

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. Kolloidale 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 gouttellettes (Starov V, Zhdanov G: J. Colloid Interface Sci, 258, 404 (2003)) a été 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 propriétés 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 gouttellettes de graisse à l'intérieur des aggrégats, de même que la viscosité relative du lait (viscosité divisée par la viscosité du lait crémeux) ne dépendent 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

texture are all governed by the flow properties of these systems. Although it is known, qualitatively, that the microstructure is related to these phenomena, a fundamental understanding is lacking. The microstructure is dependent on a number of factors: colloidal (i.e. particle-particle interactions), Brownian (the random movement of particles), hydrodynamic (i.e. particle to fluid interactions) and so on that interact in a rather complex way. It is this complexity (so called many-body interactions) that has for many years hampered the development of a unified theory relating microstructure with bulk properties.

It is usually required to relate the volume fraction of the dispersed particles with the bulk viscosity by scaling the different microstructural interactions. On the basis of a hydrodynamic consideration in the dilute limit case, Taylor [2] came up with the following equation:

$$\eta = \eta_o \left[1 + \phi \left(\frac{2\eta_o + 5\eta_d}{2\eta_o + 2\eta_d} \right) \right] \quad (1)$$

where η_o is the viscosity of the continuous liquid; η_d is the viscosity of the dispersed phase; η is the effective viscosity of the emulsion and ϕ is the volume fraction of droplets.

The hydrodynamic interaction of emulsion droplets at finite concentrations has been taken into account by Choi and Schowalter [3] and Yaron and Gal-Or [4] based on a cell model. The model due to Choi and Schowalter has been found to over predict relative viscosities for volume fractions of the dispersed phase $\phi > 0.3$ [5]. The Yaron and Gal-Or model has been shown to show significant scatter when compared to experimental data [6]. Starting from Taylor's equation and using the concept of the mean field approximation, Phan-Thien and Pham [7] have deduced the following dependency of the effective viscosity of concentrated emulsions on the volume fraction of droplets:

$$\left(\frac{\eta}{\eta_o} \right)^{2/5} \left[\frac{2\eta + 5\eta_d}{2\eta_o + 2\eta_d} \right]^{3/5} = (1 - \phi)^{-1} \quad (2)$$

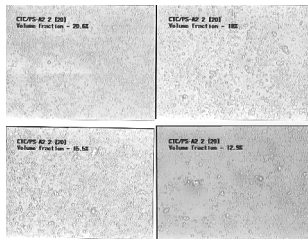
This equation, which was derived on the assumption that the droplets remain discrete, has been found to under predict the relative viscosity of

emulsions by a large amount [6]. Pal [6] noted that the existing models did not take into account the presence of surfactants (which are there by default as stabilisers). The adsorbed surfactant layer increases the volume of the droplet, by itself and also due to attractive forces on the continuous phase molecules around [8]. He deduced the following dependence wherein K (representing a hypothetical factorial increase in volume) is a fitting parameter.

$$\left(\frac{\eta}{\eta_o} \right)^{2/5} \left[\frac{2\eta + 5\eta_d}{2\eta_o + 2\eta_d} \right]^{3/5} = (1 - K\phi)^{-1} \quad (3)$$

Despite the close agreement of this equation with experimental data, it has been found [9] that such high values of K ($1.166 < K < 2.070$) signify completely immobilised droplet surfaces in which case the dependency on the viscosity of the liquid inside the droplet would disappear. Explicit in all the above equations is the assumption that the droplet particles remain discrete.

