The Effect of Nanoparticle Hydrophobicity on the Rheology of Highly Concentrated Emulsions

N.N. Tshilumbu*, I. Masalova

Department of Civil Engineering, Faculty of Engineering, Cape Peninsula University of Technology, PO Box 652, Cape Town 8000, Republic of South Africa

* Corresponding author: tshilumbun@cput.ac.za
Fax: x27.21.4603990

Received: 18.2.2013, Final version: 7.8.2013

Abstract:
A series of fumed silica nanoparticles were used as an additional emulsifier for highly concentrated (HC) water-in-oil (W/O) emulsions. These nanoparticles, with different hydrophobicity index (HI) in the 0.60 – 1.34 and HI > 3 range, were mixed with the conventional low molecular weight surfactant, sorbitan monooleate (SMO), in the oil phase prior to the emulsification process. The rheological properties of these emulsions were measured and compared with the properties of emulsions stabilized with SMO alone. In the mixed emulsifier system, the changes in rheological parameters were clearly expressed as a function of HI. The mixture of silica nanoparticles and SMO significantly increases the yield stress and plateau modulus of fresh emulsion, compared to the SMO only system. The effect was found to be more pronounced with a decrease in the HI. This is probably related to the reduction in micelle content with the decrease in HI, owing to a concomitant increase in the amount of SMO adsorbed onto the particle surface. Then, interestingly, the Foudazi-Masalova model recently developed for surfactant-stabilized highly concentrated emulsions (HCE) was found to describe successfully the rheological behavior of emulsions in the presence of a mixture of surfactant and fumed nanosilica.

Zusammenfassung:
Mehrere pyrogene Silika-Nanopartikel wurden als zusätzliche Emulgierungsmittel für hochkonzentrierte (HC) Wasser-in-Öl (W/O)-Emulsionen verwendet. Diese Nanopartikel, die unterschiedliche Hydrophobizitätsindizes (HI) im Bereich von 0.60 bis 1.34 und HI > 3 besitzen, wurden mit einem konventionellen, niedermolekularen Surfaktanten (Sorbitanmonooleat, SMO) in die Ölphase vor dem Emulsifikationsprozess gemischt. Die rheologischen Eigenschaften dieser Emulsionen wurden gemessen und mit den Eigenschaften der mit dem SMO alleine stabilisierten Emulsionen verglichen. Bei den gemischten Emulgierungsmitteln waren die rheologischen Eigenschaften eindeutig vom HI-Wert abhängig. Die Mischungen der Silika-Nanopartikel und dem SMO erhöhten in signifikanter Weise die Fließspannung und den Plateau-Modul der frischen Emulsion im Vergleich zu dem System, das mit SMO alleine stabilisiert wurde. Der Effekt trat deutlicher bei einem geringeren HI-Wert auf. Dies steht wahrscheinlich mit der Abnahme des Mizellengehaltes aufgrund der als Begleiterscheinung auftretenden Zunahme des SMO-Gehalts in Zusammenhang, das auf der Partikeloberfläche adsorbiert ist. Weiterhin beschreibt interessanterweise das Foudazi-Masalova-Modell, das kürzlich für mit durch Surfaktanten-stabilisierte hochkonzentrierte Emulsionen (HCE) entwickelt wurde, das rheologische Verhalten der Emulsionen mit Surfaktanten und pyrogenen Nanosilikapartikeln.

Résumé:
Une série de nanoparticules de fumée de silice a été utilisée comme émulsifiant additionnel d'émulsions eau-dans-huile (W/O) concentrées. Ces nanoparticules, possédant différents index d'hydrophobicité (HI) dans la gamme 0.6 – 1.34 et HI > 3, ont été mélangées avec du surfactant conventionnel de bas poids moléculaire, du mono oléate de sorbitane (SMO), dans une phase d'huile, avant le procédé émulsifiant. Les propriétés rhéologiques de ces émulsions ont été mesurées et comparées avec celles des émulsions stabilisées seulement par le SMO. Dans le système d'émulsifiant mixte, les changements des paramètres rhéologiques avec le HI sont clairement révélés. La mixture de nanoparticules et de SMO augmente significativement la contrainte seuil et le module plateau de l'émulsion fraîche, comparé au système avec le SMO seul. L'effet s'est avéré plus prononcé lorsque le HI décroît. Ceci est probablement lié à la réduction du nombre de micelles avec la baisse du HI, du à l'augmentation correspondante de la quantité de SMO adsorbé sur la surface de la particule. Ensuite, de manière intéressante, le modèle Foudazi-Masalova récemment développé pour les émulsions concentrées stabilisées par du surfactant (HCE), décrit avec succès le comportement rhéologique en présence du mélange de surfactant et de fumée de silice.

Key words: emulsions, rheology, fumed nano-silica, surfactant

 DOI: 10.3933/ApplRheol-23-62835

1 INTRODUCTION

Highly concentrated emulsions (HCE) represent a rather special class of colloids. As with any other emulsion, they are a mixture of two incompatible liquids usually stabilized with a surfactant. But in contrast to standard emulsions, the concentration of the dispersed phase in HCE exceeds the limit of the closest packing of regular spheres (app. 0.74), which is possible because of the 'compressed' state of droplets that have a polyhedral shape. The subject of this investigation is water-in-oil super-concentrated emulsions (90 vol.%), with oversaturated aqueous salt solution as dispersed phase, as in liquid explosives. The determination of the rheological characteristics of such emulsions is crucial, as they are used as the base for transport and technological applications of these systems. Moreover, in some of their technological applications, a high yield stress is usually desirable, as it enables the emulsion to resist water intrusion, retain its stability and be able to resist flow under the action of gravity [29].

The rheology of these emulsions was studied and described by the research group in several publications [1–9]. However, in all previous studies, standard surfactants usually used in technology – derivatives of poly (isobutylene) succinic anhydride – were used as emulsifiers. In this case high yield stresses are usually obtained by subjecting the emulsion to a process referred to as homogenization, whereby the droplet size is significantly reduced. The latter process, however, results in an increasing tendency of the oversaturated aqueous salt solution in the dispersed phase of the emulsion to crystallize, because of the high shear conditions. Thus, for a given composition, there is a practical limit to the degree of homogenization that can occur before crystallization of the oversaturated aqueous salt solution in the dispersed droplets becomes unacceptable [29].

