

# RHEOLOGICAL AND STRUCTURAL CHANGES DURING THE MIXING OF SUSPENSIONS AND EMULSIONS

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## ABSTRACT

The rheological effects occurring when an emulsion is mixed with a suspension can be detected using a helical ribbon stirrer. The stirrer rotates in a rheometer cup and is connected to the torque sensor of the rheometer. During mixing, microstructural changes which are related to the interactions between the continuous fluid phase and the disperse droplets (or disperse solid particles) as well as between droplets and particles will have a strong impact on the measured apparent viscosity. Phase interactions and surfactant influences can thereby be described in terms of their effect on the viscosity of the mixture. The viscosity trend during the mixing time is strongly dependent from the disperse phase concentration of the suspension, the polarity of the suspension particles and from the nature of the emulsifiers used. When a structural equilibrium is reached, the apparent viscosity as measured with the stirrer can be recalculated using the Rieger-Novak and the Metzner-Otto approach. This allows for a comparison of the apparent viscosities as determined by means of the stirrer and viscosities as determined in uniaxial shear in the concentric cylinder geometry. As microscopic observations demonstrate, the final state of the mixture of emulsion and suspension is the state with the energy minimum of the interfacial system, *i.e.* the total interfacial area is minimised by forming water containing agglomerates in a continuous oil phase.

## ZUSAMMENFASSUNG

Die rheologischen Effekte, die beim Mischen einer Suspension mit einer Emulsion auftreten, können mittels eines Wendelrührers erfasst werden. Der Rührer rotiert in einem Rheometer-Cup und ist an den Drehmomentsensor des Rheometers montiert. Während des Mischvorgangs haben mikrostrukturelle Veränderungen einen grossen Einfluss auf die gemessene scheinbare Viskosität. Die Strukturveränderungen betreffen die Wechselwirkungen zwischen der kontinuierlichen Fluidphase und den dispersen Tropfen (beziehungsweise Partikel) sowie Wechselwirkungen zwischen Tropfen der Emulsion und Partikeln der Suspension. Phasen-Wechselwirkungen und die Einflüsse von Emulgatoren können so in Bezug auf ihren Einfluss auf die Viskosität des Gemischs beschrieben werden. Der Viskositätsverlauf während der Mischzeit ist stark abhängig von der Dispersphasenkonzentration der Suspension, der Polarität der Partikel und der Art der verwendeten Emulgatoren. Wenn ein Struktur-Gleichgewicht im Gemisch erreicht wird, kann die scheinbare, mit dem Rührer gemessene Viskosität mittels des Rieger-Novak- und Metzner-Otto-Verfahrens umgerechnet werden. Dies erlaubt es, die Rührer-viskosität mit Viskositäten zu vergleichen, die unter uniaxialer Scherung in der konzentrischen Zylindergeometrie bestimmt werden. Wie mikroskopische Untersuchungen belegen, ist der Endzustand der Gemische der Zustand, der dem Grenzflächenenergie-Minimum des Systems entspricht, das heisst die gesamte Grenzfläche der Ausgangssysteme Emulsion und Suspension wird minimiert, indem sich wasserhaltige Agglomerate in einer kontinuierlichen Ölphase bilden.

## RÉSUMÉ

Les effets rhéologiques qui prennent place, lorsqu'une émulsion est mélangée avec une suspension, peuvent être détectés en utilisant un mélangeur à ruban hélicoïdal. Le mélangeur tourne dans le récipient d'un rhéomètre et est connecté au capteur de force du rhéomètre. Pendant le mélange, les changements microstructuraux, qui sont associés aux interactions entre la phase fluide continue et les gouttelettes dispersées (ou les particules solides dispersées), ainsi qu'entre les particules et les gouttelettes, auront un fort impact sur la viscosité apparente mesurée. Les interactions de phase et les influences du surfactant peuvent être ainsi décrites en étudiant leur effet sur la viscosité du mélange. L'évolution de la viscosité pendant la durée du mélange dépend fortement de la concentration de la phase dispersée dans la suspension, de la polarité des particules en suspension et de la nature de l'émulsifiant utilisé. Lorsque un équilibre structural est atteint, la viscosité apparente mesurée avec le mélangeur peut être recalculée en utilisant l'approche de Rieger-Novak et de Metzner-Otto. Ceci permet de comparer les viscosités apparentes déterminées au moyen du mélangeur avec les viscosités déterminées par cisaillement uniaxial en géométrie de cylindres concentriques. Comme le démontrent les observations microscopiques, l'état final du mélange d'émulsion et de suspension est l'état possédant l'énergie minimale du système interfacial, *c-à-d*, la surface interfaciale totale est minimisée par la formation d'eau contenant des agglomérats dans une phase d'huile continue.

