The Rheology of Binary Mixtures of Highly Concentrated Emulsions

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Abstract:
The rheological parameters (elastic modules and the yield stress) of binary mixtures of highly concentrated emulsions with different droplet sizes can be several times lower than additive values in a certain range of concentration. This is related to the proper packing of small droplets between larger ones without compression of droplets. While the yield stress is practically absent for these uncompressed droplets, the rather high storage modulus demonstrates the significance of interdroplet interaction in this system.

Zusammenfassung:
Die rheologischen Kenngrössen (elastische Module und Fließgrenze) von binären Mischungen von hochkonzentrierter Emulsionen mit unterschiedlicher Tröpfchengrösse können um ein Mehrfaches geringer sein als die rein additativen Werte der Kenngrössen. Das hängt damit zusammen, dass kleinere Tröpfchen zwischen grösseren Tröpfchen eingebunden sind, ohne dass Tröpfchen komprimiert werden. Während es für solche unkomprimierten Tröpfchen praktisch keine Fliessgrenze gibt, veranschaulicht der recht hohe Speicherungsmodul die Bedeutung der Wechselwirkung zwischen den Tröpfchen in diesem System.

Résumé:
Les paramètres rhéologiques (modules élastiques et limite d'écoulement) du mélange binaire des émulsions fortement concentrées ayant des gouttelettes de différentes dimensions peuvent être plus bas des valeurs des additifs dans une certaine gamme de concentration. Cela a trait au positionnement des petites gouttelettes autours des celles plus larges sans pour autant qu'il n'y ait aucune compression de ces dernières. Alors que la limite d'écoulement est pratiquement absente pour ces gouttelettes non comprimées, le module de stockage plutôt élevé démontre l'importance de l'interaction des gouttelettes dans ce système.

Key words: highly concentrated emulsions, binary mixtures, closest packing, yield stress, shear modulus

1 INTRODUCTION

Rheological properties of emulsions are the subject of numerous publications (see Review [1]). One of the points under discussion is the influence of droplet size on the rheological properties of emulsions, in particular, in the domain of high concentrations of a dispersed phase [2]. Generally speaking, the observed size dependencies of rheological parameters for highly concentrated emulsions (HCE) were monotonous for both narrow and wide size distributions. Besides, Pal [3] found a monotonous change in the rheological properties of HCE binary mixtures with gradual variation of the content of the two-component mixtures. However, for concentrated suspensions with bimodal size distribution of solids, it has been shown (e.g. [4]) that the shear viscosity is reduced in comparison to the properties of a suspension with a unimodal size distribution of particulates at a fixed volume fraction. A similar trend was found for suspensions with mixture of spheres and fibers in a certain range of solid content [5].

Therefore, there was a question: is this effect special for suspensions because it was not observed for emulsions? The answer to this concern was done in this study, because we succeeded to find that the dependence of the rheological parameters on the relative content of components in binary mixtures of HCE demonstrates quite different results from what was reported in [3], but similar to the behavior of bimodal suspensions [4, 5]. The experimental system was a water-in-

