Influence of Cluster Formation: Viscosity of Concentrated Emulsions

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Abstract:
Recently a new theory of viscosity of concentrated emulsions dependency on volume fraction of droplets (Starov V, Zhdanov G: J. Colloid Interface Sci, 258, 404 (2003)) has been suggested that relates the viscosity of concentrated emulsions to formation of clusters. Through experiments with milk at different concentrations of fat, cluster formation has been validated using optical microscopy and their properties determined using the mentioned theory. Viscometric studies have shown that within the shear rate range studied, both the packing density of fat droplets inside clusters and the relative viscosity of milk (viscosity over skim milk viscosity) are independent of shear-rate, but vary with volume fraction. Comparison of the experimental data with previous theories that assumed that the particles remained discrete shows wide variation. We attribute the discrepancy to cluster formation.

Zusammenfassung:
Kürzlich wurde eine neue Theorie für die Abhängigkeit der Viskosität konzentrierter Emulsionen vom Volumenbruch der Tröpfchen vorgestellt (Starov V, Zhdanov G: J. Kollodiale Schnittstelle Sci, 258, 404 (2003)), in der die Existenz von Agglomeraten ausschlaggebend ist. Anhand von Experimenten mit Milch bei unterschiedlichen Fett-Konzentrationen wurde nun die Agglomeratbildung mit optischer Mikroskopie validiert. Viskometrische Studien zeigen innerhalb des untersuchten Scherratenbereiches, dass sowohl die Packungsdichte der Fett-Tropfen innerhalb der Agglomerate, als auch die relative Viskosität der Milch unabhängig von der Scherrate sind, aber vom Volumenbruch abhängen. Ein Vergleich der experimentellen Daten mit älteren Theorien, die annehmen, dass die Partikel nicht agglomerieren, zeigt grosse Abweichungen auf. Wir können daher von einer Agglomeratbildung ausgehen.

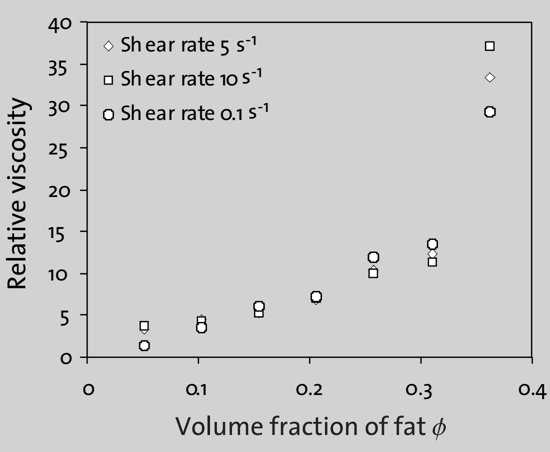
Résumé:
Récemment une nouvelle théorie pour la dépendance de la viscosité des émulsions concentrées avec la fraction volumique des goutellettes (Starov V, Zhdanov G: J. Colloid Interface Sci, 258, 404 (2003)) a ete suggérée: elle relie la viscosité des émulsions concentrées avec la formation d'aggrégats. En faisant des expériences sur du lait à différentes concentrations en graisse, la formation d'aggrégats a été validée en utilisant la microscopie optique, et leurs propriétes ont été déterminées en utilisant la théorie mentionnée ci-dessus. Les études viscosimétriques ont montré que dans le domaine de vitesse de cisaillement étudié, la densité de remplissage des goutellettes de graisse à l'intérieur des aggrégats, de même que la viscosité relative du lait (viscosité divisée par la viscosité du lait crêmeux) ne dependent pas de la vitesse de cisaillement, mais varient avec la fraction volumique. La comparaison des données expérimentales avec les théories précédentes qui supposaient que les particules restaient disconnectées montre une grande disparité. Nous attribuons cette différence à la formation d'aggrégats.

Key Words: viscosity, concentrated emulsions, clusters

1 INTRODUCTION

Emulsions are dispersions of droplets of one liquid in another immiscible liquid. Such systems are thermodynamically unstable: the droplets coalesce over time. Stability against coalescence is conferred by a surface-modifying substance (surfactant or polymer) adsorbed around the droplet surfaces.