**KEY WORDS:** Mixing of emulsion and suspension, viscosity, particle-particle interaction, structure

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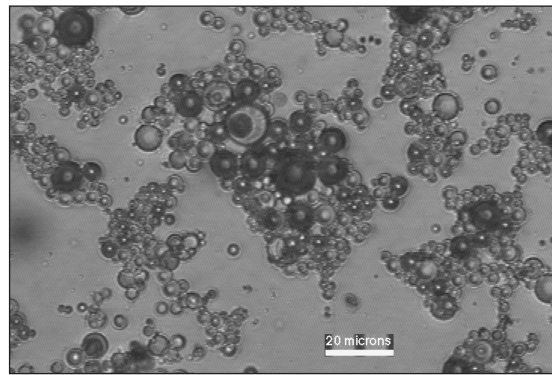
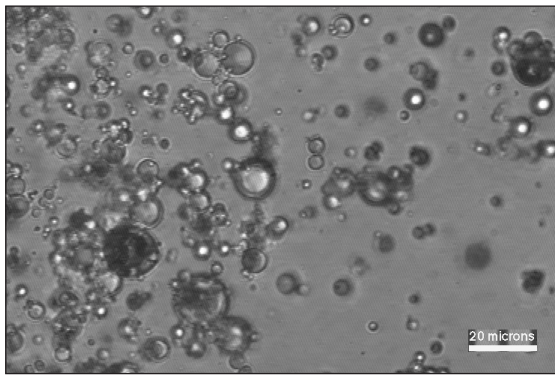


Figure 7 (left): Mixture of hydrophilic glass spheres suspension and PGPR emulsion after 1000s mixing time.

Figure 8 (right): Mixture of hydrophilic glass spheres suspension and PGPR emulsion after 18 min. mixing time.

emulsion containing PGPR at 0.48 rev/s and observed under the microscope.

The glass beads and the emulsion droplets can be recognised in the continuous oil phase. The emulsion droplets have partially adsorbed to the glass spheres. Under the microscope, coalescence phenomena can be observed, which happen between two water droplets and water droplets and beads, i.e. the mixture is not stable even at rest. The activation energy for film drainage and coalescence is provided by the thermal energy at 20°C. The identical mixture exhibits far stronger aggregation and the build-up of a particle network after 18 minutes of mixing time.

The aggregates consist of glass beads and water between the particles and on their surface. Some water droplets still remain. The spreading of the water in the agglomerate can be observed at rest under the microscope. The water wets the particles very slowly on their surfaces, but is virtually sucked into the interparticle spaces.

