# Insights into the Functional Behaviour of Lecithin in Oil-Based Suspensions

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## ABSTRACT

Model suspensions made of icing sugar and soybean oil or medium chain triglycerides (MCT) were used in rheological and forced sedimentation experiments. In general, lecithin caused a reduction in apparent viscosity, yield stress and sediment volume which was more pronounced in the case of MCT-based suspensions. Atomic force microscopy showed that the lecithin induced reduction of rheological parameters and sediment volume is in line with a decrease of adhesive interaction forces after sugar surfaces got into contact.

## INTRODUCTION

Vegetable lecithin has, among other applications, great importance as flow enhancer in confectionery production. Because of this, the impact of lecithin on rheological properties of oil-based suspensions has been extensively investigated and compared to other surfactants[1-4]. In general, the addition of lecithin results in a decrease of apparent viscosity and yield stress. These functional properties of lecithin are caused by their surface active compounds in which phospholipids dominate[5].

While the benefit of lecithin is well known, the microstructural basis of the impact of lecithin in suspensions is not thoroughly clarified. Investigations with confocal laser scanning microscopy and solvent extraction experiments denoted the adsorption of surface active compounds at the sugar/fat interface[6,7]. Sedimentation experiments revealed the influence of lecithin on particle interactions in oil-based suspensions[8,9]. However, the interactions between surface-active components of lecithin and suspension constituents, and their effects on the rheological behaviour of the bulk suspension are still not completely understood.

Aim of the study was to deepen the understanding of the interrelations between the effects of lecithin on particle interactions and suspension rheology as influenced by the dispersion medium.

## MATERIALS AND METHODS

Icing sugar *(*Pfeifer & Langen KG, Köln, Germany*)* was purchased from a local supermarket. The sugar was dried at 60 °C and 200 Pa for 24 h and subsequently stored in a desiccator until suspension preparation.

Soybean oil was purchased from a local supermarket, and AkomedR, a medium chain triglyceride (MCT), was provided by AarhusKarlshamn (Karlshamn, Sweden). To remove surface active compounds and other impurities, 6 % (w/w) silica was dispersed in soybean oil and MCT for at least 12 h, and subsequently removed by centrifugation at 10,000 g for 15 min. The supernatant was then filtered over a 520 B ½ folded filter (Whatman GmbH, Dassel, Germany).

Technical grade soybean lecithin was provided by Central Soya European Lecithins GmbH & Co. KG (Hamburg, Germany).

The pre-weighed suspension ingredients (oil, solids and surfactant) were dispersed with an axial impeller stirrer by applying a rotational speed of 1,000 rpm for 60 min. After a resting time of 30 min, the suspensions were degassed in an ultrasonic bath (Elma Hans Schmidbauer GmbH & Co KG, Singen, Germany) for 30 min. Because the phospholipids are mainly responsible for the functionality of lecithin, the incorporated amount was calculated on the basis of the target phospholipid concentration ($C_{PL}$).

As the particles exhibited different BET surfaces, and because surfactants are assumed to adhere at the solid-liquid interface in suspensions, rheological and sedimentation experiments were performed at a phospholipids/surface ratio (PL/S ratio) of 0, 3.25 or 16.26 mg/m$^2$. For rheological experiments we prepared sugar/oil-suspensions with a volume fraction $\phi$ [-] of 0.31 while, for sedimentation experiments, a volume fraction of 0.10 was used. The lower $\phi$ was selected to allow a faster sedimentation, and to ensure comparability with previous investigations[8,9].

For rheological characterization shear stress $\tau$ [Pa] was measured as a function of shear rate $\dot{\gamma}$ [1/s] which was decreased from 1000/s to 0.01/s in a logarithmic ramp within 990 s. Herschel-Bulkley model parameters extracted from stress ramp measurements, and apparent viscosity $\eta_{app}$ [Pa.s] at selected shear rates (1000/s; 10/s) were used to characterize the impact of the surfactant.

