

# Flow behaviour of highly concentrated emulsions of supersaturated aqueous solution in oil

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**Abstract** A set of highly concentrated water-in-oil emulsions with supersaturated dispersed phase were investigated in this work to verify and/or develop the models that have been presented both in the literature and in this work. The material used to form emulsions consisted of supersaturated oxidiser solution, hydrocarbon oil and PIBSA-based surfactants. The interfacial characteristics for different surfactant types were first examined. Then, the rheology of samples was studied, and different scaling methods and fitting of experimental data were studied. On the basis of flow curve measurements and observed  $\tau_v \sim \dot{\gamma}^{1/2}$  scaling, a modified version of Windhab model was suggested which showed excellent fitting of experimental results. The linear dependences of  $\tau_{y0}/\sigma$  versus  $1/d_{32}$  for studied emulsions showed non-zero intercept which implies a non-linear dependence (resulting from interdroplet interaction) to fulfil the zero-intercept requirement. It was established that the zero intercept condition was fulfilled in the

$\tau_{y0} \sim \sigma/d_{32}^2$  scaling, although the experimental results for different surfactants were not superimposed.

**Keywords** Flow curve · Yield stress · Viscous stress · Laplace pressure · Interdroplet interaction

## Introduction

Highly concentrated emulsions (HCE) are classified as high internal phase ratio emulsions (or simply HIPRE), and the dispersed phase droplets are ranged in a polyhedral closely packed configuration that is far beyond the close packing limit of spherical droplets. This closely packed configuration and the profound hydrodynamic interaction between neighbouring droplets induce mechanical interference between the droplets, thus prohibiting their free movement.

The highly concentrated emulsions have various important applications in the food and cosmetic industries, but one of the more interesting applications is their use as “liquid explosives” (Bampfield and Cooper 1985; Webber 1999). The referred explosive emulsion in this text is the base emulsion which will be sensitised by mixing with sodium nitrite solution in the later stages. The base emulsion is pumped into a mine using pipelines before it is sensitised, so its rheological properties is of special interest for industry, as well as academy (Masalova et al. 2003).

The base explosive emulsion is a water-in-oil emulsion composed of an oxidiser solution, organic fuel and an emulsifying system that is usually consisted of polymeric surfactants. The oxidiser solution forms the discontinuous phase of the explosive with a volume fraction about 80 ~ 90% and generally comprises

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inorganic oxidiser salt, in an amount from 45% to about 95% by weight of the total composition (Hales et al. 2004). The oxidiser solution is usually a supersaturated over-cooled solution of ammonium nitrate (AN) at room temperature (Hales et al. 2004), which is in the state of hydrous melt where ions can move about easily (Bengtsson et al. 1994). The supersaturated overcooled state of oxidiser solution means that it has the potential to crystallise instantly; however, explosive emulsions are stable against crystallisation for months (Masalova et al. 2006).

For high internal phase systems such as emulsion explosives, there are no published data on the behaviour of the surfactant film. It may be speculated that, for the system to flow, both distortion of droplet shape and shearing of the interdroplet layer must be involved. Indeed, in a quantitative way, this can be observed, e.g., oxazoline and amine surfactants tend to give lower viscosity emulsions than do sorbitain derivatives, but little systematic work has been done (Becher 1983). Bampfield and Cooper (1985) showed that certain polymeric surfactants dramatically increase the viscosity of emulsion explosives, while at the same time making them rubbery which could be due to the bridging of surfactant molecules at the inter droplets region.

The flow curve measurement of explosive emulsions showed the existence of a low shear rate Newtonian plateau by measuring viscosity from low to high stress, but its absence when measurements were made at decreasing stress levels (Masalova et al. 2005; Masalova and Malkin 2007a). The downward curve shows the existence of a yield stress. However, measuring the viscosity by time sweep tests at different shear rates and creep experiments demonstrated that the downward branch of the flow curve is physically meaningful, and identifies rheological properties of the emulsion in which shear-induced structure has been created by loading. Hence, the presence of yield stress for this type of emulsion is apparent (Masalova et al. 2005).

The normal stress measurement during the downward flow curve measurement as well as the microscopic studies of simple shear flow of explosive emulsions (Malkin and Masalova 2007; Masalova and Malkin 2007a) showed two different mechanisms of flow at low and high shear rates. It was seen that the flow of emulsions at low shear rates involves the rolling of larger droplets over smaller ones without any noticeable distortion of their shape, while serious distortions of droplet shape are observed at high shear rates. An inflection in the flow curve, like a hump at the intermediate shear rate of flow curve, was observed as an indication of the transition of flow behaviour from non-deformation to deformation of droplets. The

flow curve of emulsions was fitted by Herschel–Bulkley model with two different sets of coefficients below and above the hump (Malkin and Masalova 2007).

Viscoelastic properties of highly concentrated emulsions have already been studied widely, both experimentally and theoretically. It has been shown that the viscoelastic properties depend on the mean diameter of dispersed particles, polydispersity, interfacial tension and particularly on the dispersed volume fraction, although it is accepted that, in considering the area–volume mean droplet size, the polydispersity does not have a pronounced effect. Some studies showed that the osmotic pressure, shear modulus and yield stress scale with the Laplace pressure (Barry 1975; Princen et al. 1980; Princen 1983, 1985; Princen and Kiss 1989; Aronson and Petko 1993; Reinelt and Kraynik 1990, 1996; Babak et al. 2001). However, several experimental works show a discrepancy with regard to this fundamental scaling (Masalova et al. 2006; Pons et al. 1992, 1995; Otsubo and Prud'homme 1994; Dimitrova and Leal-Calderon 2004; Malkin et al. 2004; Bengoechea et al. 2006; Mougél et al. 2006; Masalova and Malkin 2007b; Romero et al. 2008). Therefore, Bengoechea et al. (2006) suggested that “*an additional source of elasticity should be considered*”.