Emulsions find widespread use in industry e.g. food emulsions, cosmetics, pharmaceuticals, agricultural sprays and so on [1]. Most of them are usually concentrated, in the sense that particle-to-particle interactions contribute significantly to observed bulk properties. Knowledge of the flow properties (the most important of which is viscosity) of emulsions is important in the design, selection and operation of the equipment involved in mixing, storage and pumping of these systems. Further, quality aspects of most food and cosmetic products (products whose properties are structure dependent) for example creaminess and



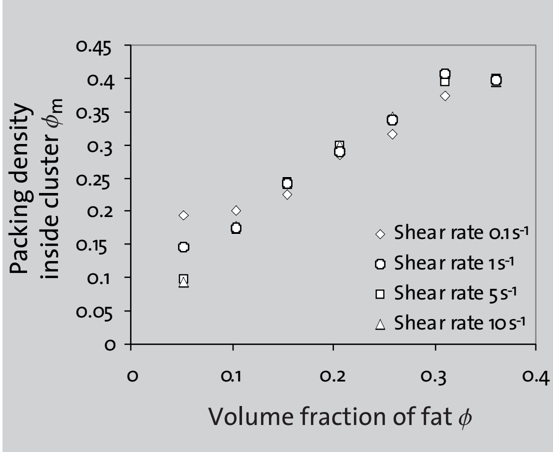


Figure 4 (left): Trend curve for relative viscosity against volume fraction of fat.

Figure 5 (right above): Variation of the packing density of droplets inside clusters with volume fraction.

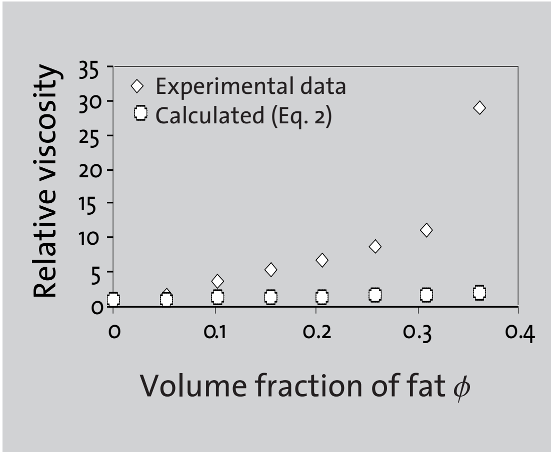
Figure 6 (right below): Comparison between experimental data and predictions of the Phan-Thien and Pham model (Eq. 2).

sents the relative viscosity plotted against the volume fraction of fat. It can be seen that the experimental points all fell on a master curve. The latter means that all shear rate dependency is accumulated in skim milk: Figure 4 shows no dependence of the relative viscosity on the shear rate.

In Fig. 5 are shown results obtained from data modelling using Eqs. 4 and 5. The packing density inside clusters is plotted against volume fraction of fat. The most remarkable feature of this figure is an independency of the packing density inside clusters of the applied shear rate. This conclusion is in line with the previous Fig. 4: clusters of fat are not influenced by the applied shear rate in the range of shear rate investigated. As the volume fraction increases the packing density inside clusters increases and levels off at about ϕ_m = 0.4. The fact that the packing density, at any volume fraction is independent of shear rate means that the influence of the mentioned above factors a) - d) are more important than the applied shear rate (in the range of shear rate investigated). The higher the particle concentration, the more the chances of collision and the greater the packing density. However, this transport effect becomes weaker with increasing agglomerate size, hence the levelling off of the packing density at higher concentrations. In Fig. 6 a comparison of experimental data with the predictions of the Phan-Thien and Pham model (according to Eq. 2) is presented. The latter under predicts the viscosity and the discrepancy is ascribed to cluster formation.

5 CONCLUSIONS

Most emulsions of technological importance are concentrated in the sense that particle-particle interactions significantly influence observed bulk properties. A structural feature of such emulsions is formation of clusters. A new theory, suggested by Starov and Zhdanov [9], relates the bulk viscosity with the cluster size distribution and the averaged packing density of droplets inside the clusters. The assumptions of this



model have been tested experimentally using milk fat in skimmed milk as a model emulsion and the experimental data modelled on the theoretical equations. The following deductions are drawn:

i) Droplets in concentrated milk emulsions form clusters even at low concentrations.
ii) The averaged packing density of droplets inside clusters and the effective relative viscosity of the milk emulsions have been found to be shear-independent at relatively low shear rates (in the range of the applied shear rate investigated).
iii) The packing density of fat droplets has been found to increase with volume fraction and to level off at higher concentrations.
iv) Comparison of experimental data with predictions of the Phan-Thien and Pham model shows a wide variation. The discrepancy can be attributed to cluster formation.

NOMENCLATURE

η	Emulsion viscosity
η_o	Viscosity of skimmed milk at a particular shear rate
η_d	Effective viscosity of milk fat
ϕ	Volume fraction of dispersed phase
η_c	Average effective viscosity of fluid inside cluster

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ϕ_m	Averaged packing density of droplets inside cluster
$\dot{\gamma}$	Shear rate
D	Diffusion coefficient
n	Number of particles per unit volume
r	Droplet radius
r_c	Radius of a casein micelle
k	Boltzmann constant
T	Temperature in °K

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