# Adhesion force and wetting behaviour of LAS acid bridges: a comparison of different neutralisation states in relation to detergent granulation

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## ABSTRACT

*LAS acid is one of the largest used surfactants in industrial detergent granulation processes. Industries are always trying to improve their products to mach the wishes of the consumer and this can be done with a good understanding of the variables and of the material's behaviour during each stage of the granulation. In this paper preliminary results on the behaviour of LAS acid used as a binder in relation to granulation of alkaline particles will be illustrated. A micromanipulator system developed at University College London and called a Micro Force Balance has been used to carry out experiments on LAS acid pendular liquid bridges between glass particles. Since LAS acid is known to react with alkali at the solid-liquid interface, the experiments are carried out using inert particles and acid that has been pre-partially neutralised with the alkaline powder. The aim is to establish the binder's wetting properties in various partially neutralised states and to investigate whether the acid phase changes influence the adhesive strength of individual pendular liquid bridges.*

## 1 INTRODUCTION

Industries using agglomeration processes are always trying to improve their product qualities by changing the formulations and operating parameters. Therefore, understanding the importance of each variable and predicting the behaviour of colliding binder-coated primary particles is necessary to model granulation processes satisfactorily. The aim of the work reported here is to study the behaviour of LAS acid used as a binder, in the manufacturing of soap. Information about the pendular stage of agglomeration can be derived from the analysis of the individual strength of a liquid bridge holding two particles together. In the literature, work has concentrated on both the experimental investigation of the force developed by a liquid bridge, and to its modelling (Willett 2000). A Micro Force Balance (MFB), developed by Fairbrother and Simons (2000), has been used successfully by Rossetti and Simons (2003) to determine the role of the capillary pressure and surface properties in the development of the liquid bridge and its geometry. In the work presented here, the MFB was used to obtain images of the separation sequence of axially strained LAS acid pre-neutralised binders. The apparatus is not designed to investigate hydrodynamic phenomena. Nevertheless, it represents a powerful tool for the determination of viscous and capillary forces. The static strength of a pendular liquid bridge, as proposed by Fisher (1926) consists of two components; the surface tension acting at the interface between solid-liquid and the capillary effects due to the curvature of the bridge. There are two different approaches to determining the bridge strength; the so called "neck" method, where the evaluation is made at the mid-point of the bridge (Lian et al., 1993) and the "boundary" method, where the evaluation is made at the contact line with one of the spheres (Adams 1985). In this work the neck equations has been used as it was found to be more suited to image analysis of the experimental data.

## 2 MICROMECHANISTIC EXPERIMENTAL APPARATUS

### 2.1 The Micro Force Balance

The experimental apparatus used in this study is known as a Micro Force Balance (MFB). It was developed at University College London and has previously been used by Fairbrother and Simons (2000), Pepin et al. (2000) and Rossetti et al. (2003) to determine the role of the liquid surface properties in the development of a liquid bridge and its geometry.