The interactions between the deformable interfaces of droplets could be (1) the work done against interfacial tension to create additional interfaces when two droplets deform as they are forced together, (2) depletion attraction and (3) the short-range repulsion (disjoining pressure) that prevents droplet coalescence (Mason 1999; Mason et al. 1996b). Since the work done against interfacial tension is already considered in Laplace pressure, the two other sources can be considered as additional source of elasticity. The significance of depletion attraction in an emulsion can result in attractive (adhesive) emulsions in which droplets flocculate or gel (Mason 1999; Mason et al. 1996b). The presence of a strong interdroplet attraction has been found to significantly influence the onset volume fraction and corresponding shear modulus compared to repulsive emulsions; however, at very high volume fractions, the rheological properties of attractive and repulsive emulsions may be quite similar, dominated by the interfacial tension of the deformed droplets (Mason 1999; Mason et al. 1996b).

In our previous works (Foudazi et al. 2010a, b), we considered the disjoining pressure as the source of additional elasticity, and we found that for explosive emulsions the electrostatic repulsion enhanced by reversed micelles could be responsible for non-scaling of shear modulus with Laplace pressure. The model supports a nonlinear dependency of shear modulus

scaled by interfacial tension versus reciprocal droplet size to satisfy the zero intercept of such dependence, which could be obtained in the presence of interdroplet interaction.

Since the structure of concentrated emulsions may depend on flow history, shear bands during flow, particularly in rheological measurements, can occur due to the irreversibly fracture of structure, creating a local weakness in the material. Therefore, any considered strain rate in this case may just be an apparent strain rate and may hide inhomogeneities in the strain rate in the sheared emulsion. The presence of shear banding in granular material is fairly studied (Schall and van Hecke 2010), although foams and concentrated emulsions have attracted researchers recently (Schall and van Hecke 2010; Bécu et al. 2006). The problem of shear banding became one of the hot spots in the rheology of multi-components systems (see the review Malkin et al. 2010). Common understanding is that the formation of banding is tightly related to the multi-valued flow curves corresponding to the co-existence of different states of a media. It has been shown (Bécu et al. 2006) that non-adhesive and adhesive emulsions have radically different flow behaviors in the vicinity of yielding: while the flow remains homogeneous in the non-adhesive emulsion and the yield stress fluid can be described by Herschel–Bulkley model very accurately, the adhesive system displays shear banding and does not follow a simple constitutive equation, suggesting that the mechanisms involved in yielding transitions are not universal.

In this work, firstly we developed a new model for flow curve of highly concentrated emulsions which is able to predict the behaviour in whole shear rate range; and secondly, the present scaling models for yield stress of highly concentrated emulsions were studied for explosive emulsions in which the interdroplet interaction is significant.

## Theory

Princen and Kiss (1989) assumed in their work that the three-dimensional equations predicting yield stress, stress of systems under flow and viscosity are functionally similar to the equation derived from their two-dimensional model. They then measured stress and yield stress behaviour of real emulsion and fitted the experimental rheological data for emulsions with different values of volume fraction  $\varphi$ , from 0.74 up to 1.0. On the basis of their modelling, they considered that the yield stress scale with Laplace pressure. Mason et al. (1996a) conducted a systematic study of highly

concentrated monodisperse emulsions and proposed the same scaling behaviour for yield stress. However, they considered the yield stress as the onset of nonlinearity in the strain sweep oscillatory experiment which was shown to be frequency dependent in our previous work (Masalova et al. 2008).

The scaling of yield stress with Laplace pressure indicates that the variation of  $\tau_{y0}$  or  $\tau_{y0}/\sigma$  against reciprocal droplet size,  $1/d_{32}$ , is linear with zero intercept, where  $\tau_{y0}$ ,  $\sigma$  and  $d_{32}$  are yield stress, interfacial tension and area-volume (Sauter) mean droplet size, respectively. This zero intercept of  $\tau_{y0} - 1/d_{32}$  dependence is physically meaningful, because when  $d_{32}$  tends to infinity (two separated phases), the yield stress will vanish ( $d_{32} \rightarrow \infty \Rightarrow \tau_{y0} \rightarrow 0$ ).

Mason (1999) studied the scaling behaviour of yield stress with volume fraction of dispersed phase of HCE as well, and proposed following experimental scaling relationship:

$$\tau_{y0} \sim \varphi(\varphi - \varphi_c)^2 \quad (1)$$

where  $\varphi_c$  is a critical volume fraction at which the yield stress rises much more dramatically.

By studying the flow curve of HCE, Princen and Kiss (1989) found that the functional dependence of capillary number,  $Ca$ , deviated from the two-dimensional model, where the viscous stress  $\tau_v \sim Ca^{2/3}$ . The viscous stress is the total stress minus yield stress as  $\tau_v = \tau - \tau_{y0}$ . They determined the viscous stress dependence experimentally, and got the flow curve prediction in terms of shear stress as follows:

$$\tau = \tau_{y0} + 64(\varphi - 0.73) \frac{\sigma}{d_{32}} Ca^{1/2} \quad (2)$$

It should be noted that this model is identical to a Herschel–Bulkley model with flow behaviour index equal to one half.