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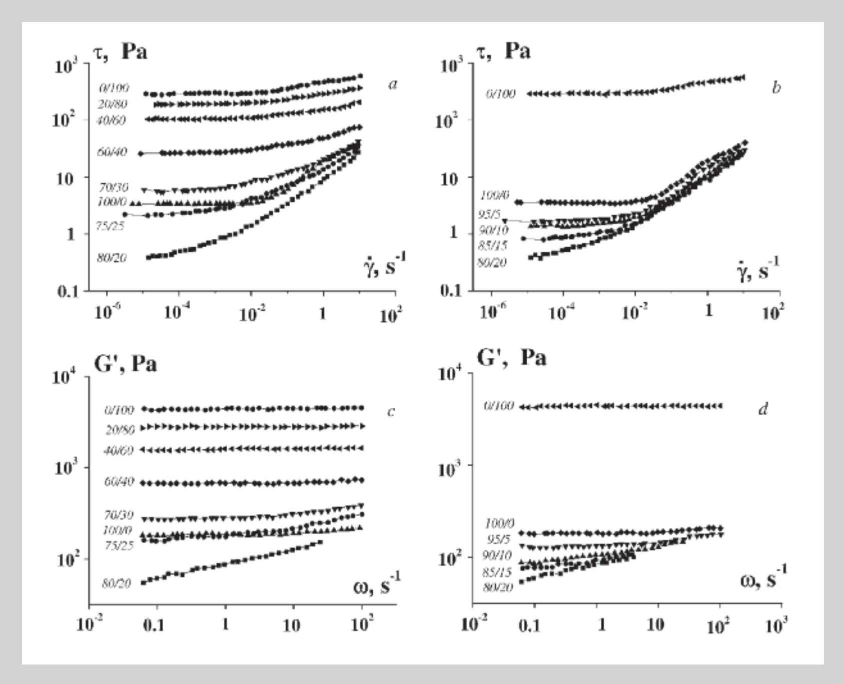

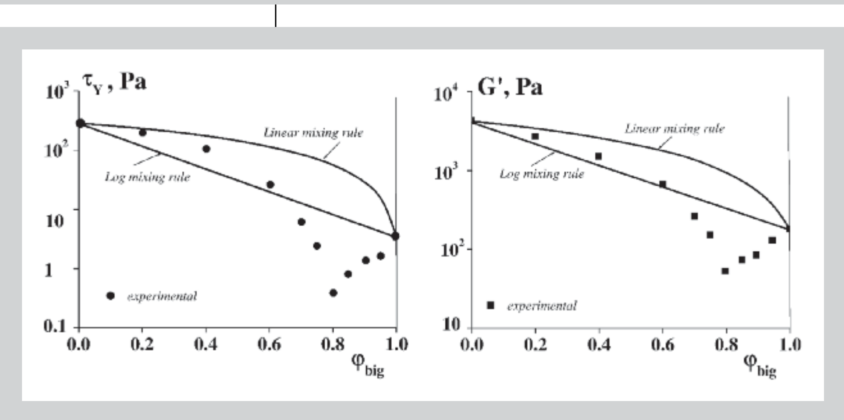

Figure 1 (above): Flow curves (a, b) and storage modulus versus angular frequency (c, d) of binary emulsions with 0.85 total volume fraction of a dispersed phase and different big/small volume ratios. The (b) and (d) parts of the figure separately demonstrate the big/small compositions behavior where the fall of rheological parameters is more significant.

Figure 2: Experimental data (points) for the yield stress (left) and elastic modules (right) in comparison with linear and logarithmic mixing rules (lines).

oil (w/o) emulsion with dispersed phase volume fraction of 0.85. This is far above the concentration of the closest packing of monodisperse spheres. The continuous phase was a dispersion of emulsifier in hydrocarbon oil. The emulsifier, poly(isobutylene succinic anhydride-urea), comprises 8 % of the paraffinic oil phase (see [6] for more information about the surfactant). The disperse phase was 60 wt% aqueous solution of ammonium nitrate. We prepared two samples with Sauter mean droplet sizes, d_{32}, of 2.7 and 16.9 μm. The size distributions in both cases are log-normal and rather narrow with uniformity of:

$$\sum \frac{V_i \left| d(v,0.5) - d_i \right|}{d(v,0.5)} \sum V_i \approx 0.31 - 0.32 \qquad (1)$$

The droplet size distributions have less than 5 % overlapping of the tails. Binary mixture of emulsion droplets with relative content of both drop size class from 100/0 to 0/100 (big-to-small volume ratio) were prepared by gently mixing using a spatula. Then the mixtures were left for a few days to allow equilibration of structure. The emulsions were gently mixed from time to time during this period. The samples were investigated using MCR300 rheometer (Anton Paar Physica). All experiments were performed at 30 °C.

