Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) 6005–6008
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Why foams containing colloidal hydrophilic particles are unstable?

D.O. Vivaldini, A.P. Luz, V.R. Salvini*, V.C. Pandolfelli

Federal University of São Carlos, Materials Engineering Department, Materials Microstructure Engineering Group (GEMM) Rod. Washington Luiz, km 235, São Carlos, SP, C.P. 676, CEP 13565-905, Brazil

Received 8 December 2012; accepted 4 January 2013
Available online 16 January 2013

Abstract

In this work, properties from colloidal silica containing foam systems were analyzed and correlated to the fundamental concepts of the particle adsorption at the gas–liquid interface, specifically for the adsorption energy and its relationship to the thermal energy of the particle. Based on the presented data, it can be pointed out that hydrophilic colloidal particles should give rise to unstable foams due to their low adsorption energy, which is below the minimum threshold required evaluated for the particle containing foam stabilization.

Keywords: Particle stabilized foams; Silica; Contact angle; Adsorption energy

1. Introduction

Foaming containing particles can result in systems having outstanding stability [1] or no foam formation due to the action of highly hydrophobic materials [2]. This opposing trend can also be attained with the same sort of particle depending on the physicochemical state of their surface, which can be modified by various techniques [3,4] (e.g., by using water-soluble amphiphilic molecules that can adsorb at the metal oxide surface and modify its aqueous wettability or by changing the morphology of the solid surface [5]).

The literature presents many studies related to the foaming behavior of colloidal silica suspensions. However, due to the various data related to the physicochemical properties of colloidal silica foams presented by Binks and Horozov [6], Blute et al. [7] and Gonzembach et al. [4] these works were selected to be explored and further analyzed in this paper.

Blute et al [7] evaluated hydrophilic (unmodified) colloidal silica suspensions (10 wt%) and analyzed the foam stability of these systems. The selected experimental procedure consisted of introducing air into the colloidal suspensions and measuring the time required for the foam to collapse (the stability time). Fig. 1 presents the stability time of foams evaluated by Blute et al. [6] as a function of the particle size (nm) of colloidal silica.

Fig. 1 shows a general trend where the smaller the particle, the higher the stability time, which is related to the higher viscosity of the suspensions containing tiny particles [7]. However, although the stability time changes are significant among those systems evaluated by Blute et al. [7], they are almost irrelevant when compared to highly stable ones [8], as the latter displays stability time values ranging from many days to years (which makes them some million to billion times more stable than those shown in Fig. 1).

In order to increase the stability time and also the system's foaminess, Binks et al. [6] reported a method to produce colloidal silica foams by changing the chemical nature of the particles in suspension. They carried out a silanization by using dichlorodimethylsilane in alcoholic medium, which resulted in the silica's contact angle (θ) increase, making a less hydrophilic particle surface. Aiming to quantify this effect, some measurements of the surface relative SiOH content were carried out. Because the SiOH chemical group is commonly present at the silica surface, this compound should be an indicative of its highly hydrophilic feature (contact angle ≈ 5–10° [9]). Furthermore, by the silanization, Binks and Horozov [6]

---

*Corresponding author. Tel.: +55 16 33518253; fax: +55 16 33615404.
E-mail addresses: pvrs@ufscar.br, vicpando@ufscar.br, vr.salvini@uol.com.br (V.R. Salvini).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.01.007

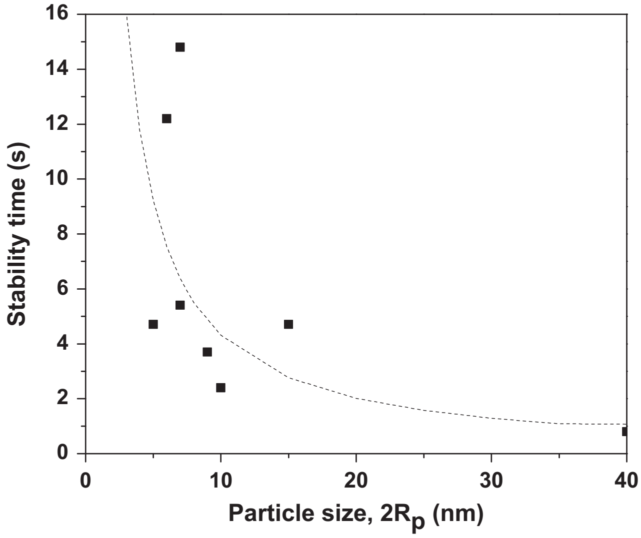

Fig. 1. Stability time (s) as a function of particle size of foams prepared with 10 wt% colloidal silica suspensions [6]. The fitting line presented is just to guide the eyes.

