Influence of nonwetting on the aggregation dynamics of micronic solid particles in a turbulent medium

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Abstract

The aim of this work was to determine and to interpret the influence of nonwetting on the aggregation dynamics of micronic solid particles in a turbulent medium. Two silica granular samples were studied: one was naturally hydrophilic; the other was made hydrophobic. Aggregation in an aqueous ethanol solution was followed by in situ turbidimetry. The influence of stirring rate and deaeration was determined. Aggregates of hydrophilic particles were small and fragile, whereas aggregates of hydrophobic particles were large and solid. Moreover, they differed greatly in optical properties. Within the proposed approach, different features of the aggregate morphology were identified: fractal dimension, maximum size, and gas content of the hydrophobic clusters. These elements are taken into account in the models of aggregation dynamics proposed here.

1. Introduction

Aggregation of hydrophilic particles in stirred liquid media can be considered a relatively well understood process despite the variety and complexity of its aspects. Good models exist in particular for representing the physicochemical interactions between aggregates and for predicting collision rates and their efficiency [1–7]. Recently, the porous character of large aggregates has been introduced in classic models of aggregation. The procedure proposed by Kusters et al. [8] has been revealed to be particularly efficient in taking into account most of the aspects of aggregation in a comprehensive dynamical model. Thanks to this model, the state of aggregation can be determined along the whole process [8–12].

Aggregation of hydrophobic particles in aqueous media, or, more generally, solid particles in nonwetting media, is less known, at least in certain aspects. A large number of ex-perimental works have proved the existence of strong long-range (20–200 nm) attractive forces between hydrophobic surfaces in water [13–15]. Previous experimental results have given rise to intensive theoretical work on the origin of the hydrophobic interaction. Several interpretations have been explored in some detail [16]. It seems that the most likely explanation focuses on the bridging of nanobubbles which preexist on the hydrophobic surface. The existence of these bubbles was first deduced from force measurements and then confirmed by direct observations [14,16–19]. Although experimental evidence and thermodynamic interpretation conclusively prove that gas bridging from preexisting nanobubbles is of major importance in hydrophobic aggregation, some theoretical aspects are less understood, in particular, spatial repartition of gas in hydrophobic aggregates.

To our knowledge, the dynamics of aggregation of solid particles in nonwetting media has not yet been the subject of systematic experimental study. The existing experimental works [20,21] do not offer the ability to compare aggregation dynamics in the cases of wetting and nonwetting. In the same way, with respect to modeling of aggregation dynamics, no

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expression of aggregation kernels is available in the case of nonwetting. Extending Kusters' procedure to the field of hydrophobic aggregation, for instance, to predict particle size distribution evolution with time, requires additional work.

In this article we present first a comparative experimental study of the aggregation of two silica samples from the same lot: one is naturally hydrophilic; the other has been made hydrophobic by surface chemical processing. The results of this study are then discussed to clearly confirm the presence of gas bridges in hydrophobic aggregates, to propose models of hydrophilic and hydrophobic aggregates relative to their morphology and optical properties, and finally, to obtain a general dynamic model of aggregation that can be applied to other situations of hydrophobicity or nonwetting.
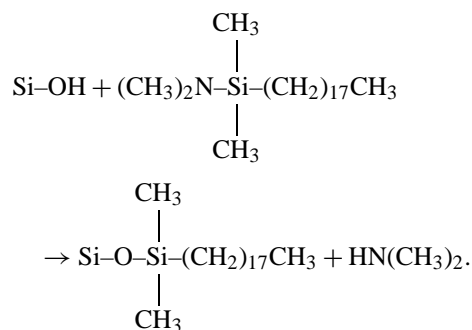
2. Materials, setup, and experimental procedures

In this work, aggregation of silica is studied in a stirred water–ethanol solution.