The main experimental results are presented in Figure 1. One can see that the unimodal emulsions, noted by 100/0 and 0/100, are typical viscoplastic media [2, 7]. The yield stress is expressed very clearly (Figure 1a, b) and in the domain of linear viscoelasticity (small amplitudes of deformations), they show a solid-like behavior and storage modulus is practically constant in a wide frequency range (Figure 1c, d). This is quite typical case for compressed HCE beyond the threshold of the closest packing. The most interesting effects are demonstrated by binary mixture with the content of small droplets about 20 %, where the viscosity is strongly reduced to a value lower than the pure 100/0 emulsion. The viscosity of a mixture of two components can be assumed to follow linear (simple) or logarithmic (Arrhenius) mixing rules, respectively [8]:

$$\eta = \phi_1 \eta_1 + (1 - \phi_1)\eta_2 \qquad (2)$$

$$\log \eta = \phi_1 \log \eta_1 + (1 - \phi_1) \log \eta_2 \qquad (3)$$

where ϕ_i and η_i are the volume fraction and viscosity of fraction *i*, respectively. The same rules might be expected for other rheological parameters of binary mixtures. The prediction of these models is compared with experimental data for the yield stress and storage modulus plateau in Figure 2. One can see that the negative deviations of the yield stress and elastic modulus from both mixing rules is an order of magnitude for binary mixtures which comprises 10 ~ 25 % of small droplets. It is interesting to note that the viscosity of concentrated binary suspensions of fiber and sphere at a similar range of fiber content was found to be even lower than suspensions of only spheres [5]. The theoretical and simulation results presented by Farr et al. [9] suggest that the threshold of the closest packing, φ^*, for a binary mixture of two monodisperse hard spheres, could be shifted up to 0.83 depending on spheres size ratio for 80/20 (big-to-small volume ratio) composition.

As seen in Figure 1, the yield stress and solid-like behavior is practically absent in the 80/20

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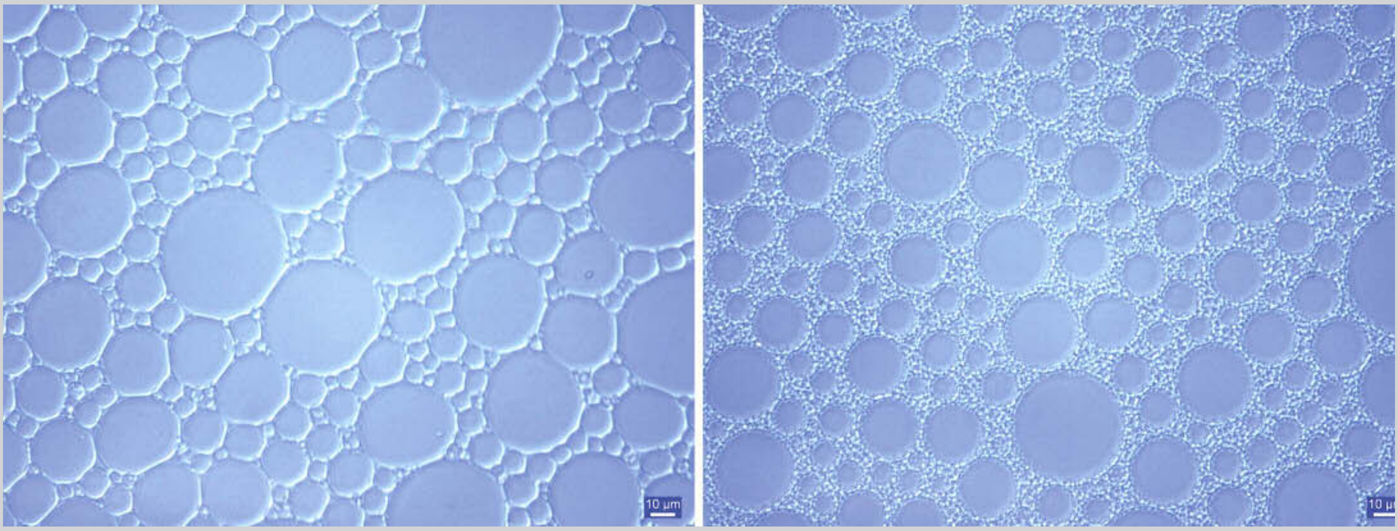