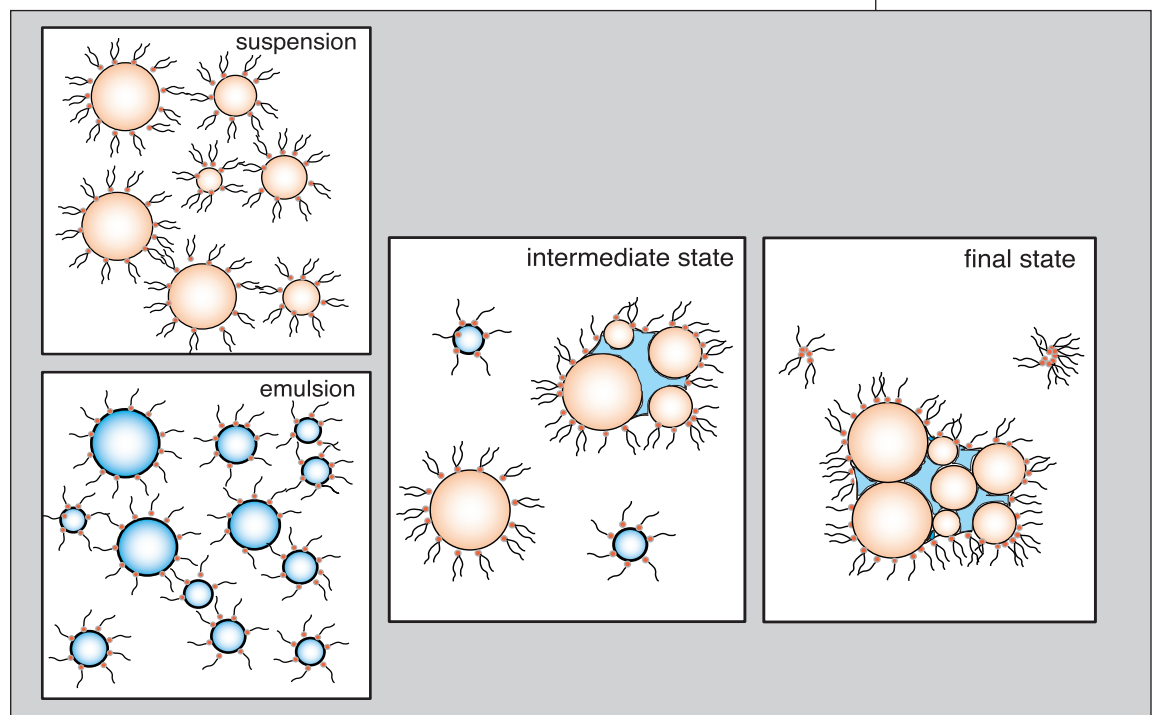
interactions with other suspension particles. Moreover, liquid bridges can form between the solids. This leads to an increasing tendency of the solids to agglomerate, thereby forming agglomerates which build up a network at higher disperse phase concentration. Hydrophobic particles undergo the same changes, but slower. They form weaker networks, which may be attributed to the incomplete wetting of the surfaces exposed to the continuous phase and hence reduced hydrophilic interactions and a lower tendency to form liquid bridges. Since attractive forces arising from liquid bridges are directly proportional to the cosine of the contact angle sphere-oil-water ( $\cos \theta$ ), the liquid bridge formed with the hydrophobic spheres will be weaker [16].

The flocculation of particles and droplets leads to a reduced interface between oil and the particles. This means that the surfaces are oversaturated and emulsifier has to desorb from the interface to form micelles in the continuous

Figure 9: Structural model of mixtures from suspensions and emulsions.

### 3.3.2 STRUCTURE MODEL

The microscopical observations can be described in a model as shown in Fig. 9. The emulsion and the suspension are stable systems with saturated interfaces at the beginning of the mixing process. The contact with the solids of the suspension destabilises the emulsion in the mixing process. The larger droplets of the emulsion are disrupted first. The free water adsorbs to particle surfaces and increases their hydrophilic



phase or multilayer structures on the surface of the particles [11], [17]. The interfacial energy of the final state of the mixture is strongly reduced and the mixture is stable except for sedimentation.

#### 4 SUMMARY / OUTLOOK

The present new approach to studying interaction phenomena occurring during the mixing of an emulsion and a suspension can quantify the effect of the particle-particle and particle-continuous phase interactions on the apparent viscosity of the mixture. The flow behavior of structurally stable suspensions can be measured using the same geometry as for the mixing. The torque and the rotational speed from the flow curves obtained can be used to calculate the representative viscosities as a function of rotational speed or – if the mixture can be measured as well in a conventional rheometer geometry – as a function of representative shear rate.

The results obtained can be helpful for studying particle-particle interactions as occurring in agglomeration in suspension processes, a separation process where fines are agglomerated using a binder liquid [18]. Our future work will concentrate on the interactions of the model suspension particles with the droplets of the model emulsion. A dependence of the interaction strength and the speed of interactions from particle coverage with emulsifiers can be presumed and was already demonstrated in preliminary experiments.

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