Current Opinion in Colloid & Interface Science 19 (2014) 575–584

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Capillary suspensions: Particle networks formed through the capillary force

Erin Koos

Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology (KIT), Straße am Forum 8, 76131 Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form 20 October 2014
Accepted 21 October 2014
Available online 15 November 2014

Keywords:
Capillary suspensions
Ternary systems
Percolation
Colloidal clusters

ABSTRACT

The addition of small amounts of a secondary fluid to a suspension can, through the attractive capillary force, lead to particle bridging and network formation. The capillary bridging phenomenon can be used to stabilize particle suspensions and precisely tune their rheological properties. This effect can even occur when the secondary fluid wets the particles less well than the bulk fluid. These materials, so-called capillary suspensions, have been the subject of recent research studying the mechanism for network formation, the properties of these suspensions, and how the material properties can be modified. Recent work in colloidal clusters is summarized and the relationship to capillary suspensions is discussed. Capillary suspensions can also be used as a pathway for new material design and some of these applications are highlighted. Results obtained to date are summarized and central questions that remain to be answered are proposed in this review.

1. Introduction

Ternary particle–liquid–liquid systems composed of particles dispersed in two immiscible liquids can form a variety of structures depending on the ratio of the three components and their material properties. The particles can stabilize emulsions forming Pickering emulsions [1], which cluster together forming spherical agglomerates that readily separate from a bulk fluid [2,3], or prevent the spinodal decomposition of the two fluids forming a Bijel [4]. Recently, it was determined that when a small amount of the second immiscible liquid is added to the continuous phase of a suspension, the rheological properties of the mixture are dramatically altered from a fluid-like to a gel-like state or from a weak to a strong gel [5••]. This transition increases the yield stress and viscosity by several orders of magnitude as the volume fraction of the second fluid increases and is attributed to the capillary forces of the two fluids on the solid particles. Thus, these systems have been termed capillary suspensions. Capillary suspensions are a new class of materials that can be used to create tunable fluids, stabilize mixtures that would otherwise phase separate, and create new materials such as low-fat foods or porous ceramics [6–8••].

1.1. Capillary suspensions

Capillary suspensions have been divided into two distinct states: the *pendular state* where the minority liquid preferentially wets the particles; and the *capillary state* where the secondary fluid wets the particles less well than the primary fluid. Both states are associated with a transition in the suspension from a fluid-like to gel-like state or from a weak gel to a strong gel. The texture and flow of these suspensions dramatically alter upon the addition of an immiscible secondary liquid at low volume fractions as shown in Fig. 1. In the pendular state, the particle network is formed through individual particles linked through capillary bridges and in the capillary state, clusters of particles surrounding secondary fluid droplets are linked together.

The creation of the network, formed by adding a preferentially wetting liquid to a suspension, has been investigated previously in higher volume fraction suspensions. Early work on sedimentation determined that the addition of a secondary fluid (usually water to an organic solvent) caused the particles to flocculate and significantly increased the sedimentation volume [9]. Later, the rheological properties of the suspensions were measured where it was observed that the admixture creates a strong gel and that the yield stress greatly increases [10]. This network structure was attributed to the formation of pendular bridges between the particles [11], though an increase in electrostatic charge on the particle surface might have contributed to some of the observed rheological changes [12]. An increase in the viscosity for lower volume fractions was also observed by McCulfor and coworkers [13]. Rheological changes due to the addition of water to an oil-based suspension of hydrophobically modified calcium carbonate (capillary state) were first observed by Cavalier and Larché [14], but they attributed the gelation to hydrogen bonding. This initial work on pendular state suspensions was extended and the first confirmation of the influence of the capillary force in capillary state suspensions was demonstrated by Koos and Willenbacher [5••] where both states were termed capillary suspensions.

E-mail address: erin.koos@kit.edu.

http://dx.doi.org/10.1016/j.cocis.2014.10.004
1359-0294/

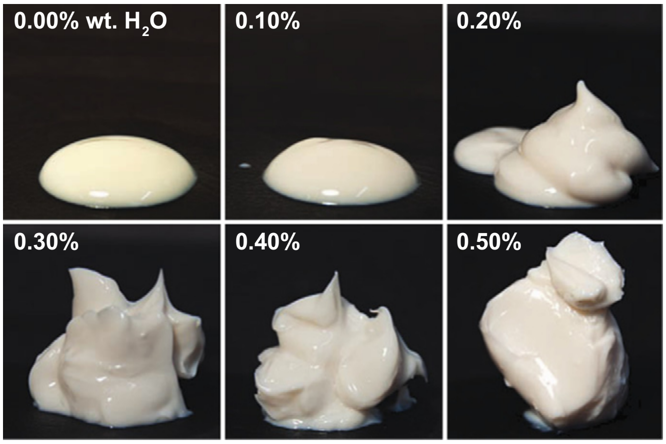

Fig. 1. The transition from weakly elastic, fluid-like behavior to highly elastic, gel-like behavior for capillary state suspension in images. (Hydrophobically modified calcium carbonate, $r = 0.8$ μm, in DINP, $\phi = 0.11$, with added water.)
Adapted from [5••].

These capillary suspensions are differentiated based on which fluid preferentially wets the particles. Using a fluorescent dye to mark the location of the secondary fluid, a diluted capillary suspension sample may be imaged, as shown in Fig. 2A. The addition of water to these oil-based suspensions of glass particles causes the particles to agglomerate tightly into clusters. In the pendular state (Fig. 2A.i), the capillary bridges are clearly visible binding particle dimers and trimers together. A shielding of the second fluid phase by particle clusters is observed in the capillary state (Fig. 2A.ii). In contrast, the glass particles without added water agglomerate slightly due to vdW attraction, but are generally well distributed throughout the sample.