The sedimentation behaviour of the suspensions was investigated using a LUMiFuge 116 (L.U.M GmbH, Berlin, Germany). Approximately 400 µl of suspension were transferred into a centrifuge tube and the settling regime was analyzed at 25 °C and a centrifugal force of 12 g. Finally, the relative volume of the sediment $V_S$ was calculated.

Interactive forces between sugar particles and a flat sugar surface (support) were determined by atomic force microscopy (AFM) using a NanoWizard II (JPK Instruments, Berlin, Germany). Colloidal force probes were prepared by attaching sugar particles to the apex of tipless V-shaped cantilevers (NP-O, Bruker, Camarillo, USA) with a two-component epoxy glue. Supports were prepared by crystallization of a sugar solution (40 g/100 g) in 35 mm petri dishes.

Force/separation (F/S) curves were determined during approach and retraction of modified cantilevers and surfaces. Additionally, the maximum force required to separate modified cantilevers and supports ($F_D$) was extracted from retraction F/S curves. Measurements were performed in soybean oil or MCT supplemented with soybean lecithin at concentrations of $C_{PL}$ = 0, 0.001, 0.01, 0.1 or 0.5 g/100 g at room temperature.

With every cantilever/support pair a total of 100 F/S curves at 10 different measurement points was recorded for each lecithin/oil dispersion. Average $F_D$ of these measurements was normalized with respect to the mean value of $F_D$ for the same cantilever/support pair in fresh oil ($C_{PL}$ = 0 g/100 g).

## RESULTS AND DISCUSSION

The addition of lecithin resulted in a drastic change of the flow curves of sugar/MCT- and sugar/soybean oil-suspensions (Fig. 1). The surfactant-induced reduction of apparent viscosity was influenced by the dispersion medium. While, in sugar/MCT-suspensions, $\eta_{app}$ decreased by 40 % ($\dot{\gamma}$ = 1000/s) and 94 % ($\dot{\gamma}$

= 10/s), the impact of lecithin in sugar/soybean oil-suspensions was weaker (reduction by 20 % respective 70 %).

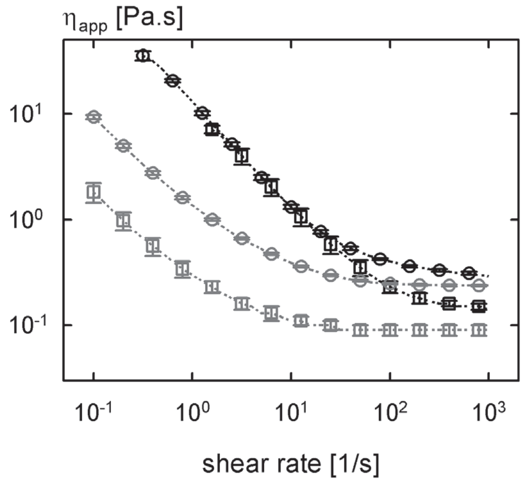


Figure 1. Viscosity functions of sugar/MCT-(squares) and sugar/soybean oil-suspensions (circles) as affected by addition of lecithin. Phospholipids/surface ratio: 0 mg/m$^2$ (black), 3.25 mg/m$^2$ (grey).

For both suspensions, the impact of lecithin depended on the shear stress in the sample. The highest influence of the surfactant was detectable for yield stress which was reduced by 99 % (in MCT) or 93 % (in soybean oil) after addition of lecithin. The results indicate that the surfactant influences particle interactions which dominate the rheological properties of suspensions at low stress. Furthermore, the results suggest that lecithin has a higher impact on particle interactions in MCT-based suspensions.

The time and space resolved transmission profiles during forced sedimentation of sugar/oil-suspensions without lecithin ($\phi = 0.1$) showed zone sedimentation (Fig. 2). The sharp transmission profiles revealed a clear boarder between settling particles and a particle-free supernatant, meaning that the particles settle with equal velocity and independent of their mass. This behaviour indicates sugar particle flocculation[10].