As mentioned, the flow curve of explosive emulsions shows a hump at intermediate shear rates (Masalova and Malkin 2007a; Malkin and Masalova 2007). A similar behaviour has been seen for dispersions and the following model for flow curve was proposed by Windhab (1993):

$$\tau = \tau_{y0} + \eta_{\infty} \dot{\gamma} + (\tau_{y1} - \tau_{y0}) [1 - \exp(-\dot{\gamma} / \dot{\gamma}^*)] \quad (3)$$

The Windhab (1993) model includes the directly measured yield stress,  $\tau_{y0}$ , and the high shear viscosity,  $\eta_{\infty}$ . It also considers the crossover point (hump),  $\tau_{y1}$ , which is usually observed in the flow curve of highly concentrated emulsions at intermediate shear rates with characteristic of  $\dot{\gamma}^*$ .

## Experimental

### Materials

#### Dispersed phase

The dispersed phase of the emulsion samples used in this study consisted of a supersaturated solution of ammonium nitrate. The water content of the dispersed phase was 20% by mass. In order to stabilise the pH of the emulsion to 4.0, the dispersed phase contained 0.5 wt.% of acetic acid and sodium acetate as buffer. The equilibrium temperature for dissolving 80 wt.% ammonium nitrate (abbreviated as AN) concentration is approximately 65°C and such a solution has a “Fudge Point” or crystallisation point of approximately 58°C. As after the preparation of emulsions, they were cooled down to room temperature, it meant that the aqueous phase of emulsions was a super-saturated over-cooled solution.

#### Surfactants

The surfactants used to stabilise the emulsion samples for this work were manufactured and provided by Lake International Technologies, South Africa. Three surfactants based on organic derivatives of poly(isobutylene) succinic anhydride (PIBSA), PIBSA–MEA, PIBSA–Imide, PIBSA–Urea, were used. The chemical structures of surfactants are shown in Fig. 1.

The hydrophobic moiety for the three PIBSA derivatives (PIBSA–MEA, PIBSA–Imide and PIBSA–Urea) is the polyisobutylene chain, with an approximate relative molecular weight of 1,050. The hydrophilic moiety is the modified succinic anhydride group, with an approximate relative molecular weight of 150. Thus the hydrophilic–lipophilic balance (HLB) leaned heavily towards lipophilicity (i.e. hydrophobicity) at less than 4, and the surfactants were soluble in hydrocarbon oils, but insoluble in water.

#### Continuous phase

When originally synthesised, the surfactants were dissolved or dispersed in Parprol 32, a paraffinic petroleum oil with no additives. Further dilution with Mosspar-H hydrocarbon-based oil (Lake International, South Africa) was performed to achieve the desired concentration.

#### Instrumentation

#### Sample preparation

The Hobart N50 mixer was used to manufacture all the samples under study. The mixer consists of an agitator unit and a bowl that was heated to 85°C. The emulsification process included the gentle pouring of pre-dissolved ammonium nitrate solution into the surfactant in the continuous phase solution contained in the bowl. The mixing performance of Hobart is facilitated by intensive shearing of the sample between the agitator and the bowl. The prepared emulsions were cooled to room temperature prior to doing any rheological or droplet size measurements.

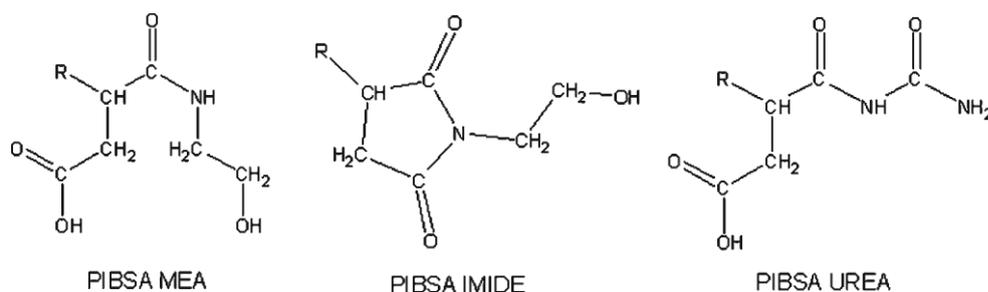
#### Microscopy observation

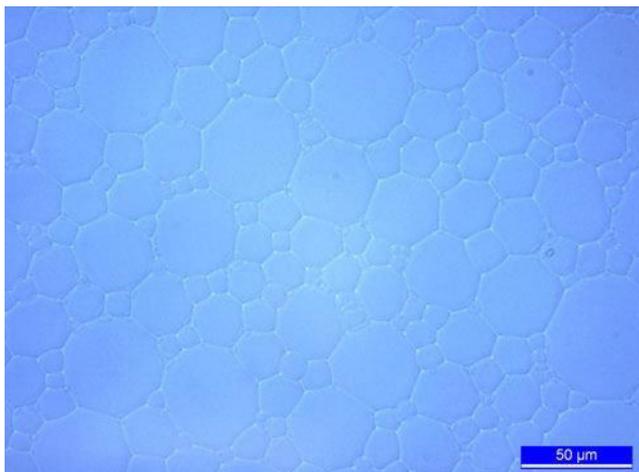
For qualitative analysis of the samples, it was checked to ensure that the emulsion was properly formed and the crystallisation of ammonium nitrate had not been started; if these criteria were not met, samples were excluded from the measurements. This analysis was achieved by using a Leica optical microscope with ×500 magnification. A typical image of a formed and uncrystallised sample is shown in Fig. 2.

#### Droplet size analysis

The droplet size distribution was measured using the Malvern Mastersizer 2000 instrument. The samples were diluted in the same oil as the continuous phase,

**Fig. 1** The chemical structure of employed surfactants where “R” indicates the polyisobutylene chain





**Fig. 2** A typical optical microscopic picture of studied highly concentrated emulsions (with PIBSA–MEA surfactant,  $\phi = 0.892$  and  $d_{32} \approx 16 \mu\text{m}$ )

just before the measurements were taken. The procedure is based on the measurement of angle dependence of the intensity of scattering of a collimated He–Ne laser beam. The angle at which the light is scattered is inversely proportional to the size of the particles. Particle size in the range from 0.5 to 2,000  $\mu\text{m}$  can be measured, which is much wider than the droplet size distribution of the real samples used in this work. The particle size distribution calculations were based on the rigorous Mie theory.