Nanosilica as an emulsifier in Pickering emulsions is well known in applications to dilute or concentrated emulsions and the resulting emulsions are reported to demonstrate outstanding stability, particularly with regard to coalescence and unusual rheological behavior [10–13, 25, 44, 48, 49]. However, only few studies have reported the possibility of forming high internal volume fraction Pickering emulsions using chemically treated nanoparticles [25, 28]. In addition, there is no data on the stability or rheological properties of such emulsions, especially when the internal phase is an oversaturated aqueous salt solution. We attempted to prepare HC W/O Pickering emulsions (90 vol.%) using fumed nanosilica particles with different hydrophobicity index (HI) as emulsifiers. Our preliminary experiments showed that nanoparticles with intermediate HI ($0.97 \leq HI \leq 1.34$) can form W/O emulsions with aqueous phase concentration of up to 77–79 vol.% only, and the resulting emulsions are characterized by high instability under shear [14]. Then we attempted to increase the dispersed phase volume fraction by mixing silica nanoparticles with a typical low-molecular weight emulsifier-sorbitan monooleate (SMO), as it is well known that SMO alone can form stable HC W/O emulsion up to 90 vol.% [34–36]. Additional interest in this kind of mixtures is related to the possibility of modifying the particle hydrophobicity in a wide range, and consequently varying its interaction with SMO and both phases of emulsions. Tambe and Sharma focused on idealized systems of naturally occurring oil-brine emulsions, using barium sulphate, calcium carbonate and silica [40–42]. Stearic acid was used as a surfactant emulsifier. It was found that surfactant addition to particle mixtures led to emulsion stability far greater than found with either particles or surfactant alone. This synergy was attributed to the surfactant's ability to increase the particle contact angle on adsorption. In a similar approach, Gosa and Uricanu found that systems of silica and PEO–PPO–PEO block copolymers caused synergistic stability [50]. They attributed the synergy to principally increased flocculation of silica with surfactant adsorption. Midmore furthered these findings, in systems of silica and both PEO [43] and HPC [38, 39] surfactants. Again clear synergy was found between silica and each of surfactants. There was evidence for increased flocculation of silica with surfactant addition, and increased contact angle. Recently Binks and co-workers looked at the synergy between moderate concentrations of nanosilica (20 nm) and non-ionic PEO type surfactants [37]. For systems with high stability clear evidence of small aggregate formation was present, confirmed with bulk rheology tests showing increases in viscosity linked to this flocculation.

Despite some activity in this area, systematic studies of stability and rheology of HC W/O emulsions using mixtures of a low-molecular weight surfactant and surface-active particles

with varying hydrophobicity are lacking. This method of HCE stabilization is especially interesting for emulsions with aqueous phase containing high concentration of salts like in liquid explosive emulsions. We studied in detail stability with time or aging, and stability under the action of high shear (during the emulsification process and pumping) of these emulsions, and the results were published elsewhere [14]. This work is completely devoted to the rheology of HCE with mixed Nanosilica/SMO emulsifier with different hydrophobicity of the solid particles as the base for transport and technological application of these systems. We intended to try to describe the rheological behavior of the emulsion with mixed Nanosilica/SMO emulsifier based on existing rheological models developed for HCE in the surfactant only systems or for particle dispersions.

1.1 RHEOLOGICAL MODELS FOR HCE OR PARTICLE DISPERSIONS

By studying the flow behavior of HCE stabilized with surfactants, Princen and Kiss [30] proposed the flow curve prediction in terms of shear stress as follows:

$$\tau = \tau_{yo} + 64(\varphi - 0.73)\frac{\sigma}{d_{32}}Ca^{1/2} \tag{1}$$

Where τ_{yo} is the yield stress, φ the dispersed phase volume fraction, σ the interfacial tension, d_{32} the area-volume mean diameter, and *Ca* the capillary number. The latter is defined as the ratio of hydrodynamic stress $\eta_c\dot{\gamma}$, which tends to stretch the droplet into a filamentary shape, to the interfacial stress σ/R which tends to contract the droplet into a sphere of radius *R*.

$$Ca = \frac{\eta_c\dot{\gamma}}{\sigma/R} \tag{2}$$

Where η_c is the viscosity of the continuous phase and $\dot{\gamma}$ is the shear rate. It should be noted that this model is identical to a Herschel–Bulkley model Equation 3 with flow behavior index *n* equal to one half.

$$\tau = \tau_{yo} + K\dot{\gamma}^n \tag{3}$$

where *n* and *K* are empirical constants. In the particular case of highly concentrated particle dispersions, Windhab [16] proposed the flow curve prediction in terms of shear stress as follows:

$$\tau = \tau_{yo} + \eta_\infty\dot{\gamma} + \left(\tau_{yl} - \tau_{yo}\right)\left[1 - exp\left(-\frac{\dot{\gamma}}{\dot{\gamma}^*}\right)\right] \tag{4}$$

The Windhab model includes the directly measured yield stress τ_{yo} and the high shear viscosity η_∞. It also considers the crossover point (hump) τ_{y1} observed at intermediate shear rate $\dot{\gamma}^*$. τ_{y1} has been introduced in this model as a secondary yield stress. A similar kind of flow curve showing a hump at intermediate shear rate has been recently reported in the flow behavior of HCE belonging to the class of HCE with a supercooled dispersed phase [6, 7]. To better describe this rather unusual kind of flow behavior of HCE of supersaturated aqueous solution in oil, the Windhab model (developed for particles dispersions) was modified by Foudazi et al. [18] and the analytical equation of the latter model is presented below:

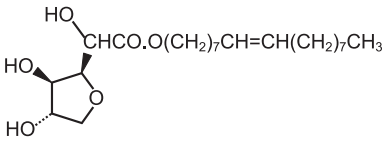
$$\tau = \tau_{yo} + K\gamma^{0.5} + \left(\tau_{yl} - \tau_{yo}\right)\left[1 - exp\left(-\frac{\dot{\gamma}}{\dot{\gamma}^*}\right)\right] \tag{5}$$

where τ_{y1} is an asymptotic value of the yield stress value that corresponds to the transition (hump) in the flow behavior at shear rate $\dot{\gamma}^*$ and *K* is an empirical constant. It is should be noted that all the above models were developed for particle dispersions or HCE stabilized by conventional surfactants, with no particles present.