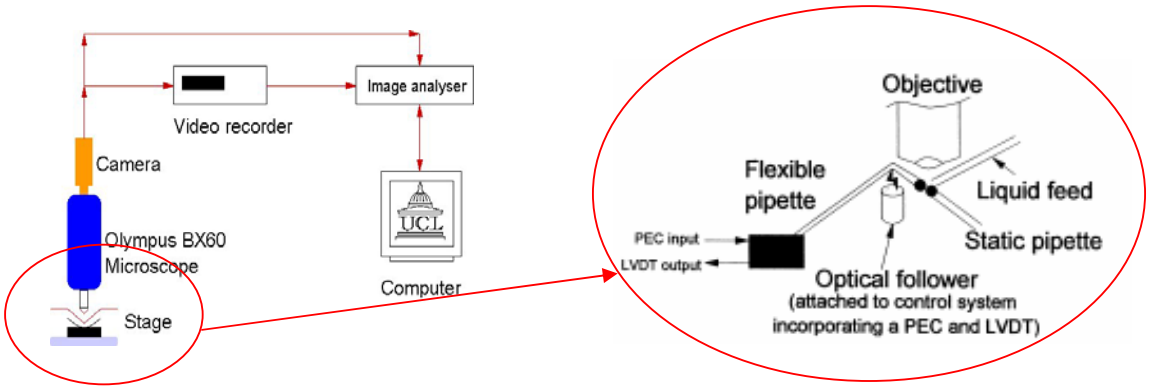


**Figure 1. Schematic of the equipment layout and of the micromanipulator stage**

The MFB consist of an optical Olympus BX60 microscope fitted with a micromanipulator stage and coupled, via a digital camera, to an image analysis and video recording system (figure 1). The optical microscope allows either transmitted or reflected illumination to be used and has a theoretical maximum resolution of 0.45 μm. On the stage two micromanipulators are employed to hold micropipettes, to the ends of which particles are attached. A third micropipette is then used to add bridging liquid between the particles. In the work presented here, MFB was used to obtain images of the separation sequence of an axially strained neutralised LAS acid bridge formed between two glass spheres. By analysing these images, adhesion force and wetting behaviour of the liquid bridge could be studied.

### 2.2 Experimental procedure

On the stage two micromanipulators are employed to hold micropipettes, to the ends of which particles are attached. Initially a straight static micropipette is clamped onto the static pipette micromanipulator, with the particle being placed under the objective lens of the microscope. Fine adjustment in all three dimensions is achieved using the individual plane micrometers. The second particle, attached to a pre-calibrated flexible micro-pipette, is then placed under the objective in contact with the first particle. Again, fine adjustment can be made using the micrometers. The bridge is formed by touching the particle on the straight pipette with a third micro-pipette covered with liquid. In this way, a drop of liquid is transferred to the particle. The particles are then put into contact and a bridge is formed (figure 2B). The particles are then separated manually (figure 2C) until the bridge ruptures (figure 2D). All the movements are imposed step by step with pauses to allow the liquid bridge to gain equilibrium. Using this separation method the influence of the dynamic force due to the liquid viscosity is negligible. The breaking sequence is captured on a video image analysis software system and individual frames are analysed using commercial software that allows pipette bending, particle separation distance and contact angles to be

calculated. The adhesive static force of the liquid bridge Fbr is eventually calculated as the product of the pipette elastic constant Ks and the pipette deflection e, as shown in equation 1:

$$F_{br} = K_s e \quad (1)$$

The volume of the bridge is calculated as the solid of revolution generated by rotating the bridge profile between the two particles about the bridge axis of symmetry.

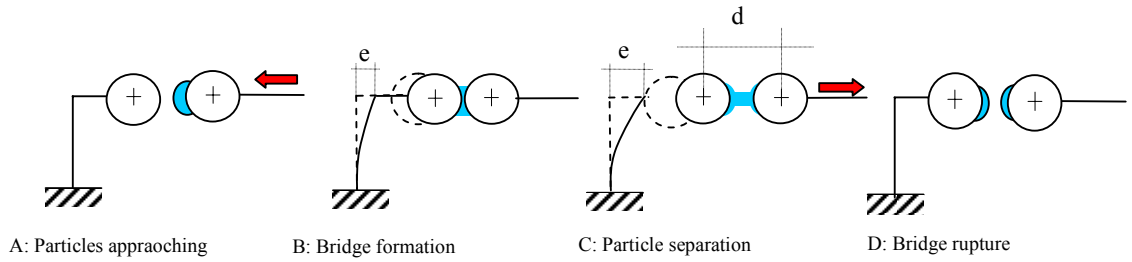


**Figure 2. Schematic of the method to calculate the strength of a liquid bridge during separation**

## 3 RESULTS AND DISCUSSION

### 3.1 Materials and experimental conditions

The experiments presented in this work have been undertaken using Linear Alkylbenzene Sulphonic acid in different neutralised states, here called Las.Na30%, Las-Na55%, Las-Na70%, Las-Na80%, Las-Na96%, as the binder between particles. These partially neutralised liquids were prepared utilising the principle of acid base neutralization reactions between LAS and Na2CO3 to form the salt, LAS-Na, along with some water. The neutralisation percentage refers to the number of moles of acid reacted to form the salt. This acid is known to react with alkaline particles. A previous investigation was carried out using the LAS acid between alkaline crystal and the results were naturally affected by the reactions at the solid-liquid interface. The images in figure 3 illustrate the crystal just after binder deposition (1), 20s later (2), after 1 minute (3) and when some excess of binder was removed 5 minutes after soaking (4). The bubbles formed on the surface of the crystal indicate that some reaction is taking place and that a gas is being given off.