#### Rheological measurements

Rheometry was conducted using the MCR 300 Paar Physica rheometer. The rheological measurements were performed by using “plate-and-plate” geometry with a plate diameter of 50 mm and sandblasted surface. It has been shown in our previous work (Masalova et al. 2006), by using different measuring gaps with sandblasted plate, the presence of slip can be neglected in rheological measurements of this type of emulsions (Masalova et al. 2006). The measuring gap between the two plates in the current work was 1 mm. All rheological measurements were conducted at 30°C.

#### Interfacial tension

The Kruss K100 tensiometer was used to measure the interfacial tension, critical micelle concentration (CMC) and surfactant concentration at interface. Static measurements with the Wilhelmy plate were used to determine the characteristics of the interfacial area between the oil (Mosspar-H) and the dispersed phase (ammonium nitrate solution).

The interfacial dilatational elasticities in the presence of different surfactants were also measured by Drop and Bubble Shape Tensiometer PAT1, Sinterface Technologies. This method works based on oscillation of a pendent droplet of dispersed phase in continuous phase.

#### Matrix of samples

Five different concentrations of the dispersed phase were employed in the formulation: 85, 88, 90, 92 and 93.5 wt.%. These weight fractions correspond to following volume fractions of the dispersed phase in emulsion: 0.764, 0.807, 0.837, 0.868 and 0.892. In this set of samples, three different surfactants, PIBSA–MEA, PIBSA–Imide and PIBSA–Urea, with same concentration of 14 wt.% in oil phase and a range of droplet sizes, 7.5 ~ 16  $\mu\text{m}$ , were studied.

#### Results and discussion

The critical micelle concentration, the interfacial tension above CMC and the concentration of surfactant at the interface obtained from the Gibbs equation are summarised in Table 1. The surfactant concentration at the interface was used to calculate the area occupied by a single surfactant molecule at the interface. The obtained CMC values show that the surfactant concentration is much higher than CMC in all prepared explosive emulsions, and therefore micelles are present in the continuous phase. Besides this, the interfacial dilatational elasticities in the presence of different surfactants measured by drop shape tensiometer are also presented in Table 1.

**Table 1** Interfacial properties of different surfactants used in this work

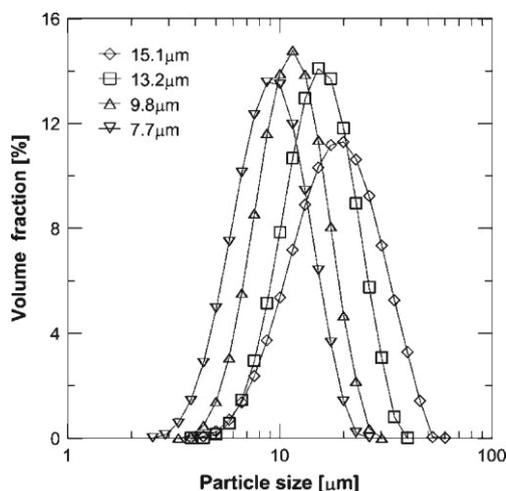
Type of surfactant	$\sigma$ (mN/m)	$E'$ (mN/m) at 0.1 Hz	CMC $\times 10^4$ (mole/l)	Area per molecule ( $\text{nm}^2$ )
PIBSA–MEA	8.4	4.3	0.9	1.5
PIBSA–Urea	5.9	3.2	1.2	1.5
PIBSA–Imide	1.0	1.2	2.2	1.4

The interfacial dilatational elasticity (dynamic elasticity) shows the same trend as the interfacial tension (static elasticity), something that is not unexpected. While the employed PIBSA-based surfactants occupy almost the same area at the interface, they show significantly different interfacial tensions and dilatational elasticities.

The results show that the following trend in interfacial elasticity is present: PIBSA–MEA > PIBSA–Urea > PIBSA–Imide. Hence, if the rheological properties of studied highly concentrated emulsions are controlled by the interfacial tension and/or dilatational elasticity, the same trend should be observed for flow curve and yield stress.

The results of typical droplet size distribution evolution for PIBSA–MEA surfactant-stabilised emulsions are shown in Fig. 3 for the volume fraction of 0.764. Similar behaviour was observed for different volume fractions and different surfactant types. It has been shown in our previous work for the same system (Mudeme et al. 2010) that below some critical droplet size, about 13  $\mu\text{m}$ , the droplet size distribution remains almost unchanged as was shown by the evolution of width of distribution obtained by fitting the Gauss function (Mudeme et al. 2010).

It can be shown qualitatively that the droplet size distribution for emulsions of the same droplet size ( $d_{32} = 7.5 \pm 0.1 \mu\text{m}$ ) stabilised with different surfactant types (Fig. 4a) and different volume fractions (Fig. 4b) is very close. However, some deviation is observed for the lowest volume fraction where we are close to the closest packing of spherical droplets. These results suggest that the effect of droplet size distribution on the rheological behaviour of studied emulsions can be



**Fig. 3** The variation of droplet size distribution for PIBSA–MEA stabilised explosive emulsions with 0.764 volume fraction

ignored.<sup>1</sup> However, this effect is somehow excluded when the area–volume mean diameter ( $d_{32}$ ) is considered in the studying the rheology of highly concentrated emulsions.<sup>2</sup>

The flow curves of explosive emulsions stabilised by PIBSA–MEA at a typical volume fraction ( $\phi = 0.868$ ) and for different droplet sizes are shown in Fig. 5. It is clear that the emulsions show a pronounced yield stress, but a hump in the flow curve at moderate shear rates ( $\dot{\gamma} \approx 0.1 - 1 \text{ s}^{-1}$ ) is seen. Similar behaviour was observed for different volume fractions and surfactant types.