2 EXPERIMENTAL

2.1 SAMPLES

Highly concentrated emulsions used for investigations in this work belong to the class of HCE with a supercooled dispersed phase. They are emulsions of the water-in-oil type. One can find the details of the composition of these emulsions in our earlier publications [1–7], therefore only their basic characteristics will be mentioned here briefly. The concentration of the disperse phase in the real technologically valid recipes is 90–96 wt.%. This phase in the standard technological formulation is a super-



Chemical composition	
Iso-paraffins [%]	85
n-paraffins[%]	4.8
Cycloparaffins[%]	10
Aromatics[%]	< 0.1
Physical properties	
Density 22°C [kg/m^3]	794
Viscosity 30°C [mPas]	2.9
Refractive index [-]	1.443
Boiling point [°C]	295

Figure 1 (left above): Structure of SMO.

Table 1 (right above): Chemical composition and physical properties of Ash-H according to the supplier (Lake International Technologies, Republic of South Africa).

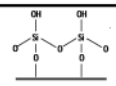
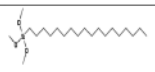
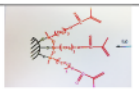
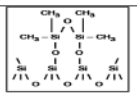
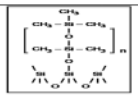
Silica type	Surface chemistry	Hydrophobicity index (HI)	Supplier
M5		0.60	Cabot Corp.
R 816		0.72	Degussa
R 711		0.97	Degussa
R 610		1.34	Cabot Corp.
TS 720		>3	Cabot Corp.

Table 2 (left below): Properties of fumed silica nanoparticles.

cooled aqueous solution of mainly ammonium nitrate (AN) salt with a minor proportion of Ca and Na nitrates in water. Water comprises < 20 % by mass of this phase. So, the salt concentration exceeds 80 %. The equilibrium temperature of dissolving for such concentration is about 65 °C. This is much higher than the room temperature at which experiments in this work have been performed.

As a low-molecular-weight surfactant, a well-known commercial product SMO was used (purity ≥ 99 %, Lake International Technologies, Republic of South Africa, commercial trade mark is Span®80).This is an ester formed between sorbitan and oleic acid (oleic acid is a C18 fatty acid with a single *cis* double bond, written as C18:1). The structure of SMO is given below in Figure 1. The molecular weight of SMO is 428, with the HLB number about 4.3. The oil phase was Ash-H, a paraffin compound (Lake International Technologies, Republic of South Africa). Table 1 summarizes the chemical composition and physical properties of Ash-H according to the supplier.

Five types of commercial fumed nano-silica powders were used as co-emulsifiers. The extent of their surface modifications was characterized by the hydrophobicity index (HI). The latter can be determined from infrared spectra [31] and is defined in terms of a ratio between the absorbance values at 2970 (due to C-H stretching, i.e., from trimethylsilyl groups, which are responsible for the hydrophobic characteristics) and 3750 cm^{-1} (representing isolated silanol groups). Simovic and Prestige [31] observed a strong correlation between HI and the contact angles at the oil-water interface. The values of HI reported in Table 2 were taken from [31]. Properties of the silica particles are summarized in Table 2. It should be noted that the primary particle diameter of the silica particles presented in Table 2 was 7–50 nm with an average specific surface area (BET) of 157 ± 35 m^2/g. All materials were used with no further purification or modification of their properties. It is worth noting that the amounts of emulsifiers (particles or SMO) used in this study are based on oil phase, not on total sample.

The protocol of sample preparation was as follows. SMO surfactant was dissolved and particles dispersed in the oil phase prior to emulsification. The emulsions were prepared with 90 vol.% of the dispersed phase. The dispersed phase of emulsion comprised 80 wt.% of ammonium nitrate (AN) in distilled water. All samples under study contained 6 wt.% of fumed silica nanoparticles and 5 wt.% of SMO in the oil phase. These optimum concentrations of emulsifiers in the oil phase were determined from our preliminary results. Indeed 5 wt.% SMO was found as the minimum surfactant concentration where, regardless of the HI, stable emulsions (with respect to the crystallization of AN in the dispersed phase) could be obtained with the mixed emulsifier system. On the other hand, the results showed that the emulsion stability increases with increasing the particles' concentration and 6 wt.% particles were found to be the upper limit above which the oil viscosity was too high to allow any emulsification in our experimental conditions. The effect of particle hydrophobicity on rheological properties was studied using nanosilica with five different hydrophobicity index listed in Table 2. The emulsification process was conducted in 2.5 kg batches by Hobart N50 mixer (manufactured and supplied by the Hobart Corporation).

The oil phase, consisting of mixtures of surfactant and fumed nanoparticles, was first placed in the bowl, mixed gently (gear 1) and heated above 80 °C. Then, the hot ammonium nitrate solution was slowly added, while stirring was maintained to ensure emulsification (average drop size d_{32} = 17 μm). Rapid mixing at higher speed of mixer (gear 3 ≈ shear rate of 380 s^{-1}) was done subsequently for all formulations to achieve the desired sample formulation for the

Figure 2:
Shear rate dependence of the shear stress for 6 wt.% nanosilica dispersion in oil with particles of different HI.

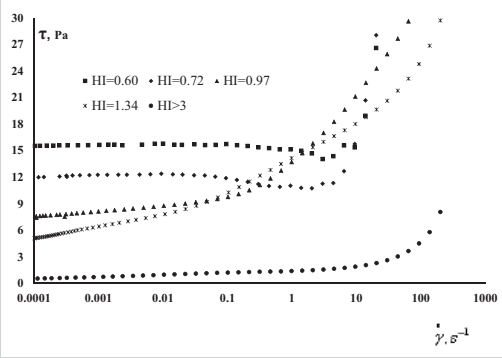


Table 3:
Refinement time (from d_{32} = 17 μm to d_{32} = 10 μm).

Emulsifier	HI > 3 + SMO	HI = 1.34 + SMO	HI=0.97 + SMO	HI=0.72 + SMO	HI=0.6 + SMO	SMO
Refinement time [min]	2.2	2.5	4	25	45	3

study (droplet refinement). Our preliminary results showed that the mixing time required during the refinement process was strongly dependent of the HI (Table 3).

2.2 INSTRUMENTATION

2.2.1 Emulsion preparation

The Hobart N50 mixer was used to manufacture all the samples under study. In it simplest form it consists of an agitator unit (a 'D' wire whisk) which can be operated at three different mixing speeds and a bowl for mixing. An annular casing of stainless steel made around the bowl, allows the glycol bath supplied by the Haake temperature controlled system to circulate around the bowl to provide heat required for the emulsification of W/O emulsion with a supercooled dispersed phase (85 °C).