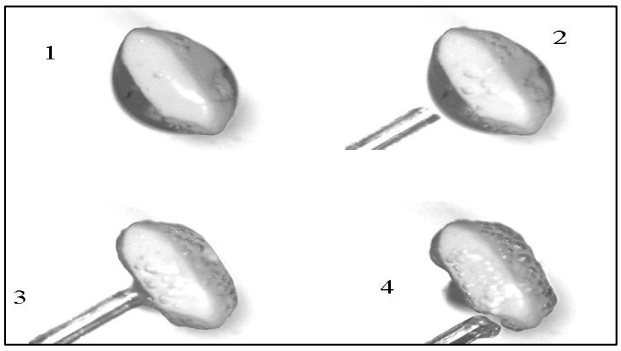


**Figure 3. Reactivity of the acid at 75 oC on a granular crystal**

In order to eliminate the influence of the reaction at the particle-bridge interface, inert particles have been selected for the current study. Soda lime glass ballotini spheres of diameters in the range 250-300 μm have been used as solid particles (Supplier: Whitehouse Scientific, Whitchurch Rd., Waverton, Chester, CH3 7PB, England). The particle diameter does not affect the bridge behaviour, only the ease of handling the spheres during the experiment. Hence, the diameters range is the largest that is possible to focus with a good resolution under a 10X microscope lens. The ballotini are cleaned with a sulphuric acid solution and dried overnight before use.

The micropipettes, used to hold the particles and feed binder during the measurements, are produced from 100mm lengths of 1.1mm O.D., 0.76mm I.D. borosilicate glass tubing (Supplier: Plowden and Thompson Ltd., Dial Glass Works, Stourbridge, West Midlands DY8 4YN.)

The behaviour of the binder is strictly related to the temperature and humidity conditions. All the experiments are carried out in room conditions. The water isotherms of the binder for such temperatures and humidity show a high capacity of the binder to take up water from the atmosphere. To avoid spoiling the binder characteristics the samples are stored in a desiccator.

### 3.2 Particle wetting for different neutralised states

The binder wettability on glass particles has been investigated with direct observations of the volume of liquid left on a particle after putting it in contact and then retracting it from a reservoir of liquid. The experiments of contact and retraction show how the degree of neutralisation affects the wetting behaviour of the binder on the particles. As shown in figure 4, the higher the degree of neutralisation, the lower the tendency of the liquid to wet the particles.