The presence of a hump in the flow curve at moderate shear rates was explained by Windhab (1993) as a secondary yield stress. As mentioned, Malkin and Masalova (2007) found that, at shear rates above the hump, the droplets are deformed during flow, while the rolling of larger droplets over smaller ones without noticeable distortion of their shape 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 (Malkin and Masalova 2007).

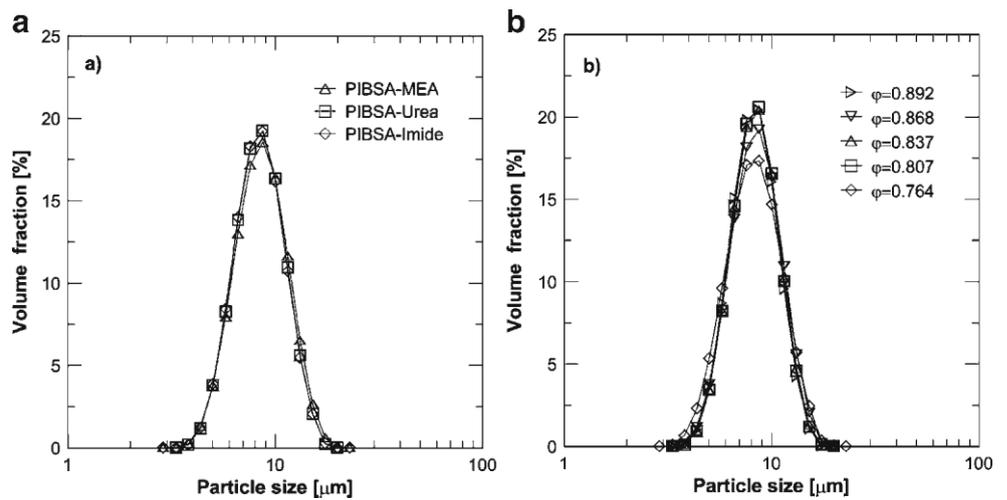
The insufficient fitting of the Herschel–Bulkley model, which is a generalised form of Princen and Kiss model Eq. 2, and Windhab model, Eq. 3, is shown in Fig. 6. It is clear that the Herschel–Bulkley model does not predict the hump at moderate shear rates, and Windhab’s model also fails to fit the measured flow behaviour.

A useful method for modelling the flow curve is fitting Herschel–Bulkley model with two different sets of coefficients below and above the hump (Malkin and Masalova 2007). This fitting method was used for the flow curves of all highly concentrated emulsions prepared by different PIBSA-based surfactants, various droplet sizes and volume fractions and it was found that, in both regions,  $n = 0.5$  results in a good fitting of flow curves. This is shown by dashed lines in Fig. 7a, and is in agreement with experimental relation  $\tau_v \sim Ca^{1/2}$  suggested by Princen and Kiss (1989). The successful fitting with the Herschel–Bulkley model in the yield stress region suggests that the investigated emulsions are not adhesive and shear banding could be

<sup>1</sup> At least in a range of droplet sizes and volume fractions

<sup>2</sup> This is because the rheological behaviour of highly concentrated emulsions is controlled by the interfacial area (total area and flattened area) of droplets.

**Fig. 4** Droplet size distribution of explosive emulsions stabilised **a** with different surfactant types but same  $\phi = 0.868$  and **b** with different volume fractions but same surfactant PIBSA–Urea



indeed neglected during rheological measurements (Bécu et al. 2006). The microscopic observation of diluted highly concentrated emulsion, Fig. 8, showed individual droplets that confirms the non-adhesive nature of these emulsions.

Since the Windhab model implies  $\tau_v \sim Ca$ , it can be modified by considering the observed dependency of viscous stress on shear rate to the power of one half as follows:

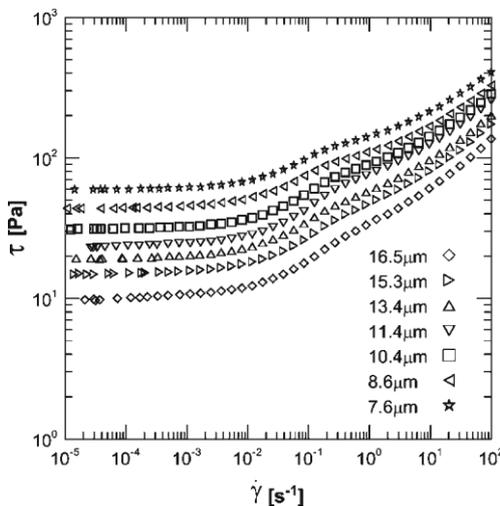
$$\tau = \tau_{y0} + K\dot{\gamma}^{0.5} + (\tau_{y1} - \tau_{y0}) 1 - \exp(-\dot{\gamma} / \dot{\gamma}^*) \quad (4)$$

This model shows excellent fitting of experimental results in the whole shear rate range, as shown by the dashed line in Fig. 7b; however, the  $\tau_v \sim Ca^{1/2}$  scaling is not exactly valid for this proposed model due to the presence of exponential term. Excellent fittings of Eq. 4

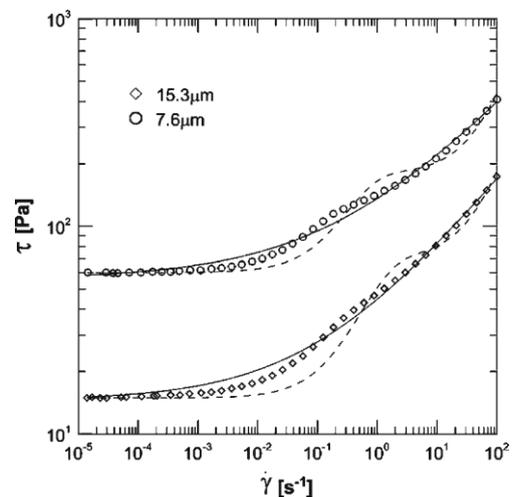
were observed for all samples with different droplet sizes, volume fractions and surfactant types as shown in Fig. 9.