2.2.2 Optical methods

The optical microscopy was used for visual observation of any structural change in the emulsion (change in droplet size or crystallization of salt in the dispersed phase) before and after rheological measurements. The analyses were carried out with a Leica optical microscope equipped with a digital camera. Laser diffraction for measuring the size distribution of dispersed droplets was carried out with the Mastersizer 2000 device (Malvern Instruments Co.). The procedure for measuring is based on sample dispersion under software control and the measurement of angle dependence of the intensity of scattering of a collimated He-Ne laser beam. Particle size can be measured in a range from 0.26 to 1500 μm. Each emulsion sample (a small amount of sample was taken) was dispersed in the large volume of oil to reach a very dilute concentration of aqueous droplets in oil and to avoid the formation of agglomerates. The average value d_{32} was used as a measure of droplet size in this study.

2.2.3 Rheological methods

All rheological studies were conducted using a rotational stress rheometer MCR 300 (Paar Physica) with bob-in-cup measuring units with a sand blasted bob surface in order to minimize the possibility of slip [4].The experiments were carried out at 30 °C in mainly the following two deformation modes:

- Scanning (sweep) shear rate measurements, with decreasing shear rate from 10^2 to 10^{-5} s^{-1}, which were found to be physically meaningful and which identify the flow curve of the emulsion [3, 5],
- Amplitude sweep oscillations in the range of strains from 0.1 to 200 % at the constant frequency of 1.59 Hz.

2.2.4 Bottle test

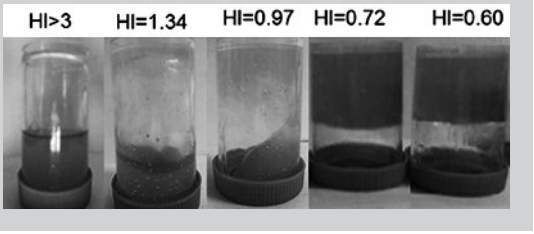
A rapid indication on oil aggregation properties of particle dispersions in oil was given by the bottle test method by monitoring the extent of flow five minute after the bottle have been fully inverted [44].

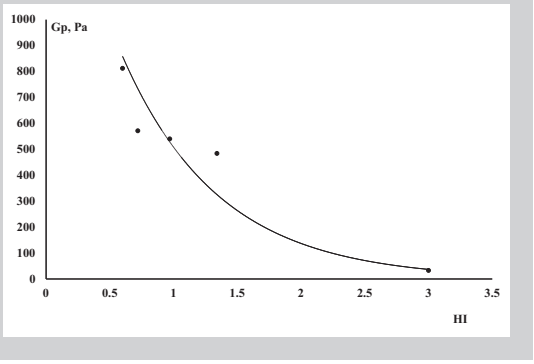
3 RESULTS AND DISCUSSION

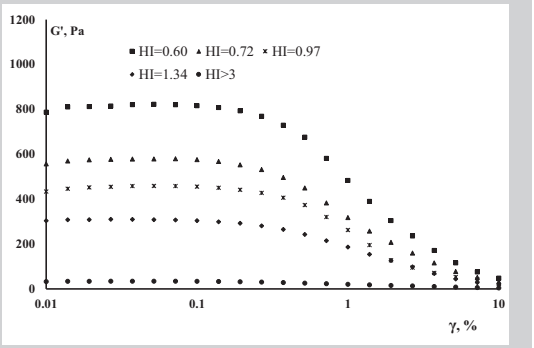
3.1 RHEOLOGICAL PROPERTIES OF THE OIL PHASE

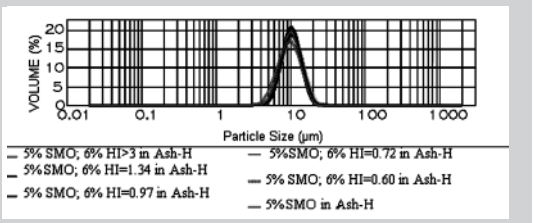
Firstly, the flow properties of pure paraffin oil and paraffin oil in the presence of 5 wt.% SMO were determined. Measurements of the apparent viscosity as a function of the shear rate demonstrated that the oil is a purely Newtonian fluid with a viscosity of 3 mPas at 30 °C. It was further found that the addition of 5 wt.% SMO has virtually no effect on the flow properties of paraffin oil (viscosity 3.15 mPas at 30 °C). Then, the rheological properties of paraffin oil dispersions in bulk were measured for particles with and without SMO. In this case a shear rate sweeping in the decreasing mode from 10^2 to 10^{-5} s^{-1}, was used. The flow curves obtained for silica dispersions (Figure 2) demonstrate the existence of the yield stress τ_{yo} and solid-like behavior at low stresses.

The existence of the solid-like behavior is visually demonstrated by the following experiment (Figure 3). Vessels were filled with 6 wt.% silica particles of different HI dispersed in the oil phase and then inverted. Particle dispersions containing the most hydrophilic silica did not show any flow 5 min after inverting the vessels (right section in Figure 3). It is thus evident that silica nanoparticles create









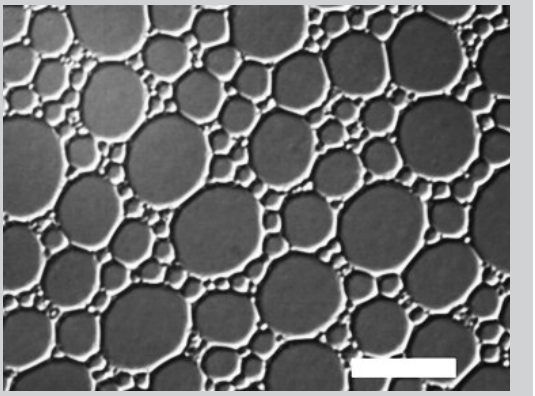


Figure 3 (left above): Photograph of 6 wt.% nanosilica dispersion in oil 5 min after inverting the vessels.

Figure 4 (right above): Amplitude dependence of the elastic modulus for 6 wt.% nanosilica dispersion in oil with particles of different HI.

Figure 5 (left below): Dependence of dispersion elasticity on hydrophobicity of silica nanoparticles.

Figure 6 (right middle): Histogram of drop size distribution of the emulsion prepared with SMO alone and the SMO/nanoparticles mixtures (d = 10 μm).

