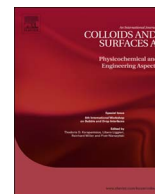




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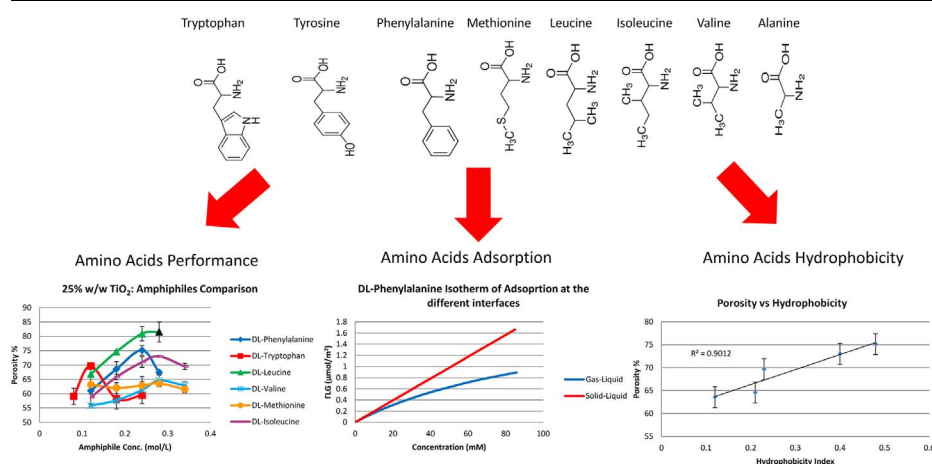
## Colloids and Surfaces A

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## Formulation of Ceramic Foams: a New Class of Amphiphiles

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## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, amino acids are proposed and assessed as a new class of amphiphiles that is more environmentally benign and present a wider operational window than those reported in the literature. The effects of the amphiphile concentration and structure on the foam properties were investigated (e.g. porosity, bubble size distribution). These were classified depending on their different hydrophobicity by establishing a hydrophobicity index. Monotonic relationships between the hydrophobicity index and the foam structural properties (e.g. porosity, bubble size) were found. In addition, the more suitable amino acid to be used at larger scales was identified and it was used as a model amphiphile to have a deeper insight into the foaming process. In particular, the repartition of the amino acids among the different interfaces and the minimum amphiphile concentration to obtain stable foams were identified.

## 1. Introduction

In recent years ceramic foams have been receiving an increasing interest thanks to their applicability in several technology fields. Among others, ceramic porous materials are used as refractory

insulators, catalyst supports and filters for molten metals [1,2]. Several techniques have been developed for the production of ceramic foams; these include replica technique, sacrificial templating and direct foaming [3]. The replica technique consists in the impregnation of a natural (e.g. wood [4], coral [5]) or a synthetic template (e.g. polymer

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foam [6]) with a ceramic suspension. In order to obtain a thin ceramic coating on the template surface, the suspension in excess is removed by passing the template through rollers. After drying and calcination a ceramic positive replica of the template is obtained. Sacrificial templating uses a biphasic mixture of a template and ceramic slurry to generate the porous structure inside the ceramic body. The sacrificial material can be natural [7] or synthetic [8] and either in solid [9] or liquid form [10]. These are then either extracted or decomposed to form a negative replica of the sacrificial template in the ceramic material. Direct foaming is an ostensibly straightforward method for the production of ceramic foams. In this process, air is directly entrained into the ceramic suspension causing the attachment of the previously modified particles at the air/water interface, leading to stable foams [11]. Particles surface properties are modified in order to reduce their hydrophilicity. This is realized through the addition of an amphiphile; namely a chemical that has a polar head which electrostatically interacts with the particles surface and a hydrophobic tail that is directed toward the aqueous phase. Several classes of chemicals have been proposed as amphiphiles, these include among others carboxylic acids, amines and gallates [11]. The selection of the suitable amphiphile is largely governed by the particle's surface charge where carboxylic acids are used with positively charged particles, amines with negatively charged particles and gallates with either positively charged or neutral particles. It has been demonstrated that both the structural characteristics of the amphiphile and its concentration strongly affect foam properties such as porosity, stability and bubble size distribution [12,13].

Although the use of the previously mentioned amphiphiles is widely reported in the literature, the use of these amphiphiles is limited to a certain pH range dictated by the particle surface charge. In addition, many of these amphiphiles present acute toxicity limiting their usage at production scale. The aim of this work is to investigate the possibility of using amino acids as amphiphiles. Amino acids are organic compounds containing an amine group ( $-\text{NH}_2$ ), a carboxylic group ( $-\text{COOH}$ ) and a side chain specific to each amino acid. There are about 500 natural occurring amino acids [14]; these can be classified according to the position of the functional groups in alpha- ( $\alpha$ ), beta- ( $\beta$ ), gamma- ( $\gamma$ ) or delta- ( $\delta$ ). In this work attention was posed on the alpha- amino acids; in these molecules the carboxylic and the amino groups are attached to the first carbon or alpha- ( $\alpha$ ) carbon. The selection of this class of amino acids was based on their lower cost relative to hydrophobic  $\beta$ -,  $\gamma$ - and  $\delta$ -amino acids making them more economically suitable for the scale up of the process in the future. This class of molecules is environmentally friendly and allows a wider pH operational window courtesy of the presence of both the carboxylic and the amino group on the same molecule. In the present study the amino acids are classified according to their different hydrophobicity. This is then shown to influence both the porosity and the bubble size distribution of the obtained foams. Among the tested amino acids the best amphiphile in term of operability is identified; then its adsorption at the different interfaces and the minimum amphiphile concentration necessary to obtain stable foams is identified.