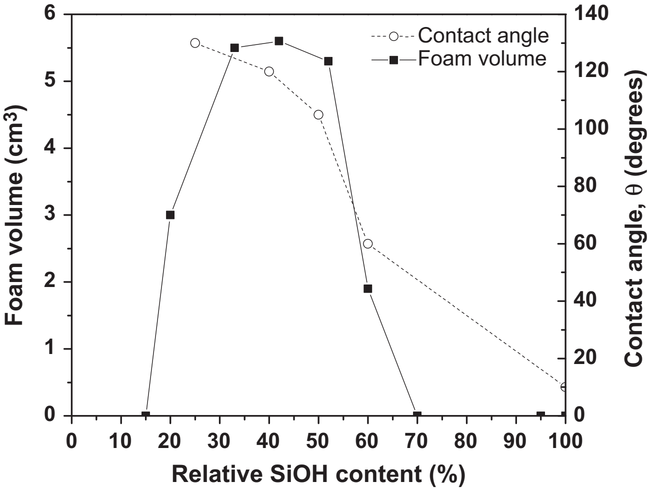

Fig. 2. Contact angle (°) [10] of silica particles as a function of the relative SiOH content on their surface and the foam volume (cm^3) [6] attained for each system.

were able to produce highly stable foam systems and to achieve high foaminess values (measured by the stable foam volume) with 20 nm colloidal silica particles suspensions. Their results are shown in Fig. 2, which presents the foam volume as a function of the relative SiOH content on the silica surface. It is important to emphasize that the foams that could be generated by Binks et al. [6] presented very high stability times (dozens of hours), much higher than the few seconds attained by Blute et al. [7] (see Fig. 1).

Fig. 2 shows that there are ranges of SiOH content that allows foam generation and stabilization, whereas SiOH values higher than 70% or lower than 15% inhibit the foam formation and stabilization process. In order to elucidate this aspect, the contact angle (θ), which is a function of the relative SiOH content, is also shown in Fig. 2 (based on Kostakis et al. [10]). The θ value is very important for the production of foams containing particles as it controls their adsorption at the gas–liquid interface, affecting the foam stabilization.

Gonzembach et al. [4] applied another method to increase the stability time and foaminess of colloidal silica suspensions. They carried out in-situ modification of the silica particles surface in suspension by adding hexylamine as a surface modifier. Fig. 3 shows their results based on the volumetric gas fraction (P) incorporated in the suspensions, which is a direct measure of the system foaminess. It is possible to observe that as the hexylamine concentration increases above a certain level, foam generation takes place. Analogous to the Binks and Horozov [6] system, the physicochemical parameter changed was the particle contact angle with water (θ), which also varies with the hexylamine concentration and is also shown in Fig. 3 [11]. It is important to emphasize that the foams that could be generated ($P > 0\%$) by Gonzembach et al. [4] presented very high stability times (dozens of hours), which are also much higher than those attained by Blute et al. [7] (see Fig. 1).

Figs. 1–3 show that the physicochemical properties are relevant for the behavior of particle containing foams, either due to the particle size effect or the wettability one. These fundamental concepts regarding foam systems containing particles have already been discussed in the literature [12], nevertheless a comprehensive quantitative analysis to allow the comparison among different systems is still required, such as for particular particle size values, wettability or another property that depend on them. This systemic view may result in novel concepts that can elucidate the required conditions to attain foamability and, additionally, explain why foams containing colloidal hydrophilic particles are so unstable, as shown in Fig. 1 by