Figure 7 (right below): Microscopic image depicting the typical structure of HCE (Scale bar = 10 μm).

spatial structure with quite discernible strength. The maximal values of the yield stress achieved for compositions with low HI is 15.5 Pa, while the increase in HI (left photographs in Figure 3 or bottom part in Figure 2) leads to the decrease in τ_{yo} down to 0.3 Pa. Evidence for the solid-like structure can be also obtained by measuring the elastic modulus. It is worth mentioning that the elastic modulus does not depend on the frequency, which is usual for solid-like structures in dispersions below the yield stress [45, 46]. Figure 4 demonstrates the amplitude dependencies of the elastic modulus at constant frequency (f = 1.59 Hz). As was expected from the yield stress values, the plateau modulus at low strains with maximal elastic modulus was found for hydrophilic particles and its values decrease with the increase of HI. The latter is presented in Figure 5. As seen, highly hydrophobic particles cannot create structure in an oil medium. This is a consequence of the mechanism of formation of the structure via hydrogen bond [47], and this possibility decreases with the increase in hydrophobicity on nanoparticles [15, 44].

The disappearance of the plastic solid-like behavior of oil dispersion with the addition of SMO seems to be the result of a combination of two mechanisms. Firstly, adsorption of SMO onto silica nanoparticle surface increases the particles' hydrophobicity and consequently reduces their ability to create a spatial structure via hydrogen bonding. Secondly, keeping in mind that 1–2 wt.% SMO are required to fully cover the particle surface [26], and that the CMC of SMO is 0.003 wt.% [14], one can conclude that the amount of surfactant used in this study (5 wt.%) is enough to generate spherical micelles in the oil phase as evident from Small Angle Neutron Scattering (SANS) studies [19–21]. It is well known that a fraction of micelles could become charged via a disproportionation process in which two neutral micelles interact to form one positively-charged and one negatively-charged micelle [22, 23, 27]. In this case the cations are expected to be very small compared to the anions. By adding silica particles in such environment, positive charges together with single SMO molecules adsorb onto particles surfaces, leaving the anions and neutral micelles in the oil phase [26]. The presence of electrical charges on the particle surfaces is expected to generate a strong electrostatic repulsion between them, consequently destroying their gelling ability.

3.2 RHEOLOGICAL PROPERTIES OF EMULSIONS STABILIZED WITH MIXED NANOSILICA/SMO EMULSIFIER

The volume fraction of the dispersed phase was fixed at 90 % for all samples. The droplet size distributions of samples used in this study are given below (Figure 6).It is clear that all samples for which the mixed emulsifier systems were used, as well as the one for which the SMO alone was used, had same droplet size(10 μm) and similar droplet size distributions. The typical structure of HCE under study is shown in Figure 7.

Figure 8 (left above): Flow curves of emulsions prepared with 5 wt.% SMO and 6 wt.% particles of different HI.

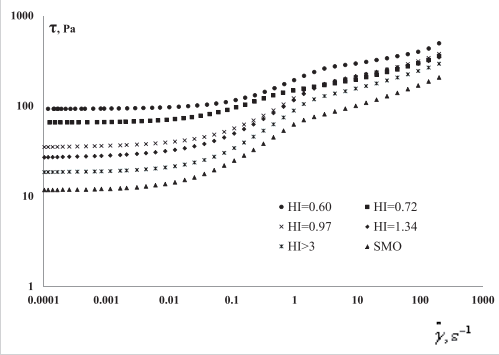
Figure 9 (right above): Typical best fittings of Herschel-Bulkley, Windhab and Foudazi-Masalova's models on flow curves of particles/SMO stabilized emulsions.

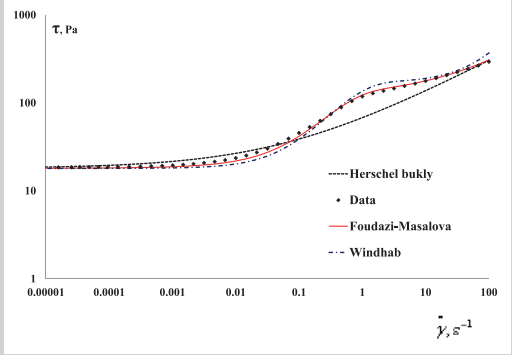
Figure 10 (left below): Best fittings of Foudazi-Masalova's (continuous line) modelon flow curves of particles/SMO stabilized emulsions.

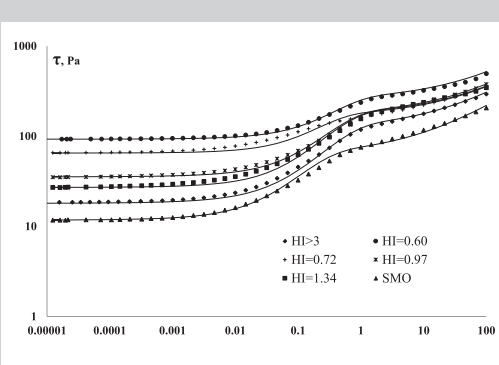
Figure 11 (right below): Effect of HI of nanoparticles on viscoelastic properties of HCE stabilized with SMO/particles mixtures.

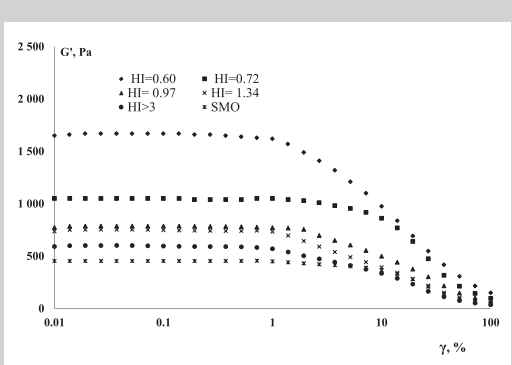
Table 4 (above): Plateau modulus of oil dispersions with and without SMO (6 wt.% of silica, ** 6 wt.% of silica and 5 wt.% of SMO).*

Table 5 (below): The yield stress of oil dispersions with and without SMO (6 wt.% of silica, ** 6 wt.% of silica and 5 wt.% of SMO).*