Current evidence suggests that even at sufficiently low concentrations diffusion results in droplets collision and formation of clusters. Berli and Quemada [10] have studied the steady and unsteady rheological behaviour of cutting oil emulsions with the view of establishing possible specific relations between structure and properties. They report that even for low oil concentrations, the droplets were aggregated together. The interpretation of the viscosity of concentrated emulsions can therefore significantly be improved if i) the systems are considered as emulsions of clusters, ii) the internal microstructure of a typical cluster is considered as reflecting the properties of a particular system at the micro-scale especially those of primary particles. To this end a new theory has recently been published [9]. In particular, the cluster size distribution and the packing density of droplets inside clusters are envisaged to be the main parameters. The latter in turn affects the effective viscosity, η_c , of 'liquid' inside clusters. These parameters are assumed to be both volume fraction and shear rate dependent. According to the theory [9], if the dependence of the averaged packing density, $\phi_c(\phi, \dot{\gamma})$, on the volume fraction of the dispersed phase and the shear rate is specified, the following pair of algebraic equations allows



calculation of the dependence of the effective viscosity of emulsions, η , on the volume fraction of droplets, ϕ :

$$\left(\frac{\eta_c}{\eta_o}\right)^{2/5} \left[\frac{2\frac{\eta_c}{\eta_o} + 5\frac{\eta_d}{\eta_o}}{2 + 5\frac{\eta_d}{\eta_o}} \right]^{3/5} = (1 - \phi_m)^{-1} \quad (4)$$

and

$$\left(\frac{\eta}{\eta_o}\right)^{2/5} \left[\frac{2\eta + 5\eta_c}{2\eta_o + 5\eta_c} \right]^{3/5} = \left(1 - \frac{\phi}{\phi_m}\right)^{-1} \quad (5)$$

where η_c is the effective viscosity inside clusters. The purpose of this work was to experimentally test this theory. At the same time the level of the presumed flocculation was monitored. A somewhat related line of consideration of concentrated suspensions, which is based on fluid immobilisation has recently been discussed by Windhab [11].

3 EXPERIMENTAL

Milk fat (as double cream) in skimmed milk was used as a model emulsion because the fat globules are nearly spherical and it also represents a real life emulsion with all the complexities of the extra components. The skimmed milk and double cream were purchased from Safeway Supermarket, UK. The double cream had a fat content of 47.5 g/100 ml. The skimmed milk and the double cream were mixed in different ratios to vary the fat content. The volume fraction was determined using the Coulter Multisizer II equipped with a tube of 30 μm . Viscometric tests were carried out on each of the samples using the TA Instruments AR-1000N constant stress-constant strain rheometer equipped with a concentric double gap geometry. The samples were initially pre-sheared at 100 s^{-1} for 5 minutes to drive off dissolved air. At this shear rate the samples were well within the high shear steady state region. The samples were then left to relax for 30 minutes in order that the structure is re-established, but not long enough for ageing to start. This duration is more than the time required for the structure to be re-established as ascertained from a separate time ramp test. This was further

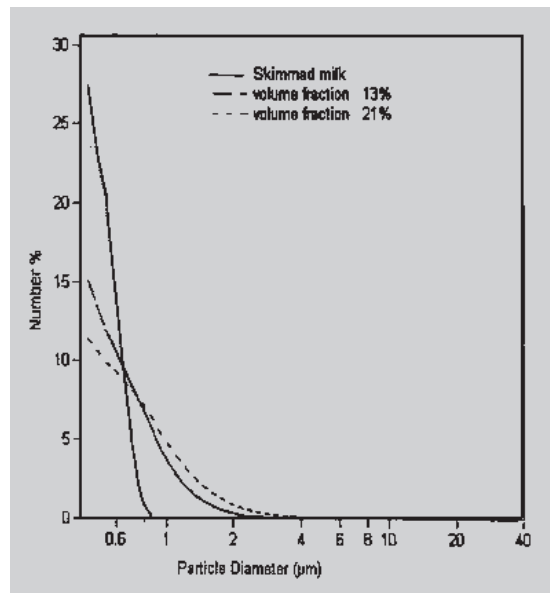


Figure 1 (left): Photomicrographs of milk fat in skimmed milk emulsions at different concentrations (magnification x200).

Figure 2 (right): Evolution of particle size distribution with increase in fat content in milk emulsions.

confirmed when the test sample did not show any thixotropy between up and down curves with this time interval allowed.