The viscosity of the surfactant-in-oil solution averaged over the range 6.49 to 25.8 s<sup>-1</sup> for all surfactant type was found to be 6.1 ± 0.1 mPa s. Therefore, the differences in flow behaviour of emulsion samples stabilised with different surfactant types cannot be attributed to the viscosity of continuous phase, but may be attributed to the micellar structure of surfactant in the thin film layer of oil phase between aqueous droplets and/or interdroplet interaction (Foudazi et al. 2010a, b) of disperse phase.

It was widely accepted that the shear stress in simple shear flow below which the material does not flow (which corresponds to  $\tau_{y0}$  in the proposed model)

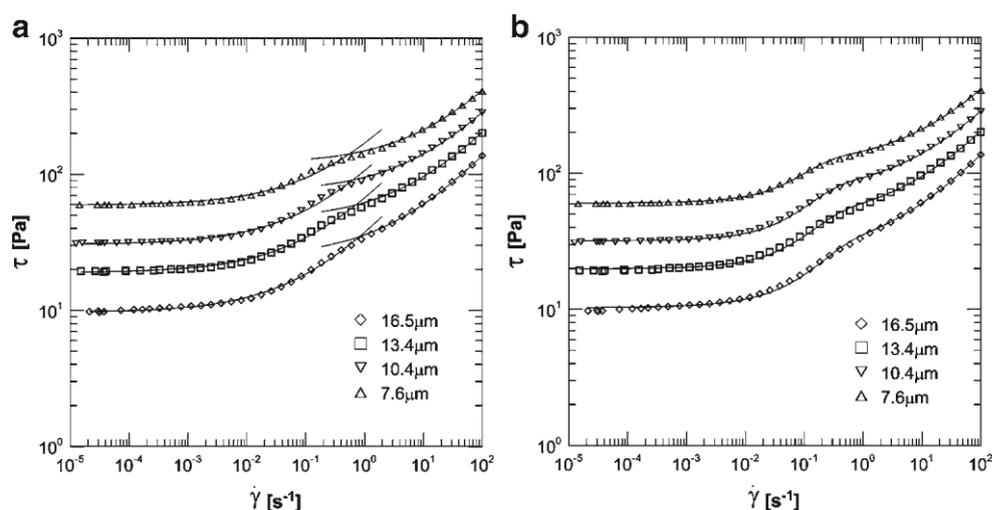


**Fig. 5** Typical flow curves for explosive emulsions of different droplet sizes ( $\phi = 0.868$ ) stabilised with PIBSA–MEA



**Fig. 6** Typical best fittings of Herschel–Bulkley (*continuous line*) and Windhab’s (*dashed line*) models on the flow curve of PIBSA–MEA stabilised emulsions

**Fig. 7** Typical fittings of **a** Herschel–Bulkley model with two different sets of  $\tau_{y0}$  and  $K$  coefficients but the same  $n = 0.5$  and **b** the proposed model, Eq. 4, on the flow curve of PIBSA–MEA stabilised emulsions



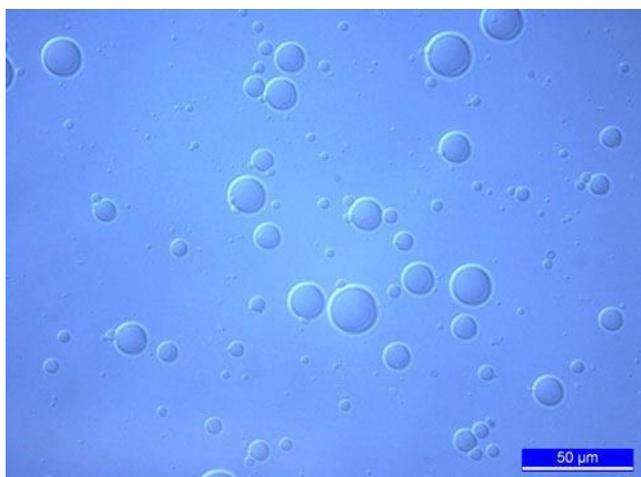
has some physical meaning and technological benefits. However,  $\tau_{y1}$  is only an asymptotic yield stress value that corresponds to the transition (crossover point, hump) in the flow behaviour at shear rate  $\dot{\gamma}^*$ . Based on the work by Malkin and Masalova (2007), this stress could be associated with the transition point from the rolling to the deformation mechanism of droplet motion.