Flow curves obtained for emulsions stabilized with mixed emulsifier (5 wt.% of SMO and 6 wt.% of silica) with nanoparticles of different HI are shown in Figure 8. As is seen, the emulsions show a pronounced yield stress and a hump in the flow curve in the range of moderate shear rates (0.4 – 0.6 s^{-1}).The stress associated with the hump has been described by the Windhab model [16] as a secondary yield stress. The physics of this phenomenon was explained in publications [5, 7]. It was found that at shear rates above the hump, the droplets are deformed during flow, while the rolling of droplets over one another is the dominant mechanism of flow at shear rates below the hump. It was suggested that this transition is controlled by the capillary number of systems under flow [5] and the inter-droplet interaction [17]. To better describe the flow behavior of HCE of supersaturated aqueous solution in presence of the mixed emulsifier system, we tried to fit our experimental data using three different models of flow curves (Herschel-Bulkley, Windhab and Foudazi-Masalova). It is worth mentioning that all the above models were developed either for particles dispersions or for HCE stabilized by conventional surfactants, with no particles present. So choosing one of these models to describe emulsion flow in the presence of a mixture of traditional surfactants and nanoparticles was not fortuitous. As it can clearly be seen from Figure 9, the Foudazi-Masalova model fits our experimental data well. Thus this model was used to describe the flow curves (Figure 10). The fitting values of the model parameters are summarized in Table 6.

These data allow us to compare the rheology of different compositions and the role of hydrophobicity of nanoparticles.It is seen that while emulsions prepared with SMO alone have relatively low yield stress, the addition of nanosilica significantly increases the magnitude of the true and secondary yield stress. The effect of nanoparticles on the yield stress of SMO-based emulsion is amplified with reduction of HI (decrease in hydrophobicity).The yield stress of samples has the following trend in the HI influence: HI = 0.60 > HI = 0.72 > HI = 0.97 > HI = 1.34 > (HI > 3). Treating the yield stress as the measure of the strength of a structure formed in emulsions, one can say that HI = 0.60 provides the highest rheological characteristics of HCE.

As evidenced by the qualitative bottle test and the rheology of oil dispersions in the presence of 5 wt.% of SMO (Table 4 and Table 5), the nanosilica network in the interfacial layers between droplets is broken. Moreover, HCE can exist only because SMO covers the interface. Therefore we may conclude that the formation

HI	0.60	0.72	0.97	1.34	> 3
G_p [Pa] (silica)*	812	571	540	484	33
G_p [Pa] (silica/SMO) **	6	0.7	2.5	0	0

HI	0.60	0.72	0.97	1.34	> 3
τ_y [Pa] (silica)*	15.5	11.9	7.1	4.5	0.3
τ_y [Pa] (silica/SMO) **	0.07	0.03	0.02	0	0

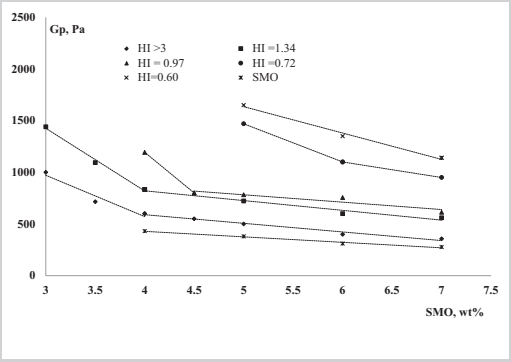


Figure 12:
Dependence of HCE elasticity on SMO, wt.% for silica nanoparticles with different hydrophobicity index.

Table 6:
Parameters of the Foudazi-Masalova model for emulsions with nanoparticles of different HI.

of a network of silica particles in the bulk phase, and the interfacial tension or elasticity, are not the (only) controlling parameters of the flow behavior in accordance with the model advanced in [17]. Structure formation in HCE in the presence of mixtures of SMO and different HI is confirmed by the results of measurements of the elastic modulus. The frequency dependence of the elastic modulus is absent in a wide frequency range that is typical for solid-like behavior of emulsions at low amplitude of deformation. Therefore we can consider the plateau modulus values as the characteristic of elasticity of emulsions with a mixed emulsifier system. Then, as in Figure 4, it is reasonable to consider the amplitude dependence of the elastic modulus, bearing in mind that the values obtained at low amplitudes correspond to the linear viscoelastic behavior of emulsions. Experimental data obtained for HCE stabilized with mixtures of SMO and particles of different HI are presented in Figure 11.

It is seen that the low-amplitude plateau modulus G_p pursues the same trend as for the yield stress, decreasing with an increase of HI. It is clear that scaling of the storage modulus by Laplace pressure does not result in superimposition of values corresponding to different compositions. Again we can conclude that the formation of a network of silica particles in the bulk phase, and the interfacial tension or elasticity, are not the (only) controlling parameters of the HCE elasticity that is in accordance with the model advanced in [17]. The following evaluations are interesting in comparing the role of SMO in mixed emulsifier systems. Calculations show that about 0.65 wt.% of the full amount of SMO is sufficient to cover completely the area of dispersed droplets for emulsion with d_{32} = 10 μm. The other share remainder of a surfactant remains in the oil phase adsorbed onto particles, and forms micelles. Keeping in mind that small-angle neutron-scattering studies have revealed a spherical shape for SMO micelles with a mean radius of 22 A° [19, 20], particles sized 7–50 nm, and assuming the inter-droplet thickness of the order of 100 nm [6], one can expect the presence of micelles and silica nanoparticles in the inter-droplet layer. A reduction in micelle content is expected as the particle HI decreases. Indeed, as HI decreases, more surfactants are likely to adsorb onto particles' surface due to the concomitant increase of both the surface density of OH-groups [31] and their surface activity [14, 32]. It is worth mentioning that our previous publication [33] demonstrated that for an HCE prepared with surfactant only, any decrease in micelle concentration increases both the yield stress and the plateau modulus of an HCE. It is worth checking the validity of the latter statement in the presence of a mixture of surfactant and nanoparticles. A new set of HCE was then prepared where the particles' concentration was kept constant, 6 wt.%, in the oil phase, while the HI was varied in the range 0.60–1.34 and HI > 3. The SMO concentration in the oil phase was varied in the 3–7 wt.% range while the dispersed phase volume fraction, the droplet size and droplet size distribution of the resultant emulsions were controlled and kept the same in all samples. The rheological properties of the fresh emulsions were then investigated and the main results are presented below.