2.1. Silica

Silica beads of diameters 0.5 and 1.5 μm were used in this study. These are Geltech Inc. products with a nearly monodisperse particle size distribution. Their solubility in water and ethanol is practically zero. Their refractive indexes have been determined by index matching in water–glycerol solutions and found to be 1.4408 for 0.5-μm silica and 1.4416 for 1.5-μm silica at a wavelength of 589 nm. These silica samples were not submitted to preliminary hydration as many authors do. This intentionally avoids dealing with the specificity of silica surface behavior relative to other oxides (see further under Qualitative Discussion).

2.1.1. Silica hydrophobization

To confer hydrophobic character to the silica surface we used the procedure proposed by Duchet et al. [22]. This method consists of surface grafting of carbon chains of various lengths. Its main steps are: (1) preliminary hydroxylation and formation of silanol groups by 160 h boiling in water; (2) drying and elimination of adsorbed water at 140 °C; (3) wetting with a N,N-dimethyloctadecylaminosilane solution for 48 h. Thanks to this processing, silanization takes place and strong Si–O–Si bonds are formed at the silica surface according to the reaction

$$Si\text{--}OH + (CH_3)_2N\text{--}\underset{\overset{\displaystyle |}{CH_3}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}\text{--}(CH_2)_{17}CH_3$$

$$\rightarrow Si\text{--}O\text{--}\underset{\overset{\displaystyle |}{CH_3}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}\text{--}(CH_2)_{17}CH_3 + HN(CH_3)_2.$$

Samples of hydrophibized silica so prepared are directly usable for aggregation experiments.

2.1.2. Hydrophobicity characterization

For hydrophobicity characterization, hydrophilic silica powder in the form of pellets undergoes sintering at 1050 °C. To reactivate the possibly deactivated Si sites, the pellets are plunged for 5 min in sulfochromic mixture and then made hydrophobic by means of the same procedure described previously. The hydrophobicity of the samples processed in this way is characterized by the contact angle of a pellet with a drop of the liquid phase. Angles higher than 90° correspond to hydrophobicity of the solid or, equivalently here, to nonwetting by the liquid phase. Contact angles θ are measured using a Digidrop apparatus from GBX.

Results for different water–ethanol mixtures are illustrated in Fig. 1. Contact angle and, thus, hydrophobicity decrease with ethanol yield. Nonwetting ends beyond a volume fraction of 15% in ethanol. From a practical point of view, dispersion of hydrophobized silica in nonwetting ethanol–water solutions requires a first step of dispersion in an ethanol-rich (wetting) solution, then a second step of dilution of this suspension in water to reach the required composition.

In the absence of silanisation processing, contact angles of 0° are measured whatever the composition of the solution. This confirms the hydrophilic character of the unprocessed silica. In the follow-up to this work, original silica samples will be qualified as "hydrophilic" or "unprocessed," whereas samples submitted to silanization will be denoted as "hydrophobic" or "processed."

Remark. In a recent paper [23], Nguyen et al. proved that attraction forces between silanated glass surfaces globally decrease with the volume fraction in ethanol. This attractive interaction, however, remains significant in the concentration domain that should correspond to hydrophilic conditions ($\theta < 90°$). The wettability threshold (15%) in ethanol is probably not as sharp a boundary as expected. This is also apparent in [23], where force amplitude rapidly changes when ethanol is added to pure water, but, however, does not
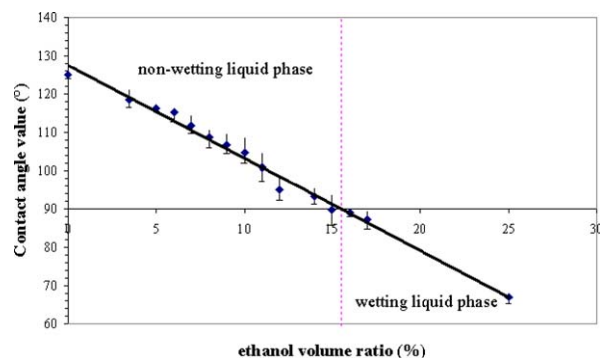

Fig. 1. Contact angle of hydrophobized silica pellets in ethanol–water mixtures.