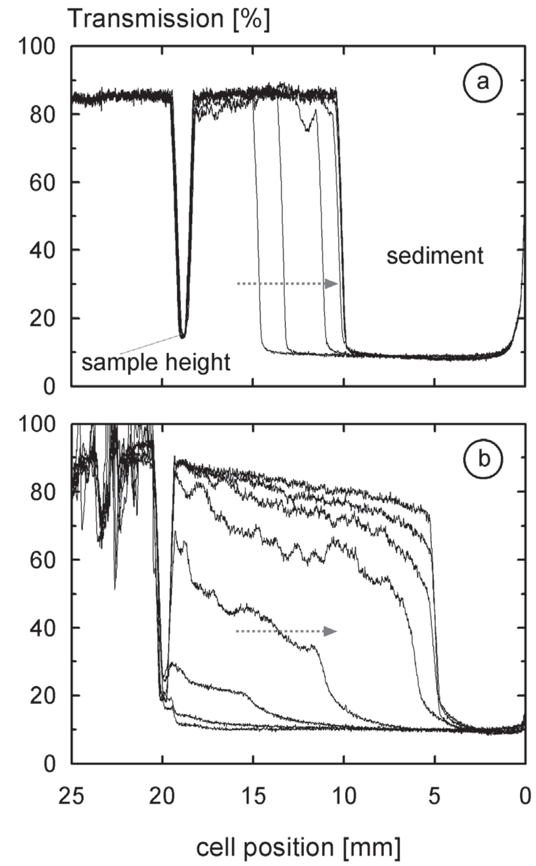


Figure 2. Progress of transmission profiles during sedimentation of a sugar/oil-suspension as affected by addition of lecithin. Phospholipids/surface ratio: 0 mg/m$^2$ (a), 3.25 mg/m$^2$ (b). The arrow indicates the progress of sedimentation.

The addition of lecithin resulted in a change of the sedimentation behaviour (Fig. 2). A polydisperse sedimentation was detectable in which particles showed different sedimentation velocities which indicates a higher particle stability against aggregation due to addition of lecithin[11].

As shown in Figure 3, the addition of surfactant also caused a reduction of the sediment volume ($V_S$). In general the effect of lecithin during forced sedimentation is comparable to the action of the surfactant during sedimentation under gravity and is dedicated to the reduction of attraction between particles that makes them pass each other more easily[8,9]. Again the impact of lecithin was more pronounced in MCT-based suspensions. In this suspensions $V_S$ decreased by 55 % while in sugar/soybean oil-suspensions $V_S$ was reduced by 45 %.

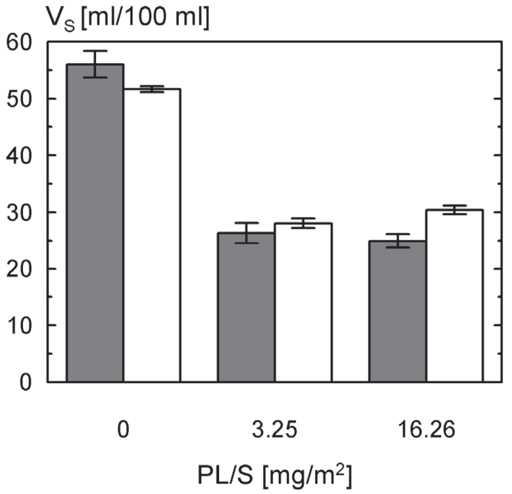


Figure 3. Sediment volume of sugar/MCT- (grey bars) and sugar/soybean oil-suspensions (open bars) as affected by the presence of soybean lecithin (expressed as phospholipids/surface ratio (PL/S)).

Although sedimentation analysis showed that lecithin influenced the interactions between sugar particles, it is not possible to attribute these changes to variations in attractive respective repulsive forces before or after the particles get into contact.