The following can be clearly seen from Figure 12. Firstly, regardless of the particle HI, the elastic modulus was found to decrease with the increase of SMO concentration. Then, interestingly, low values of HI give rise to a high elastic modulus in the entire range of SMO concentration as fewer micelles are expected to remain in the oil phase due to a large adsorption of SMO molecules onto the particles' surface. Thirdly, emulsions prepared with SMO only, showed the lowest elasticity for the entire range of SMO concentration. Again the significant effect of micelles is evident in both the plateau modulus and the yield stress (not shown here), even in the presence of nanoparticles. Based on the above arguments, one might suggest the following to explain the observed influence of HI of nanoparticles. Firstly, we can presume that the increase in the micelle concentrations with an increase in

HI	τ_y [Pa]	γ^*	τ_{y1} [Pa]	K
0.60	92	0.55	250	27
0.72	48.3	0.5	190	33
0.97	39	0.4	172	25
1.34	34	0.4	151	23
> 3	24.2	0.4	122	22
SMO	11.7	0.2	60	16

HI enhances the rolling mechanism because of decreasing the friction between interfacial layers [33]. Secondly, as was mentioned previously, particle surfaces are expected to carry positive charges in the presence of SMO micelles. The electrostatic interaction generated by charged particles in the thin film between drops can be considered as a possible additional source of elasticity in HCE. Thus, the higher concentration of micelles (higher HI) increases the possibility of charged micelles, resulting in a decrease in Debye length of electrostatic forces, and hence the decrease in electrostatic repulsion. Less electrostatic repulsion leads to less stored additional energy and resistance to flow [17]. Thirdly, it was demonstrated experimentally [24] that, in the presence of silica, SMO builds up lamellar structures between the droplets and the silica blocks. This layer ordering can be considered as another source of elasticity.

4 CONCLUSION

We have investigated the influence of particle hydrophobicity on the rheological properties of highly concentrated water-in-oil emulsions with a super-cooled dispersed phase. The fumed silica nanoparticles were mixed with a low molecular weight conventional surfactant SMO. The results obtained were compared with the properties of emulsions where only SMO was used as emulsifier. When only SMO acts as the emulsifier, stable HC W/O emulsion up to 90 vol% can form. In the mixed emulsifier system, the changes in rheological parameters were clearly expressed as a function of HI, despite the fact that all the investigated emulsions seem to present similar interfacial properties (SMO alone is likely to cover the interface) and the silica particle network in the thin film between droplets is in a completely broken state (because of SMO adsorption onto the silica surface).

Indeed, the mixing of SMO and silica nanoparticles significantly increased rheological properties responsible for solid-like behavior of emulsions (the yield stress and plateau modulus) compared to the SMO only system. The effect was found to be more pronounced with a reduction of HI. Thus the formation of a network of silica particles in the bulk phase, and the interfacial tension or elasticity, are not the (only) controlling parameters of the flow behavior that is in accordance with the model advanced in [17]. The observed effect of HI on the rheological properties of emulsions is probably related to the reduction in micelle content, with the decrease in HI due to a concomitant increase in the amount of SMO adsorbed onto the particle surface. Interestingly, the Foudazi-Masalova model recently developed for surfactant-stabilized HCE was found to describe the rheological behavior of emulsions successfully in the presence of a mixture of surfactant and fumed nanosilica.

REFERENCES

[1] Masalova I, Malkin AYa, Slatter P, Wilson K: The rheological characterization and pipeline flow of high concentration water-in-oil emulsions, J. Non-Newton. Fluid Mech. 112 (2003) 101–114.

[2] Masalova I,Malkin AYa, SlatterP, Wilson K: Effect of droplet size on the rheological properties of highly-concentrated w/oemulsions, Rheol. Acta 43 (2004) 584–591.

[3] Masalova I, Taylor M, Kharatiyan E, Malkin AYa: Rheopexy in highly concentrated emulsions, J. Rheol. 49 (2005) 839–849.

[4] Masalova I, Malkin AYa, Ferg E, Kharatiyan E, Haldenwang R: Evolution of rheological properties of highly-concentrated emulsions with ageing – emulsion-to-suspension transition, J. Rheol. 50 (2006) 435–451.

[5] Masalova I, Malkin AYa: Peculiarities of rheological properties and flow of highly concentrated emulsions – The role of concentration and droplet size, Colloid J. 69 (2007) 185–197.

[6] MasalovaI I, Malkin AYa: Rheology of highly concentrated emulsions – concentration and droplet size dependencies, Appl. Rheol. 17 (2007) 42250–42259.

[7] Masalova I, Malkin AYa: Shear and normal stresses in flow of highly concentrated emulsions, J. Non-Newton. Fluid Mech. 147 (2007) 65–68.

[8] Kovalchuk K, Masalova I, Malkin AYa: Influence of electrolyte on interfacial rheological properties and shear stability of highly concentrated emulsions, Colloid J. 72 (2010) 860–814.

[9] Foudazi R, Masalova I, Malkin AYa: The rheology of binary mixtures of highly concentrated emulsions: effect of droplet size ratio, J. Rheol. 56 (2012) 1299–1314.

[10] Midmore BR: Preparation of a novel silica-stabilized oil/water emulsion, Colloids and Surfaces A: Physicochem. Eng. Aspects 132 (1998) 257–265.

[11] Binks BP, Lumsdon SO: Catastrophic phase inversion of water-in-oil emulsions stabilized by hydrophobic silica, Langmuir 16 (2000) 2539–2547.

[12] Wolf B, Lam S, Kirkland M, Frith WJ: Shear thickening of an emulsion stabilized with hydrophilic silica particles, J. Rheol. 51 (2007) 465–478.