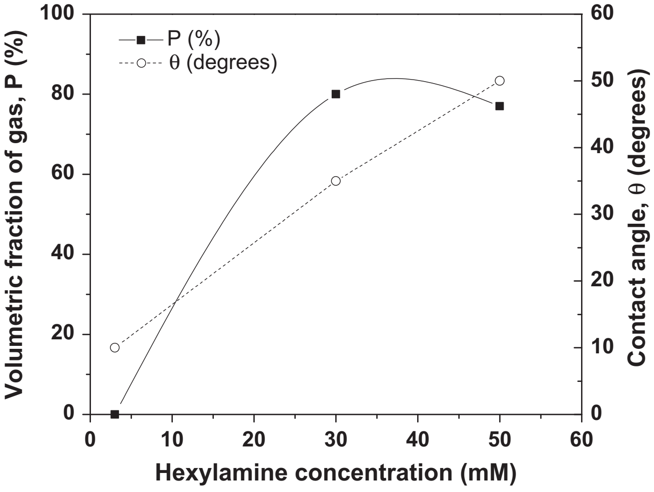

Fig. 3. Volumetric fraction of gas (P) and the contact angle (θ) as a function of hexylamine concentration (mM). The contact angle data was taken from Vilkova et al. [11]. The particle size was fixed in 200 nm. The fitting lines presented are just to guide the eyes.

their low stability time values. This broader view may also provide explanations for the great stability/foamability attained by colloidal partial hydrophobic silica particle foams, as shown in Figs. 2 and 3.

Therefore, the present communication aims to explore and analyze the fundamental concepts leading to the foaming behavior of suspensions containing colloidal particles by correlating experimental data with fundamental physicochemical concepts. In order to do so, this work focused on colloidal silica containing foams based on experimental data presented in the literature. The colloidal silica particle containing foam was selected for this study as it has been one of the most investigated regarding its foam formation ability. The main objective was to understand the fundamental reasons of why some colloidal silica foams attain good stability whereas others do not.

2. Mathematical approaches

For a suitable evaluation of nanoscaled particles containing foams, it is necessary to select a foam property sensitive to the presence of such particles, which could then explain the observed macroscopic behavior.

It is known that when a particle is attached to a gas–liquid interface, the overall Gibbs free energy of the system is reduced, resulting in a more favorable thermodynamic condition. The energy decrease due to this adsorption process at a flat interface can be mathematically described by Eq. (1) [1].

$$\Delta G_{\text{ads}} = \pi R_{\text{p}}^2 \gamma (1 \pm \cos\theta)^2 \tag{1}$$

where, ΔG_{ads} is expressed in joules (J), γ is the gas–liquid interfacial tension (N/m) and R_{p} is the particle radius (*m*). Additionally, when $0^\circ \leq \theta \leq 90^\circ$ the positive sign in Eq. (1) is used or the negative one for $\theta > 90^\circ$.

Nevertheless, the ΔG_{ads} value cannot be used to state whether the interface is stable or not. That argument can only be sustained when the energy released due to adsorption of the particles is compared to their own thermal energy, which is the origin of the Brownian motion of colloidal particles in suspension [13]. If the thermal energy value is close to the adsorption energy, then this process may not take place, as the particles will have enough energy to break loose from the gas–liquid interface.

The thermal energy of suspended colloidal particles is described by the product of the Boltzmann constant (K_{B}) and the absolute temperature (T) [14]. Therefore, by the ($K_{\text{B}}T$) value, also expressed in Joules (J), it is possible to define the stability of the particles adsorption at gas–liquid interface, as presented by Eq. (2) [1]:

$$\text{Interface Stability} = \frac{\Delta G_{\text{ads}}}{K_{\text{B}}T} = \frac{\text{Adsorption Energy}}{\text{Thermal Energy}} \tag{2}$$

Eq. (2) allows the comparison among different foam systems regarding their particle size and wettability. This tool will be used in this work to discuss and explain the experimental foam properties shown before (Figs. 1–3).