Shear rate was ramped up, logarithmically, from 0.06 s^{-1} to 30 s^{-1} . The 'wait for equilibrium' option was used and the tolerance was set at 2%. The maximum point time was 1 minute and the instrument also set to correct for inertia. The temperature was controlled at $20 \pm 0.04^\circ\text{C}$ using an external circulating system. For each volume fraction, the test was repeated three times, each time using fresh samples. The extent of cluster formation was monitored directly using a Leica ATC 2000 optical microscope equipped with a video camera and indirectly using static light scattering (Coulter Laser Sizer, Model LS 130).

The data obtained from the experimental work was then modelled on the theoretically derived equations using Microsoft Excel Solver add-in [12 - 13]. Packing density inside clusters, ϕ_m , was made the subject in Eq. 4 and substituted in Eq. 5 to give an expression which is a function of η_c/η_o . The solver add-in is then used to solve for η_c/η_o subject to the constraint that $\eta_c/\eta_o > 1$. The generated value of η_c/η_o is then substituted in Eq. 4 to give ϕ_m . This was done for each volume fraction and shear rate.

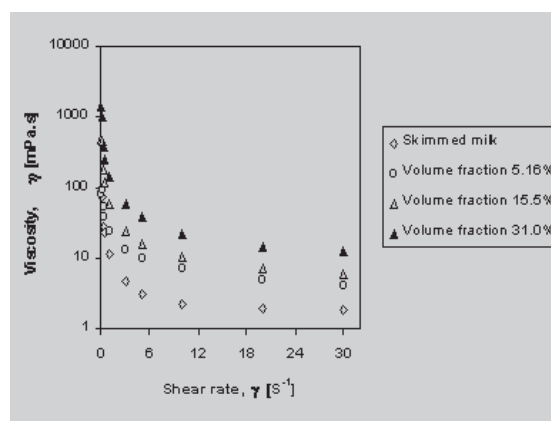
4 RESULTS AND DISCUSSION

Figure 1 shows typical micrographs taken at different values of the volume fraction of milk fat. It is evident that the emulsions form doublets, triplets and so on, even at low concentrations. Figure 2 shows results obtained from static light scattering experiments (Coulter laser sizer, model LS 130). It shows an increase in the cluster size as the concentration of fat is increased. Cluster formation can be explained in terms of the translational and rotational motions of the

Figure 3: Flow curves of milk fat in skimmed milk emulsions.

droplets and the interaction forces between them during their approach and collisions, which include:

- Partial coalescence:** The fat globule in milk consists of a range of triglycerides with varying melting points. At 20°C the globules are semi crystalline. Semi crystalline droplets can destabilise through a partial coalescence. It occurs by penetration of fat crystals from a crystalline droplet into another similar droplet. The liquid portions of the two droplets then flow together, but the solid fraction acts as a skeleton to support the distinct shape of the doublet against the Laplace pressure [14]
- Inter droplet pair potential:** The droplets in emulsions are in continual motion because of the effects of thermal energy, gravity or applied shear forces, and as they move about, they frequently collide with their neighbours. After a collision, emulsion droplets may either move apart or remain aggregated, depending on the relative magnitude of the attractive and repulsive interactions between them. The droplets will aggregate if they have sufficient energy to fall in either the primary or secondary minimum [15]. In quiescent systems, the collisions between droplets are mainly a result of their Brownian motion. According to von Smoluchowski, the collision frequency due to Brownian motion is $F_b = 16\pi D n^2$, where D is the diffusion coefficient of a single particle, n is the number of particles per unit volume and r is the droplet radius. $D = kT/6\pi\eta r$, where k is Boltzmann constant and T is the absolute temperature in °K. The latter expressions show that the frequency of collisions rapidly increases with fat concentration. Perikinetic transport [16] which results from Brownian motion, leads to the formation of clusters. Droplet-droplet encounters can also occur because of the different creaming rates of the different sized droplets. The collision frequency increases as the difference between the creaming velocities of the particles increases
- Depletion interactions:** The presence of non-adsorbing casein micelles in the continuous phase of the emulsions causes an increase in the attractive force between the droplets due to an osmotic effect associated with the exclu-