The Princen and Kiss (1989) theory predicts that the variation of  $\tau_{y0}$  or  $\tau_{y0}/\sigma$  against reciprocal droplet size,  $1/d_{32}$ , is linear with zero intercept. As mentioned, this zero intercept of  $\tau_{y0} - 1/d_{32}$  dependence is physically meaningful, because when  $d_{32}$  tends to infinity (two separated phases), the yield stress will vanish ( $d_{32} \rightarrow$

$\infty \Rightarrow \tau_{y0} \rightarrow 0$ ), although this dependence can deviate from the simple linear relationship. The variation of yield stress,  $\tau_{y0}$ , against droplet size for explosive emulsions of  $\phi = 0.868$ , stabilised with different surfactant types, is shown in Fig. 10. The non-zero intercept of  $\tau_{y0} - 1/d_{32}$  dependence for studied emulsions implies the existence of a non-linear dependence to fulfil the zero intercept requirement. The condition of non-linear dependence cannot be associated with the variation of droplet size distribution for different droplet sizes, because it was shown that droplet size distribution remains almost unchanged in a certain range. In other words, even if we exclude the first few points in Fig. 10 which correspond to big droplet sizes with dissimilar distributions (slightly broader), the non-zero intercept of linear dependence will be still present.

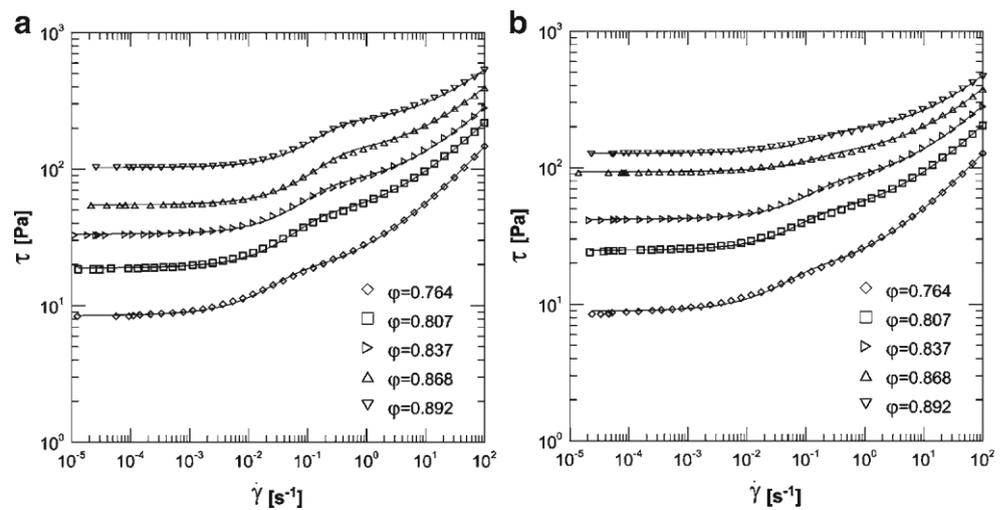
If the interfacial energy controls the yield stress of prepared highly concentrated emulsions, the same trend as interfacial tension and dilatational elasticity should be observed for yield stress values. However, a completely different trend is observed: PIBSA–Imide > PIBSA–Urea  $\approx$  PIBSA–MEA. Moreover, the Princen and Kiss (1989) theory predicts  $\tau_{y0}/\sigma - 1/d_{32}$  linear dependence should be superimposed for different surfactant types, but depends on the volume fractions. The non-superimposition of this dependence for different surfactants is shown in Fig. 11.

The scaling of rheological properties with reciprocal squared droplet size has been suggested by Masalova and Malkin (2007a), due to the non-zero film thickness between droplets, and attributed to Van der Waals forces between droplets by Mougel et al. (2006). However, both of them predict the scaling of rheological



**Fig. 8** Typical image of a diluted highly concentrated emulsion ( $\phi = 0.892$  and  $d_{32} \approx 16 \mu\text{m}$ ) to volume fraction about 10%

**Fig. 9** Typical flow curves of explosive emulsions of different volume fractions but similar droplet sizes ( $d_{32} = 7.5 \pm 0.1 \mu\text{m}$ ) stabilised with **a** PIBSA–Urea and **b** PIBSA–Imide

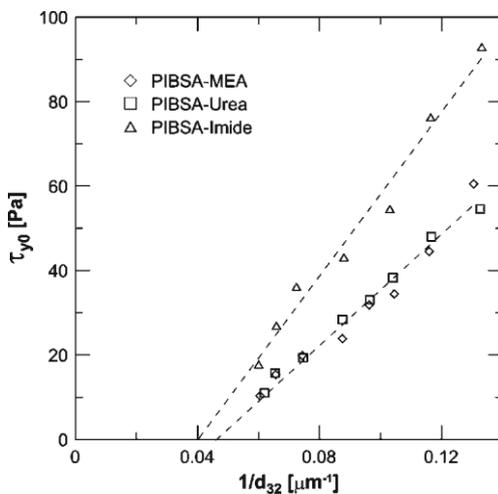


properties with interfacial tension, too. Thus, the idea is to check the  $\tau_{y0} \sim \sigma/d_{32}$  scaling, or the linear dependence and superimposition of  $\tau_{y0}/\sigma$  against  $1/d_{32}^2$  for different samples, as shown in Fig. 12.

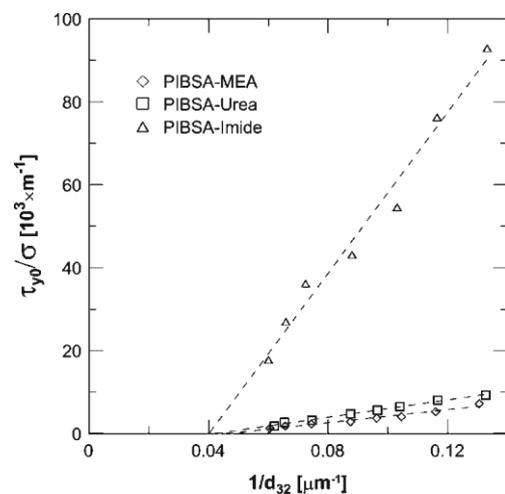
It is seen that the zero intercept condition is fulfilled in this scaling type, although the experimental results for different surfactants are not superimposed. This deviation reveals that models presented by Mougel et al. (2006) and Masalova and Malkin (2007b) are not satisfactory for prepared highly concentrated emulsions and some other phenomena control the rheological behaviour of these samples. This could be due to the presence of a significant interdroplet interaction which

was introduced in the modelling of shear modulus of highly concentrated emulsions in our previous work (Foudazi et al. 2010a, b). While shear modulus is obtained from the gel-like state and yield stress is acquired from the fluid-like state, both of them are controlled by droplet deformation and related to solid-like behaviour. The interfacial dilatational elasticity cannot be the controlling mechanism of observed behaviour, because it has the same trend as interfacial tension.

