared by weighing solvent, Bindzil 30/220 and PVP in a vial and the mixtures were left to equilibrate on a roller-mixer for 24 h. Stock solutions of NaPA were then added and the samples were left to equilibrate for a further 24 h.