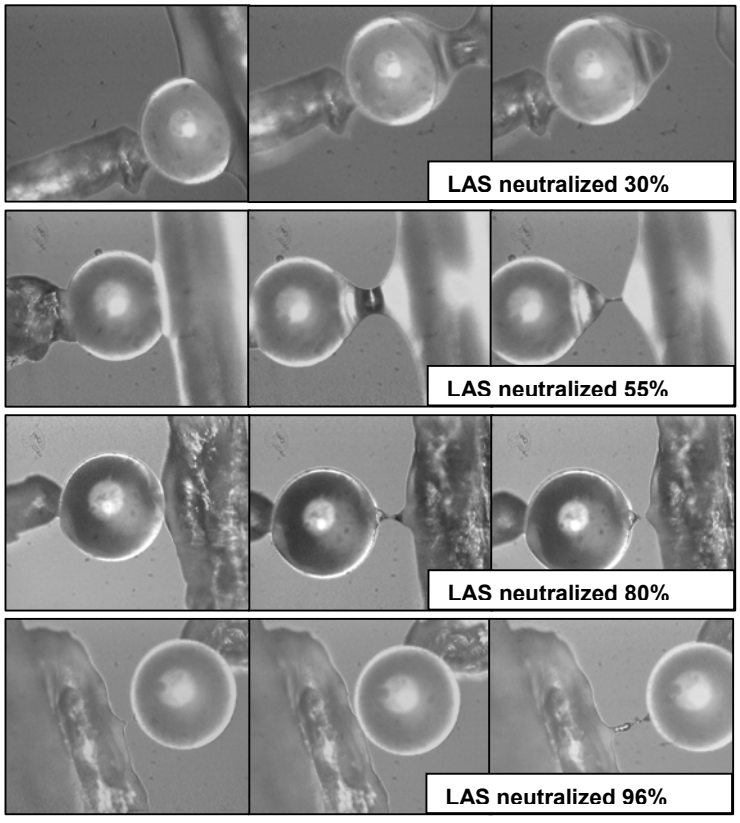

**Figure 4. Wetting sequence for 30%, 55%, 80% and 96% neutralised binder. The sequences are taken during the first attempt to contact and retract.**

Indeed, in order to get adequate wetting in the cases of 80% and 96% neutralised binder, it is necessary to force the particles into the liquid and repeat the wetting action several times. In contrast, with the 30% and 55% neutralised samples, it is possible to wet the particles on first contact. The liquid distribution in these cases is more uniform, which under process conditions would enable the binder to spread uniformly amongst the particles during mixing.

### 3.3 Liquid bridge adhesive force

Measurements of the adhesive force of each neutralised sample were carried out using the experimental procedure described in section 2.2. In figure 5 the static force of each binder has been plotted versus the separation distance between spheres.