3. Results and discussion

Based on Eq. (2) it is possible to evaluate the influence of R_{p} and θ on the particle adsorption stability. Fig. 4 shows the results attained for an aqueous low temperature ($T = 373$ K) system:

It is possible to observe that as the contact angle changes from 5° to 10° or from 5° to 89°, the ($\Delta G_{\text{ads}}/K_{\text{B}}T$) ratio increases many orders of magnitude. Furthermore, the dotted parallel line to the *x* axis shown in Fig. 4 defines the condition where the adsorption energy is equal to the thermal energy, which implies that the system is unstable as the thermal energy is high enough to withdraw particles from the interface of the bubbles. Therefore, it is possible to point out the inherent instability associated with unmodified colloidal silica foams, just like those prepared in Blute et al. [7], as the low contact angle (5–10°) associated with such small particles results in very low (sometimes less than 1) values for the ($\Delta G_{\text{ads}}/K_{\text{B}}T$) ratio (Fig. 4). This is the key aspect that explains the low stability time attained in colloidal ($2R_{\text{p}} < 40$ nm) silica foam systems by Blute et al. [7] (Fig. 1).

In order to explain the results attained by Binks and Horozov [6] (Fig. 2) and Gonzembach et al. [4] (Fig. 3) the ($\Delta G_{ads}/K_B T$) ratio for those systems was calculated using Eq. (2) and the values of θ presented in Figs. 2 and 3. The surface tension (γ) values were assumed to be close to plain water, 72 m N/m. The results are shown in Fig. 5.

Fig. 5 correlates the attained foam volume or volumetric gas fraction (P) with its corresponding ($\Delta G_{\text{ads}}/K_{\text{B}}T$) value. Although the correlation between ($\Delta G_{\text{ads}}/K_{\text{B}}T$) and foam volume or with P is not quite clear, no foam was attained with a ($\Delta G_{\text{ads}}/K_{\text{B}}\text{T}$) value below approximately 300. This result indicates that foams stabilized with particles require an adsorption energy (ΔG_{ads}) a few hundred times greater than the thermal energy (K_{B}T), which can be regarded as a

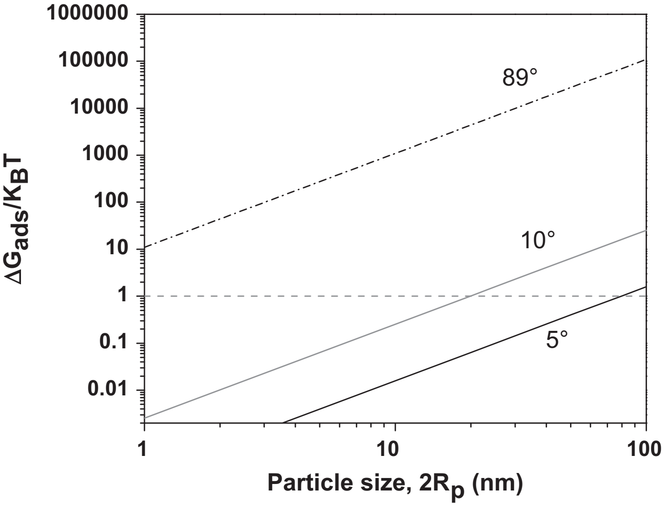

Fig. 4. ($\Delta G_{\text{ads}}/K_{\text{B}}T$) relation as a function of particle size (nm) for three different contact angles (5, 10 and 89°). The dotted line represents ($\Delta G_{\text{ads}}/K_{\text{B}}T$) = 1.

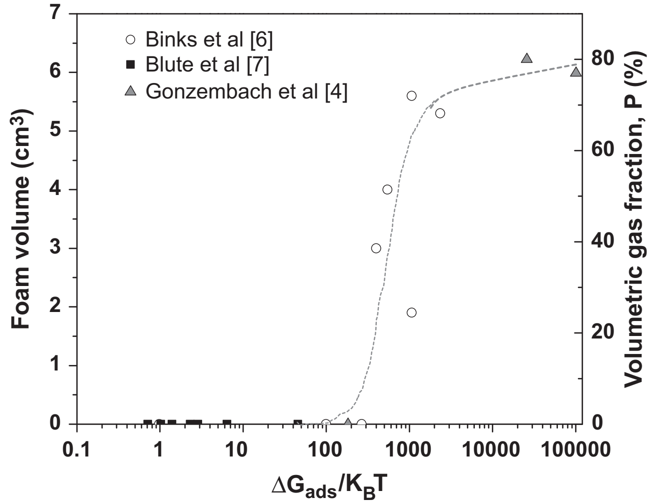

Fig. 5. Correlation between the ($\Delta G_{\mathrm{ads}}/K_{\mathrm{B}}T$) ratio and the foam volume (cm^3) (by Binks and Horozov [6] and Blute et al. [7] on the left) or with the volumetric gas fraction, P (%) (by Gonzembach et al. [4] on the right). The fitting line presented is just to guide the eyes.