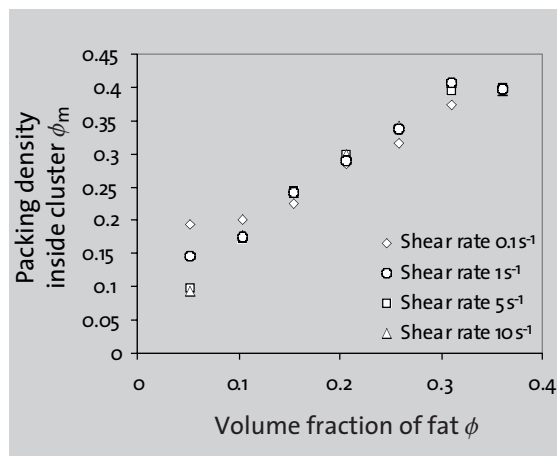
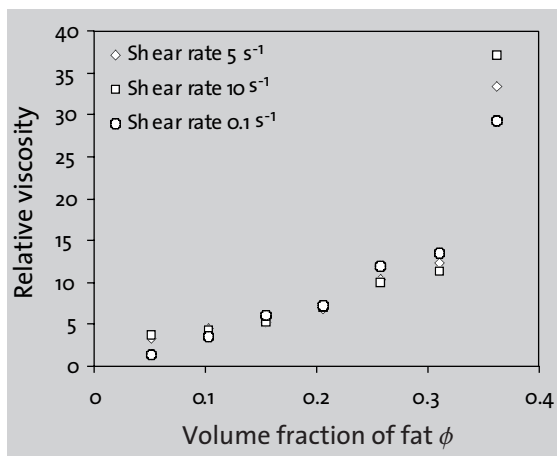


sion of these particles from a narrow region surrounding each droplet [17]. The origin of this interaction is the exclusion of the casein micelles from a narrow region surrounding each droplet. This region extends a distance approximately equal to the radius, r_c , of a casein micelle away from a droplet surface. The concentration of casein micelles in this depletion zone is effectively zero, while it is finite in the surrounding continuous phase. As a result there is an osmotic potential difference which favours the movement of solvent molecules from the depletion zone into the bulk liquid so as to dilute the casein micelles and thus reduce the concentration gradient. The only way this process can be achieved is by two drops aggregating and thereby reducing the volume of the depletion zone, which manifests itself as an attractive force between the droplets. Grotenhuis et al. [18] have studied the interaction between fat globules in milk and casein micelles. They report that the oil droplets and the casein micelles phase separate as a result of depletion interaction

- Milk also contains other small quantities of ingredients that are necessary for nutritive and prophylactic purposes in rearing the infant calf. Some of these are immunoglobulins. One of these IgM can act as a weak adhesive between fat globules forming bridges between them so that they link up into small clusters [19]. This immunoglobulin is especially effective below 40°C.**

Figure 3 shows the evolution of viscosity with shear rate for different concentrations of the dispersed phase (fat). As the volume fraction of fat increases, the flow curves shift upwards toward the high side of viscosity. It can also be seen that the emulsions are shear thinning [19] and high shear limit is reached above shear rate $\sim 10 \text{ s}^{-1}$ at all fat concentrations investigated.

