Journal of Colloid and Interface Science 455 (2015) 93–100

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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Influence of binary microgel phase behavior on the assembly of multi-functional raspberry-structured microgel heteroaggregates

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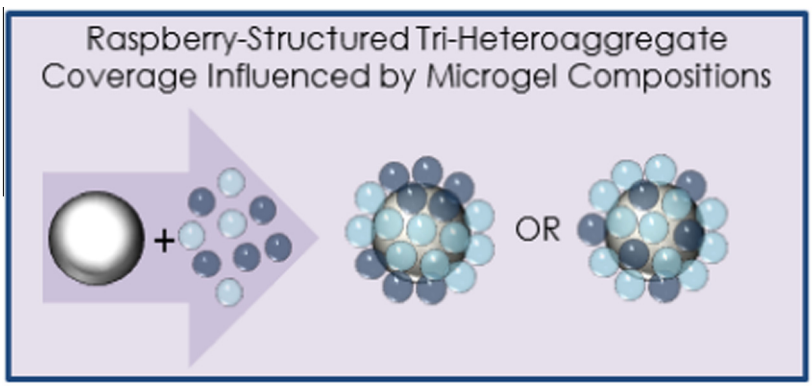
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2015
Accepted 18 May 2015
Available online 22 May 2015

Keywords:
Heteroaggregation
Multi-functional delivery vehicles
Microgel phase behavior

ABSTRACT

We investigate the influence of microgel composition on phase behavior of binary microgel dispersions using poly(*N*-isopropylacrylamide) microgels cross-linked with 5 mol% and 1 mol% *N*,*N*′-methylenebis(acrylamide), or poly(*N*-isopropylmethacrylamide) microgels cross-linked with 5 mol% *N*,*N*′-methylenebis(acrylamide). We then explore the dispersion phase behavior in the context of microgel deposition at a planar interface. These results are then compared to the observed assembly of microgels at curved interfaces, in the form of raspberry-like patchy particles (RLPPs) consisting of a polystyrene core surrounded by a (two-component) microgel shell. Results suggest that microgel composition has a large influence on the ability of binary dispersions to coat planar and curved interfaces. In particular, we demonstrate that binary dispersions of microgels containing higher cross-linker content exhibit decreased packing densities that are very pronounced at a curved interface. To enhance packing density we also explore the use of a two-step coating process to fabricate RLPPs with enhanced control over topography. Development of these complex vehicles is potentially beneficial in the modulation of biological systems where spatial and temporal presentation of molecules can have a large influence on cellular behavior.
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Abbreviations: AFM, Atomic Force Microscopy; RLPs, raspberry-like particles; RLPPs, raspberry-like patchy particles; SEM, Scanning Electron Microscopy; ϕ_{eff}, effective volume fraction; NIPAm, *N*-isopropylacrylamide; pNIPAm, poly(*N*-isopropylacrylamide); NIPMAm, *N*-isopropylmethacrylamide; pNIPMAm, poly(*N*-isopropylmethacrylamide); BIS, *N*,*N*′-methylenebis(acrylamide); AAc, acrylic acid; SDS, sodium dodecyl sulfate; APS, ammonium persulfate; EDC, 1-ethyl-2-[2-di methylaminopropyl]carbodiimide hydrochloride; NHS, *N*-hydroxysuccinimide; AB, 4-aminobenzophenone; EtOH, ethanol; DMSO, dimethylsulfoxide; PS, polystyrene; PBS, phosphate buffer saline.

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http://dx.doi.org/10.1016/j.jcis.2015.05.031
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1. Introduction

Microgels are colloidal hydrogel nano- or microparticles that have been proposed for a variety of applications including tissue engineering scaffolds [1,2], drug delivery [3,4], biomimetic constructs [5,6], and separations [7,8]. Microgel dispersions exhibit rich phase behavior due to the softness of the individual colloidal particles [9]. In particular, the phase behavior of thermoresponsive poly(*N*-isopropylacrylamide) (pNIPAm) microgels has been investigated in detail, revealing that the softness imparted on these colloids increases the thermodynamic parameter of interest, the effective volume fraction, required for crystallization and narrows the coexistence region in comparison to hard spheres [10]. While the phase behavior of single-component pNIPAm microgel dispersions has been investigated in detail [11–14], the phase behavior of binary microgel dispersions has received markedly less attention. Though there has been investigation of other hard sphere colloidal mixtures including latex particles [15–18], it is reasonable to predict that binary microgel dispersions will exhibit unique behavior due to the softness of the building blocks.

Previously, our lab has investigated the behavior of colloidal crystals composed of two microgel components. In one study, we formed colloidal crystal lattices from pNIPAm microgels containing acrylic acid (AAc) ($R_H \sim 375 \pm 20$ nm) and observed that such crystals were able to seamlessly integrate large, "defect microgels," ($R_H \sim 873 \pm 66$ nm) doped in at 0.1 wt% [19]. Our lab has also explored how binary microgel dispersions respond at an interface through centrifugal (active) and passive deposition on a planar glass surface [20]. We observed decreases in microgel footprints during deposition for both passive and active methods, which was an indication of how particle–particle repulsion dictated microgel spreading at solid substrates. However, these studies were not designed to capture colloidal phase behavior in solution.