## 2. Materials and Methods

### 2.1. Materials

Fumed  $\text{TiO}_2$  particles (grade AEROXIDE P25) were obtained from Evonik Industries (Essen, Germany). The supplier technical data sheet states that the primary particles have a mean diameter of approximately 21 nm while their aggregates are several hundred nm in size. Density and surface area are  $4 \text{ g/cm}^3$  and  $50 \text{ m}^2/\text{g}$  respectively. The AEROXIDE P25 is characterised by an anatase/rutile ratio of 80/20 with both crystal structures having a tetragonal geometry.

The amino acids used to modify the particles surface were DL-Alanine 99%, DL-Valine 99%, DL-Isoleucine 99%, DL-Leucine 99%, DL-

Methionine 99%, DL-Phenylalanine 99%, DL-Tyrosine 98% and DL-Tryptophan 99% (Alfa Aesar, Heysham, United Kingdom). Other chemical used in the experiments were demineralised water, nitric acid 70% v/v (Alfa Aesar, Heysham, United Kingdom) and potassium hydroxide solution 40% v/v prepared by dissolving potassium hydroxide pellets (Alfa Aesar, Heysham, United Kingdom) in demineralised water.

### 2.2. Suspension Preparation

Titania suspensions were prepared by stepwise addition of the powder to deionised water continuously stirred using an IKA EUROSTAR power control-visc overhead mixer. The pH of all suspensions was adjusted to electrostatically stabilise the particles. Titania particles are stable at pH either below 4 or above 7. To favour the dissolution of amino acids the pH was kept either below 2 or above 10 through the addition of small aliquots of 70% v/v  $\text{HNO}_3$  and 40% v/v KOH respectively. The solid loading of titania suspensions was set to 25% w/w. In a typical formulation, carried out at acid pH, 99.7 g of titania was added to 250 ml of demineralised water containing 50 ml of 5% v/v  $\text{HNO}_3$ . After powder dispersion the suspension pH was dropped below 2 through the addition of 5 ml of 70% v/v  $\text{HNO}_3$ . Then an amino acid was added to the titania suspension to obtain the required concentration in the range 0.08 and 0.36 mol/L.

### 2.3. Foaming and Foam Characterisation

Foaming of 300 mL suspension was carried out using an overhead stirrer equipped with a gas inducing impeller [15]. The vessel diameter and impeller diameter were  $T = 12 \text{ cm}$  and  $D = 6 \text{ cm}$  respectively ( $D/T = 50\%$ ). The vessel was fitted with 4 baffles 1 cm wide ( $B/T = 8.3\%$ ). Mixing was carried out at 2000 rpm for 20 minutes. The foam was dried under ambient conditions and then calcined in a Carbolite Furnace CWF at  $600^\circ\text{C}$  for 4 hours. During the ramping step and for the first 45 minutes the furnace was purged under  $\text{N}_2$  followed by air. The heating rate was  $2^\circ\text{C}/\text{min}$ .

The porosity of the calcined foam was initially evaluated by both mercury intrusion porosimetry and water pick-up. The average difference between the two techniques was 4% so the quicker water pick-up experiment was used for further analysis; for this reason, only the porosity values determined by water pick-up are reported herein. In this technique, the initial weight of four foam samples was recorded then these were immersed in water and the weight of the wetted samples was recorded over a four days period. The average amount of water picked up was determined by difference between the weight of the wet foam and the initial weight. From this value the foam porosity and pore volume were calculated.

Foam bubble size distribution was determined by acquiring optical microscope (Nikon Eclipse E200) images of the foam cross section. Bubble's diameters were obtained by analysing the acquired images with Fiji ImageJ 1.50a (Wayne Rasband, National Institute of Health, USA) [16]. The obtained diameters were corrected by dividing them by 0.79 in order to take into account the random position of the bubbles during sample sectioning. The correction factor was determined by Williams et al.; they identified that the mean pore diameter determined from 2D images is 79% of the actual pore diameter. This factor was derived from numerical methods that they developed and described in order to correct the underestimated pore size obtained from 2-D cross section [17].

### 2.4. SS-NMR

Titania suspensions having pH of 1, 4 and 10 were prepared using the procedure described in Section 2.2. Titania particles were modified by the addition of 0.2 mol/L of DL-Phenylalanine. The suspensions were dried at ambient condition and then ground using mortar and pestle. The SS-NMR spectrum was acquired at a static magnetic field

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