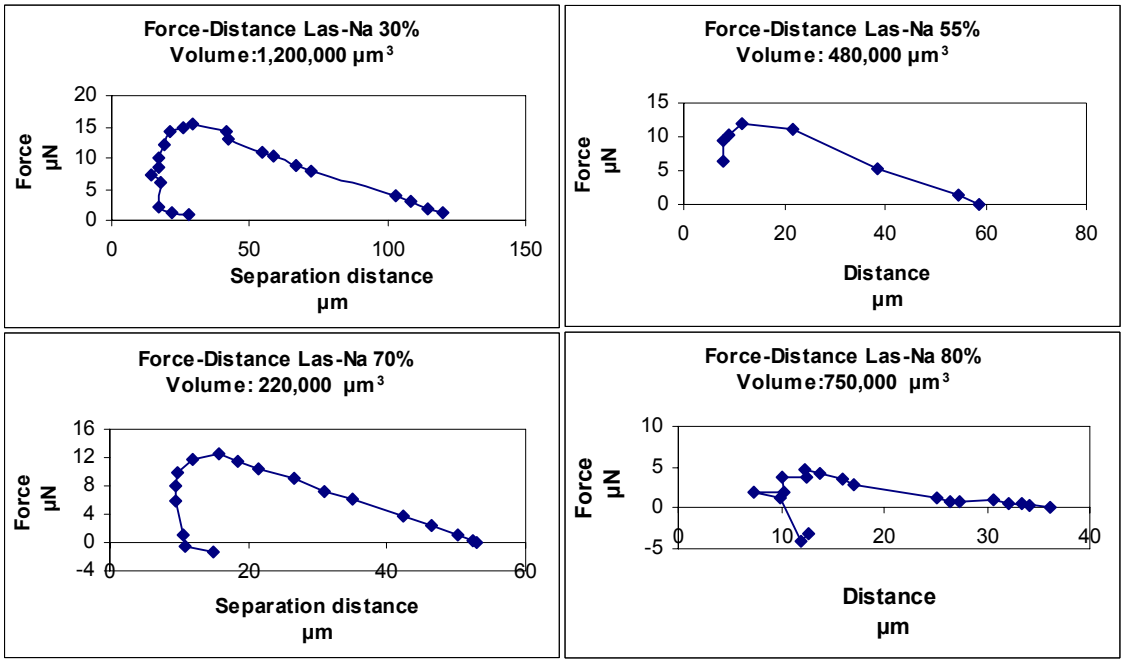


**Figure 5 Force of adhesion versus separation distance for 30%, 55%, 70% and 80%% neutralised samples.**

The trend of the curve is comparable to those presented by Mason and Clark (1965), The particles were not put in contact at the start of each experiment. This explains why the initial separation distance is not zero. The initial separation distances shown in figure 5 are the distances between the spheres at the moment of bridge formation and before the beginning of the separation sequence. The difference in value is due to the difference in the bridging volumes and to the wetting properties expressed by each different sample. The low neutralised samples (30%, 55%) express better wettability and higher ability to flow from the feed pipette. This results in a higher amount of bridging volume and therefore in a higher initial and final separation distance. The experimental force of adhesion Fbr can be explained using the neck method (Lian et al. 1993):

$$Fn = 2\pi r\gamma - \pi r^2 \Delta P \quad (2)$$

In equation 2 Fn is the bridge force, r is the bridge neck radius, $\gamma$ the liquid surface tension and $\Delta P$ the capillary pressure. Due to the particle dimensions, the effect of gravity is ignored in this work (Princen 1968)

The force shows a maximum that corresponds to the configuration where the capillary pressure is at its minimum. As separation distance increases, the diminution of the neck radius and increase in the capillary pressure lead to the decrease in force. In fact, near to rupture the meniscus is similar to an umbilical cord, the radius of the bridge is at its lowest, the capillary pressure increases and the force runs to zero.

Figure 6 shows a preliminary comparison of forces expressed by bridges of different samples at the same separation distance of 30 μm. Each force has been normalised in respect to the bridge volume $F/V^{1/3}$. The trend indicates that force and rupture energies decrease with increasing degree of neutralisation. This is indicative of the overall effect of neutralisation. The effects on surface tension and viscosity are currently unknown, as the actual values are yet to be measured experimentally. This will be done in the near future.

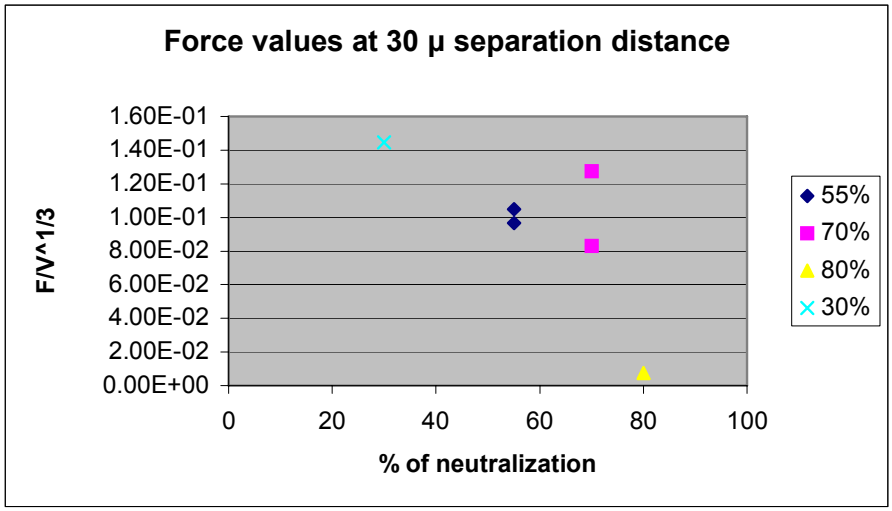


**Figure 6 Comparison between forces expressed at 30 μm separation distance**

## 4 CONCLUSIONS AND FUTURE WORK

The wetting is responsible for the distribution of liquid binder during particle-binder mixing. The lower neutralized binders show the best wetting behaviour. Difficulties exhibited by the 96% and 80 % neutralised samples in depositing on the glass spheres indicate that during granulation the binder would not be uniformly distributed. Since at this stage it is not possible to use sodium carbonate particles, because of the reaction taking place with the acid binder, the effect of wetting behaviour on different surfaces will be studied by silanising the glass to varying degrees of hydrophobicity. The future work will include also testing and calibrating a new device that allows dynamic separation, the viscosity of each sample will be measured and its contribution will be added to the static bridge force.

## 5 ACKNOWLEDGEMENTS

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