[13] Binks BP, Desforges A, Duff DG: Synergistic stabilization of emulsions by a mixture of surface-active nanoparticles and surfactants, Langmuir 23 (2007) 1098 – 1106.
[14] Tshilumbu NN, Kharatyan E, Masalova I: Effect of nanoparticle hydrophobicity on stability of highly concentrated emulsions, J. Dispers. Sci. Technol. Accepted for publication.
[15] Simovic S, Prestidge CA: Nanoparticle layers controlling drug release from emulsions, Eur. J. Pharm. Biopharm. 67 (2007) 39 – 47.
[16] Windhab E: Bericht der IV. Tagung der Lebensmittelrheologie, Detmold (1993).
[17] Foudazi R ,Masalova I, Malkin AYa: Effect of interdroplet interaction on elasticity of highly concentrated emulsions, Appl. Rheol. 20 (2010) 45096 – 45106.
[18] Foudazi R, Masalova I, Malkin AYa: Flowbehavior of highly concentrated emulsions of supersaturated aqueous solution in oil, Rheol. Acta 50 (2011) 897 – 907.
[19] Reynolds AP, Gilbert PE, White WJ: High internal phase water-in-oil emulsions studied by small-angle-scattering, Phys. Chem.B 104 (2000) 7012 – 7022.
[20] Reynolds PA, Gilbert PE, White WJ: High internal phase water-in-oil emulsions and related microemulsions studied by small angle neutron scattering, J. Phys. Chem. B 105 (2001) 6925 – 6932.
[21] Zank J, Reynolds PA, Jackson AJ, Baranyai KJ, Perriman AW, Barker JG, Kim M-H, White WJ: Aggregation in a high internal phase emulsion observed by SANS and USANS, Physica B 385 – 386 (2006) 776 – 779.
[22] Espinosa CE, Guo Q, Singh V, Behrens SH: Particle charging and charge screening in nonpolar dispersions with nonionic surfactants, Langmuir 26 (2010) 16941 – 16948.
[23] Hsu MF, Dufresne ER, Weitz DA: Charge stabilization in nonpolar solvents, Langmuir 21 (2005) 4881 – 4887.
[24] Reynolds PA, Henderson MJ, Zank J, White JW: Complex layering observed in high internal phase emulsions at a silicon surface by neutron reflectometry, J. Colloid Interface Sci. 364 (2011) 539 – 545.
[25] Arditty S, Schmitt V, Lequeux F, Leal-Calderon F: Interfacial properties in solid-stabilized emulsions, Eur. Phys. J. B 4 (2005) 381 – 393.
[26] Dukhin AS, Goetz PJ: How non-ionic "electrically neutral" surfactants enhance electrical conductivity and ion stability in non-polar liquids, J. Electroanal. Chem. 588 (2006) 44 – 55.
[27] Poovarodom S, John CB: Effect of particle and surfactant acid-base properties on charging of colloids in a polar media, J. Colloid Interface Sci. 346 (2010) 370 – 377.
[28] Menner A, Ikem V, Salgueiro M, Bismarck A: High internal phase emulsion templates solely stabilised by functionalised titania nanoparticles, Chem. Comm. (2007) 4274 – 4276.
[29] Richard HH, Don HC, Heldon KH, Scott BP: Emulsion phase having improved stability, US Patent (2004) 6808573.
[30] Princen HM, Kiss AD: Rheology of foams and highly concentrated emulsions. A: An experimental study of the shear viscosity and yield stress of concentrated emulsions, J Colloid Interface Sci. 128 (1989) 176 – 187.
[31] Simovic S, Prestidge CA: Nanoparticles of varying hydrophobicity at the emulsion droplet-water interface: adsorption and coalescence stability, Langmuir 20 (2004) 8357 – 8365.
[32] Smitha S, Shajesh P, Mukundan P, Warrier KGK: Synthesis of mesoporous hydrophobic silica microspheres through a modified sol-emulsion-gel process, J. Sol-Gel Sci. Technol. 48 (2008) 356 – 361.
[33] Masalova I, Foudazi R, Malkin, AYa: The rheology of highly concentrated emulsions stabilized with different surfactants, Colloids and Surfaces A: Physicochem. Eng. Aspects 375 (2011) 76 – 86.
[34] Yates DE, Dack SW: Determination of emulsion explosives with Span-80 as emulsifier, US Patent (1987) 4710248.
[35] Sudweeks W: Physical and Chemical Properties of Industrial Slurry Explosives, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 432 – 436.
[36] White WJ, Henderson JM, Perriman A: The crystallization of supersaturated emulsions, Isis Experimental Report (2004): 14591.
[37] Binks BP, Desforges A, Duff DG: Synergistic Stabilization of Emulsions by a Mixture of Surface-Active Nanoparticles and Surfactant, Langmuir 23 (2007) 1098 – 1106.
[38] Midmore BR: Preparation of a novel silica-stabilized oil/water emulsion, Colloids and Surfaces A: Physicochem. Eng. Aspects 132 (1998) 257 – 265.
[39] Midmore BR: Effect of aqueous phase composition on the properties of a silica-stabilized W/O emulsion, J. Coll. Interf. Sci. 213 (1999) 352 – 359.
[40] Tambe DE, Sharma MM: Factors controlling the stability of colloid-stabilized emulsions. I. An experimental investigation, J Coll. Interf. Sci. 157 (1993) 244 – 53.
[41] Tambe DE, Sharma MM: Factors controlling the stability of colloid-stabilized emulsions. II. A model for the rheological properties of colloid-Laden interface, J Coll. Interf. Sci. 162 (1994) 1 – 10.
[42] Tambe DE, Sharma MM: The effect of colloidal particles on fluid–fluid interfacial properties and emulsion stability, Adv Coll. Interf. Sci. 52 (1994) 1 – 65.
[43] Midmore, BR: Synergy between silica and polyoxyethylene surfactants in the Formation of O/W Emulsions, Colloids and Surf. A: Physicochem. Eng. Aspects 145 (1998) 133 – 143.
[44] Binks BP, Philip J, Rodrigues JA: Inversion of Silica-Stabilized Emulsions Induced by Particle Con-

centration, Langmuir 21 (2005) 3296–3302.
[45] Khan SA, Zoeller NJ: Dynamic Rheological Behavior of Flocculated Fumed Silica Suspensions, J. Rheol. 37 (1993) 1225–1235.
[46] Raghavan SR; Walls HJ, Khan SA: Colloidal Interactions between Particles with Tethered Nonpolar Chains Dispersed in Polar Media: Direct Correlation between Dynamic Rheology and Interaction Parameters, Langmuir 16 (2000) 7920.
[47] Barthel H: Surface interactions of dimethylsiloxy group-modified fumed silica, Colloids Surf. A 101 (1995) 217.
[48] Binks BP, Clint JH, Whitby CP: Rheological Behavior of Water-in-Oil Emulsions Stabilized by Hydrophobic Bentonite Particles, Langmuir 21 (2005) 5307–5316.
[49] Lagaly G, Reese M, Abend S: Smectites as colloidal stabilizers of emulsions – II. Rheological properties of smectite-laden emulsions, Appl. Clay Sci. 14 (1999) 279.
[50] Gosa KL, Uricanu V: Emulsions stabilized with PEOPPO-PEO block copolymers and silica, Colloids and Surf. A: Physicochem. Eng. Aspects 197 (2002) 257–269.