Figure 3: Optical microscopic picture of (left) emulsions containing only big droplets d_{32} = 16.9 μm and (right) 80:20 binary mixture of two fractions with d_{32} = 16.9 and 2.7 μm

mixture in contrast to the viscoplastic behavior of "unimodal" fractions. The presence of yielding in non-adhesive HCE is evidently caused by the formation of compressed droplets [10], while we can suppose that such structure is absent in the mixtures due to the possibility for volume to be filled with spherical droplets of different size (as was calculated in [9]). Indeed, this supposition was confirmed by direct microscopic observations, Figure 3, which demonstrates that compressed droplets in the 80/20 binary mixture comprise the negligible part of the structure, while the rest of uncompressed droplets are arranged in a closely packed structure. Therefore, the volume fraction of dispersed phase 0.85 appears to be about φ^* in this case, which explains the observed results.

It may be questioned why the experimental results in [3] did not show a minimum in the rheological properties of binary mixtures. The reason is that the droplet size ratio of binary mixtures studied by Pal [3] was about 1.95 μm/1.28 μm $\approx$ 1.6, while the big-to-small droplet size ratio was much higher, approximately 6, in this work. In other words, it could be suggested that in order to see the viscosity reduction effect in binary mixtures, the droplet size ratio should be high enough to provide negligible overlapping of the droplet size distributions of mixed fractions. It is also worth mentioning that high G' values were observed for 80/20 binary mixture though droplets in this emulsion are not compressed. It means that the origin of elasticity in our case is not the increase in interfacial area provided by compressed droplets (as in the standard model [10]) but interfacial interaction as was described in [6].

SUMMARY

A strong decrease in the viscosity, elastic modulus and yield stress was found in binary mixtures of HCE (disperse phase content of 0.85), which comprises 10 ~ 25 % of small droplets with the big-to-small size ratio of 1:6. This effect was explained by more complete spatial filling of such binary mixture that allowed us to avoid the consequences of droplet compression in highly concentrated emulsions.

REFERENCES

[1] Derkach SR: Rheology of emulsions, Adv. Colloid Interface Sci. 151 (2009) 1 – 23.

[2] Masalova I, Malkin AYa: Rheology of highly concentrated emulsions – concentration and droplet size dependencies, Appl. Rheol. 17 (2007) 42251.

[3] Pal R: Rheology of high internal phase ratio emulsions, Food Hydrocolloids 20 (2006) 997 – 1005.

[4] Chang C, Powell RL: Effect of particle size distributions on the rheology of concentrated bimodal suspensions, J. Rheol. 38 (1994) 85 – 98.

[5] Fischer P, Pollard M, Erni P, Marti I, Padar S: Rheological approaches to food systems, C. R. Physique 10 (2009) 740 – 750.

[6] Foudazi R, Masalova I, Malkin AYa: Effect of interdroplet interaction on elasticity of highly concentrated emulsions, Appl. Rheol. 20 (2010) 45096.

[7] 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.

[8] Kendall J, Monroe KP: The viscosity of liquids. II. The viscosity-composition curve for ideal liquid mixtures, J. Am. Chem. Soc. 39 (1917) 1787 – 1802.

[9] Farr RS, Groot RD: Close packing density of polydisperse hard spheres, J. Chem. Phys. 131 (2009) 244104.

[10] Mason TG, Lacasse M-D, Grest GS, Levine D, Bibette J, Weitz DA: Osmotic pressure and viscoelastic shear moduli of concentrated emulsions, Phys. Rev. E 56 (1997) 3150 – 3166.

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