For this reason, we characterized interactions between sugar surfaces in soybean oil or MCT by the use of AFM. Figure 4 shows examples of a force/separation function between sugar surfaces in soybean oil without lecithin or a lecithin/oil-dispersion ($C_{PL}$ = 0.01g/100g). During approach, no interactions were detectable until surfaces got into contact and a linear increase of the force was measured. After contact, the cantilever was retracted. At low distances a hysteresis between the force signal of approach and retreat was obvious, indicating attractive forces between the sugar surfaces. Hence we can conclude that the interactions of sugar particles in oil-based systems are dominated by adhesive forces after the particles got into contact.

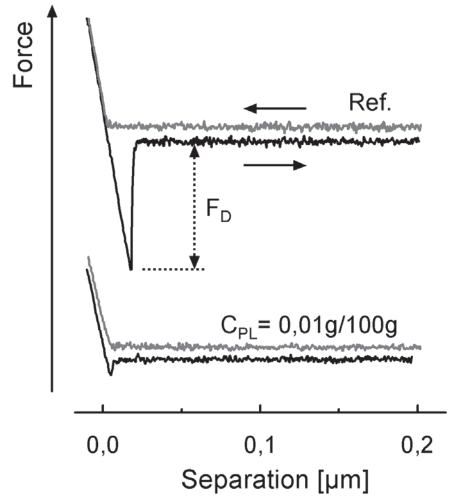


Figure 4. Force/separation function between sugar surfaces in soybean oil without lecithin (Ref.) and a lecithin/soybean oil dispersion ($C_{PL}$ = 0.01 g/100 g)

The addition of lecithin resulted in a clear decrease of $F_D$, indicating the impact of the surfactant on adhesive interactions. The amount of reduction was influenced by the concentration of the surfactant and the dispersion medium (Fig. 5).

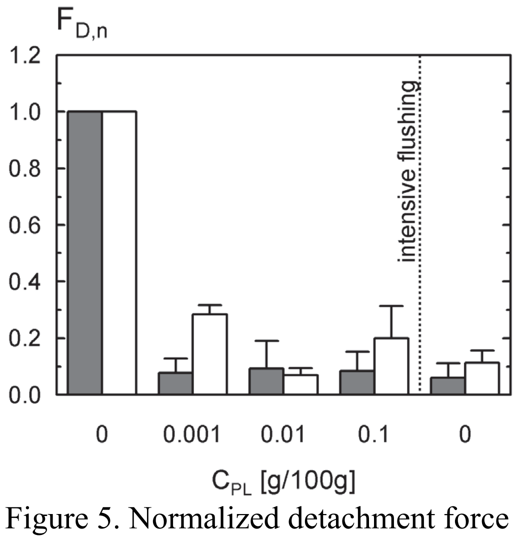


Figure 5. Normalized detachment force between sugar surfaces in lecithin/MCT- (grey bars) and lecithin/soybean oil-dispersions (open bars) with increasing phospholipid concentration and after intensive flushing with lecithin free oil.

While, in MCT, $F_D$ was reduced by 90 % at $C_{PL}$ = 0.001 g/100 g, the minimum of $F_D$

in soybean oil was reached at $C_{PL}$ = 0.01 g/100 g. A further increase of $C_{PL}$ resulted in insignificant changes of $F_D$.

After interactions between sugar surfaces at highest $C_{PL}$ were determined the measuring setup was intensively flushed with fresh oil, followed by a repetition of the measurements. The determined $F_D$ was similar to that of lecithin enriched dispersions as measured before. Hence the impact of lecithin on adhesive forces is caused by the action of molecules which are strongly adsorbed to the solid surface. The results of AFM are in line with the findings of Harris[6] and Vernier[7] who determined that the influence of lecithin on the rheology of sugar/oil-suspensions is based on the surfactants firmly adsorbed to the sugar surface.

The results indicate the relationship between decreasing adhesive forces and a reduction of rheological parameters. The more pronounced effect of lecithin on rheology of MCT based suspensions correlates with its higher impact on particle interactions as characterised with AFM and sedimentation analysis. As reasons for the impact of the dispersion medium on the behaviour of lecithin, differences in aggregation, adsorption and structuring at the interfaces have to be considered and will be examined in further work.

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