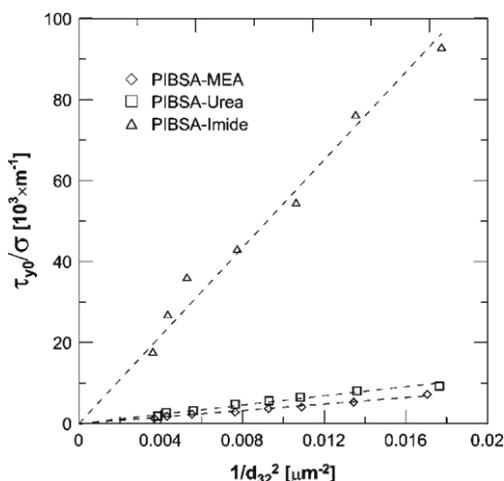
The scaling relationship, Eq. 1, which was suggested by Mason (1999), is considered in Fig. 13. For big droplet sizes—where the contribution of interdroplet interaction is less significant—a sufficient superimposi-



**Fig. 10** Variation of yield stress against reciprocal droplet size for explosive emulsions with different surfactant types ( $\varphi = 0.868$ )



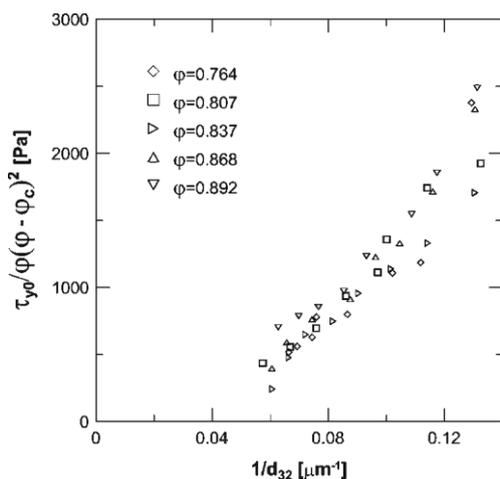
**Fig. 11** Variation of yield stress scaled with interfacial tension against reciprocal droplet size for explosive emulsions with different surfactant types ( $\varphi = 0.868$ )



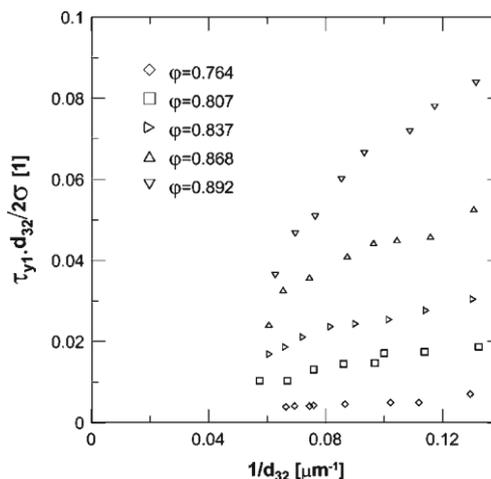
**Fig. 12** Scaling of yield stress with reciprocal squared droplet size ( $\varphi = 0.868$ )

tion is observed with  $\varphi_c = 0.695$ . In other words, when the interdroplet interaction becomes significant, deviation from this scaling behaviour is observed. This is reasonable, because Mason's scaling relationship was proposed for the case where the interfacial energy is the sole source of elasticity.

Since it was suggested that the hump in the flow curve is associated with a critical capillary number (Malkin and Masalova 2007), the variation of its stress,  $\tau_{y1}$ , divided by Laplace pressure as a function of droplet size is shown in Fig. 14. It is seen that this capillary number is dependent on both the volume fraction and the droplet size, thus the proposed theory does not work in this case. This shows that the interfacial energy is not the only controlling mechanism against rolling to deformation transition, but the interdroplet interaction may contribute to this transition.



**Fig. 13** Scaling of yield stress with  $\varphi(\varphi - \varphi_c)^2$



**Fig. 14** The capillary number of the stress of hump for PIBSA–MEA stabilised emulsions with different volume fractions and droplet sizes

## Conclusion

The flow curves of prepared highly concentrated emulsions with supersaturated overcooled aqueous dispersed phase showed a pronounced yield stress, but a hump in the flow curve at moderate shear rates was also seen. By fitting the Herschel–Bulkley model with two different sets of coefficients below and above the hump, it was found that  $n = 0.5$  resulted in a good fitting of flow curves. This was in agreement with scaling relation suggested by Princen and Kiss (1989) for viscous stress, and was considered in developing a modified version of Windhab model. This new model showed excellent fitting of experimental results in the whole shear rate range of all emulsion samples. The deviation of yield stress results from scaling relationship suggested by Princen and Kiss (1989) and Mason (1999) supported the significance of interdroplet interaction for explosive emulsions as it was observed for shear modulus behaviour (Foudazi et al. 2010a, b). The results showed that the yield stress scales with reciprocal squared droplet size; however, the experimental results for different surfactants were not superimposed which suggested that the interfacial tension is not the parameter controls the rheology when the interdroplet interaction is significant.