minimum threshold for the formation and stabilization of foams containing particles. This threshold is lower than that often stated in literature, which is suggested to be thousands of times greater [1]. If one compares the 300 ratio value with that generated by unmodified colloidal silica suspensions (such as Blute et al. systems [7]), which is in the range of 5 to 10^{-3} (see Fig. 4 and the curves where $\theta = 5°–10°$ with $2R_{\mathrm{p}} = 20$–40 nm), it is possible to understand why those systems presented such low stability times (smaller then dozens of seconds) and are shown in Fig. 5 with P values very close to null.

4. Conclusions

Colloidal particle stabilized silica foams were investigated based on the variables that control the system foaminess and stability, such as the particle size and wettability. It was concluded that the ratio between the adsorption energy of a particle at gas–liquid interface (bubble's interface) and the thermal energy of the particles is an important parameter that helps to explain the experimental results in the literature. The correlated data presented in this work suggested that the adsorption energy must be at least few hundred times greater than the thermal energy in order to allow foam stabilization, which is the reason why hydrophilic colloidal particles containing foams are unstable, as their adsorption energy are either lower or just above the thermal energy value.

Acknowledgments

The authors are grateful to the Brazilian research funding institution CNPQ, FIPAI and FIRE (Federation for International Refractory Research and Education) for supporting this work.

References

[1] A.R. Studart, U.T. Gonzenbach, E. Tervoort, L.J. Gauckler, Processing routes to macroporous ceramics: a review, Journal of the American Ceramic Society 89 (2006) 1771–1789.
[2] R. Pugh, Foaming, foam films, antifoaming and defoaming, Advances in Colloid and Interface Science 64 (1996) 67–142.
[3] C. Chuanuwatanakul, C. Tallon, D.E. Dunstan, G.V. Franks, Controlling the microstructure of ceramic particle stabilized foams: influence of contact angle and particle aggregation, Soft Matter 24 (2011) 11464–11474.
[4] U.T. Gonzenbach, A.R. Studart, E. Tervoort, L.J. Gauckler, Stabilization of foams with Inorganic colloidal particles, Langmuir 22 (2006) 10983–10988.
[5] W. Lee, B. Park, K. Lee, Fabrication of superhydrophobic surface of alumina with nanoporous structure, Bulletin of the Korean Chemical Society 31 (2010) 1833–1834.
[6] B. Binks, T. Horozov, Aqueous foams stabilized solely by silica nanoparticles, Angewandte Chemie 117 (2005) 3788–3791.
[7] I. Blute, R. Pugh, J. van de Pas, I. Callaghan, Silica nanoparticle sols 1. Surface chemical characterization and evaluation of the foam generation (foamability), Journal of Colloid and Interface Science 313 (2007) 645–655.
[8] U.T. Gonzenbach, A.R. Studart, E. Tervoort, L.J. Gauckler, Tailoring the microstructure of particle-stabilized wet foams, Langmuir 23 (2007) 1025–1032.
[9] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley, Wetting and spreading, Reviews of Modern Physics 81 (2009) 739–805.
[10] T. Kostakis, R. Ettelaie, B. Murray, Effect of high salt concentrations on the stabilization of bubbles by silica particles, Langmuir 22 (2006) 1273–1280.
[11] N. Vilkova, S.I. Elaneva, K. S.I., Effect of hexylamine concentration on the properties of foams and foam films stabilized by Ludox, Mendeleev Communications 22 (2012) 227–228.
[12] T.S. Horozov, Foams and foam films stabilised by solid particles, Current Opinion in Colloid and Interface Science 13 (2008) 134–140.
[13] M. Haw, Colloidal suspensions, Brownian motion, molecular reality: a short history, Journal of Physics: Condensed Matter 14 (2002) 7769–7779.
[14] S. Blundell, K. Blundell, Concepts in Thermal Physics, Oxford University Press, 2006 368-385.