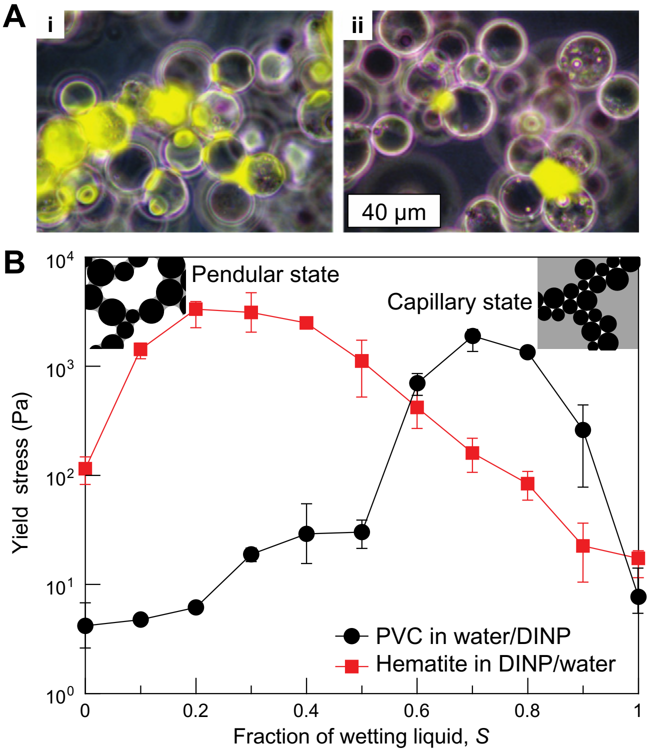

Fig. 2. (A) Images of the (i) pendular and (ii) capillary states. (A.i: Clean glass, $\theta = 49.4°$, and A.ii treated glass, $\theta = 99.3°$ in DINP with 1 wt.% added water. For both samples, $r = 12.3$ μm and $\phi = 0.3$.) (B) Dependence of the yield stress on the fraction of the wetting liquid. For this PVC, the yield stress is greatest in the capillary state. For hematite, the yield stress is greatest in the pendular state.
Adapted from [5••].

Following the convention of wet granular materials, each sample was characterized using the saturation S,

$$S = \frac{V_{\text{wetting fluid}}}{V_{\text{total fluid}}} = \frac{V_w}{V_b + V_l} \tag{1}$$

which is close to zero for the pendular state ($V_w = V_l$) and approaches one for the capillary state ($V_w = V_b$). The gel-like transition in capillary suspensions dramatically increases the yield stress and viscosity above the corresponding values of the single-fluid suspensions. The full dependence of yield stress on the saturation is shown in Fig. 2B for PVC ($r = 16.4$ μm) and hematite, both in various percentages of water and diisononyl phthalate (DINP). For PVC and similar systems, the greatest yield stress occurs in the capillary state at a fraction of $S \approx 0.7$, but for systems similar to hematite (for instance, silica and hydrophilic glass), the yield stress was the greatest in the pendular region ($S \approx 0.2$). While the formation of capillary suspensions is a general phenomenon, each material combination appears to have a preference for either the capillary state or the pendular state. While this may be a physical restriction depending on, for example, how well the secondary fluid can re-wet the particle surface, it may also depend on the droplet breakup as the suspension is created.

The pendular and capillary states are shown on a ternary diagram with other particle–liquid–liquid systems in Fig. 3. In capillary suspensions, the secondary fluid droplets are typically smaller than the particles and the total secondary fluid volume is a small fraction of the total volume. In Pickering emulsions, solid particles stabilize the emulsion droplets; hydrophilic particles tend to form stable oil-in-water (o/w) emulsions and hydrophobic particles tend to form water-in-oil (w/o) emulsions. To create stable Pickering emulsions, the particle size must be much smaller than the droplet size. The opposite behavior is demonstrated in spherical agglomerates where many particles are enveloped by a larger droplet of preferentially wetting liquid. Gelation in Pickering emulsions and from spherical agglomerates is caused primarily through the van der Waals interaction among the particles on the surface of adjacent droplets. The capillary force causes gelation in capillary suspensions. The available states for ternary systems depend on the specific material properties and on the processing history. Key among these material properties are the interfacial tension and contact angle, both of which contribute to the strength of the capillary force.

1.2. Capillary force

When a liquid meniscus forms between two surfaces, an attractive force between these surfaces results. In suspensions, this capillary force usually dominates over other forces, such as the van der Waals force [15]. The capillary force, which plays an important role in a wide range of natural phenomena and technical processes [16,17], is composed of two parts: the Laplace pressure inside the liquid and the surface tension acting at the solid–liquid–gas contact line. The capillary force F_c between two solid particles connected by a pendular bridge depends on the radius r of the particles, their separation distance S, the surface tension of the liquid Γ, the wetting angle θ, as well as the volume V_l and shape of the liquid bridge. Analytical as well as computational solutions for F_c assume a certain bridge shape (e.g. toroidal, cylindrical, etc.) or solve the Laplace–Young equation. For a finite particle separation of equally sized spheres connected by a fluid bridge, the capillary force is given by

$$F_c = \frac{2\pi r \Gamma \cos\theta}{1 + 1.05\hat{s} + 2.5\hat{s}^2}, \quad \text{with } \hat{s} = s\sqrt{\frac{r}{V_l}} \tag{2}$$

which simplifies to the well-known expression $F_c = 2\pi r \Gamma \cos\theta$ for spheres that are in contact [18]. The equations for the capillary force