Skim milk has been selected as a continuous phase and the relative viscosity below means “viscosity over skim milk viscosity”. Figure 4 pre-

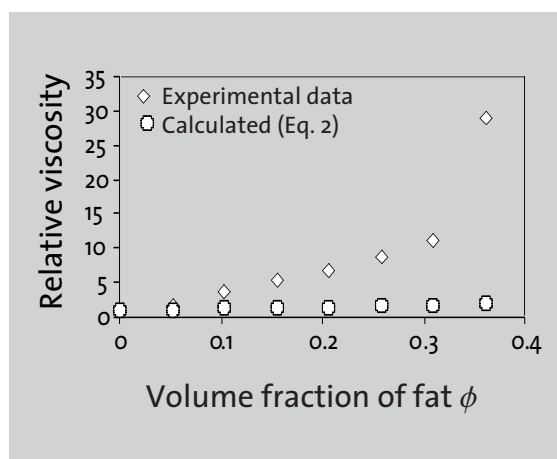


sents the relative viscosity plotted against the volume fraction of fat. It can be seen that the experimental points all fell on a master curve. The latter means that all shear rate dependency is accumulated in skim milk: Figure 4 shows no dependence of the relative viscosity on the shear rate.

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 $\phi_m = 0.4$. 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

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).

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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REFERENCES

- [1] Becher P: Emulsions: Theory and Practice, Oxford University Press, New York (2001) 429-456.
- [2] Taylor GI: The Viscosity of a fluid containing small droplets, Proceedings of the Royal Society of London, Series A 138 (1932) 41-48.
- [3] Choi SJ, Schowalter WR: Rheological Properties of non-dilute Suspensions of Deformable Particles, Physics of Fluids 18 (1975) 420-427.
- [4] Yaron I, Gal-Or B: On viscous flow and effective viscosity of concentrated suspensions and emulsions. Effect of particle concentration and surfactant impurities, Rheological Acta 11 (1972) 241-252.
- [5] Pal R: Shear viscosity behaviour of emulsions of two immiscible liquids, Journal of Colloid and Interface Science 225 (2000) 359-366.
- [6] Pal R: Viscosity-Concentration equation for emulsions of nearly spherical droplets, Journal of Colloid and Interface Science 231 (2000) 168-175.
- [7] Phan-Thien N, Pham DC: Differential multiphase models for polydisperse suspensions and particulate solids, Journal of Non-Newtonian Fluid Mechanics 72 (1997) 305-318.
- [8] Pal R and Rhodes E: Viscosity/Concentration Relationships for Emulsions, Journal of Rheology 33 (1989) 1021-1045.
- [9] Starov VM, Zhdanov VG: Viscosity of Emulsions: Influence of Flocculation, Journal of Colloid and Interface Science 258 (2003) 404-414.
- [10] Berli CLA, Quemada D: Rheological modelling of microgel suspensions involving solid-liquid transition, Langmuir 16 (2000) 7968-7974.
- [11] Windhab EJ: Fluid immobilisation - A Structure Related Key Mechanism for the Viscous flow Behaviour of Concentrated Suspension Systems, Applied Rheology 10 (2000) 134-144.
- [12] Roberts GP, Barnes HA, Mackie C: Using the Microsoft excel 'Solver' tool to perform non-linear curve fitting, using a range of non-Newtonian flow curves as examples, Applied Rheology 11 (2001) 271-276.
- [13] John EG: Simplified Curve Fitting using Spreadsheet add-ins, International Journal of Engineering Education 14 (1998) 375-380.
- [14] McClements DJ: Food Emulsions: Principles, Practice and Techniques, CRC Press, Florida (1999) 221-226.
- [15] Verwey EJW, Overbeek, JThG: Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam (1948).
- [16] Sonntag H: Coagulation kinetics, in Coagulation and Flocculation: Theory and Applications, Bohuslav Dobias (Ed), Marcel Dekker Inc., New York (1993) 57.
- [17] Jenkins P, Snowden M: Depletion Flocculation in Colloidal Dispersions, Advances in Colloid and Interface Science 68 (1996) 57-96.
- [18] ten Grotenhuis E, Tuinier R, de Kruif CG: Phase Stability of Concentrated Dairy Products, J. Dairy Sci. 86 (2003) 764-769.
- [19] Prentice JH: Dairy Rheology: A Concise Guide, VCH Publishers, New York (1992).