In the present contribution, we explore the deposition of binary microgel mixtures with defined effective volume fractions (ϕ_{eff}) onto planar and curved interfaces (Scheme 1). We investigate how microgel stiffness influences film formation using a mixture of pNIPAm microgels containing either 1 mol% or 5 mol% *N*,*N'*-methylenebis(acrylamide) (BIS). We also explore how microgel network structure influences film formation from a binary mixture of pNIPAm microgels and poly (*N*-isopropylmethacrylamide) (pNIPMAm) microgels both containing 5 mol% BIS. Understanding of binary microgel mixtures can shed light on development of complex microgel coatings or microparticles, which are of particular interest for biomedical applications, including drug delivery and tissue engineering scaffolds [21], where sensitive biological systems are highly influenced by mechanical properties [22–24], topographical features [25,26], microstructure [27,28] and spatial/temporal presentation of biomolecules. [29,30]

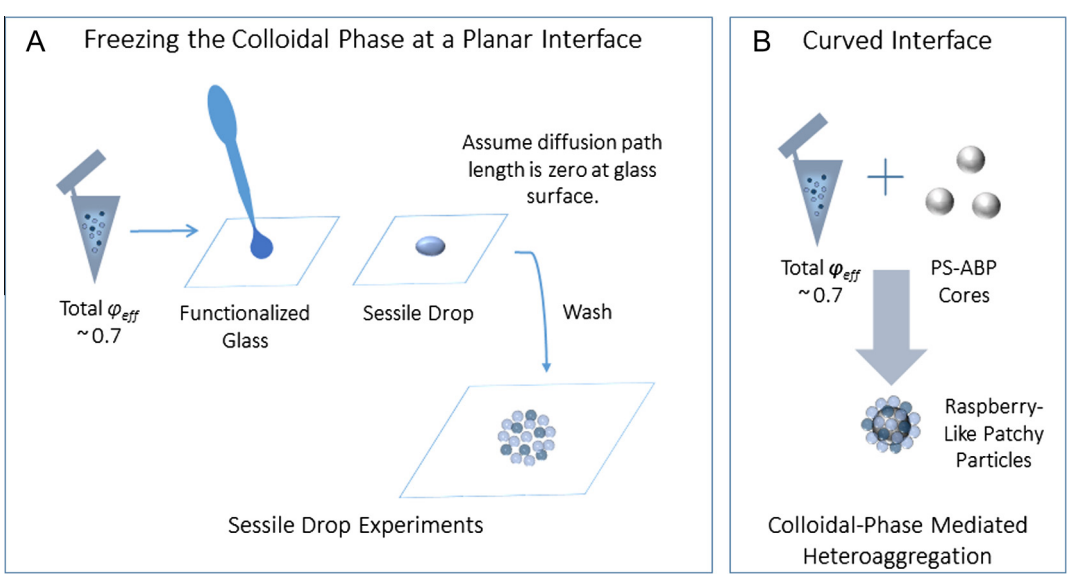
2. Materials and methods

2.1. Materials

All reagents were purchased from Sigma–Aldrich (St. Louis, MO) and used as received, unless otherwise noted. Reagents *N*,*N'*-methylenebis(acrylamide) (BIS), acrylic acid (AAc), sodium dodecyl sulfate (SDS), ammonium persulfate (APS), 1-ethyl-2-[2-di methylaminopropyl]carbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS), 4-aminobenzophenone (AB), 95% v/v ethanol (EtOH), dimethylsulfoxide (DMSO), sodium chloride (NaCl), (3-aminopropyl)-trimethoxysilane (APTMS) and sodium phosphate monobasic monohydrate were all used as received. The monomers *N*-isopropylacrylamide (NIPAm) and *N*-isopropylmethacrylamide (NIPMAm) were recrystallized from hexanes (VWR international, West Chester, PA) and dried *in vacuo* prior to use. Carboxyl modified polystyrene (PS) spheres were purchased from Polysciences, Inc. (Warrington, PA). Deionized water used in all reactions, purifications, and buffer preparations was purified to a resistance of 18 MΩ (Barnstead E-Pure system), and filtered through a 0.2 μm filter to remove particulate matter.

2.2. Microgel synthesis

Microgels were synthesized as previously described using precipitation polymerization [31]. For pNIPAm microgels, the total monomer concentration was 100 mM with molar compositions of 95 mol% pNIPAm and 5 mol% BIS [denoted pNIPAm:BIS (95:5)] or 99 mol% pNIPAm and 1 mol% BIS [pNIPAm:BIS (99:1)]. For



Scheme 1. (A) Behavior of binary concentrated microgel dispersions was evaluated by placing a drop of highly packed microgel dispersions on coverslips. (B) Behavior of binary concentrated microgel dispersions at a curved interface was evaluated by fabricating raspberry-like patchy particles using colloidal-phase mediated heteroaggregation.

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