

# EFFECT OF INTERDROPLET INTERACTION ON ELASTICITY OF HIGHLY CONCENTRATED EMULSIONS

R. FOUDAZI, I. MASALOVA\*, A. YA. MALKIN

Institute of Material Science and Technology, Cape Peninsula University of Technology,  
Cape Town, South Africa

\* Email: [masalovai@cput.ac.za](mailto:masalovai@cput.ac.za)  
Fax: x27.21.4603990

Received: 16.12.2009, Final version: 30.4.2010

## ABSTRACT:

We present a model for osmotic pressure and shear modulus of highly concentrated emulsions by including the interdroplet interaction in terms of disjoining pressure. The results show that even a small addition in interdroplet interaction can lead to significant deviations from the classical Princen-Lacasse-Mason models that take into account only the surface energy as the sole source of elasticity. The newly proposed model predicts new effects, in particular the possibility of nonlinear dependency of elastic modulus on the droplet size, and can be used to discuss the elasticity sources of highly concentrated emulsions. In the second part of this article, the unusual elasticity of highly concentrated explosive emulsions is discussed by using the proposed model.

## ZUSAMMENFASSUNG:

Wir stellen ein Modell für den osmotischen Druck und Schubmodul von hochkonzentrierten Emulsionen, durch Einbeziehen der Tröpfchenwechselwirkung im Hinblick auf den Abstoßungsdruck, vor. Die Ergebnisse zeigen, dass bereits eine geringe Erhöhung der Tröpfchenwechselwirkung zu erheblichen Abweichungen von den klassischen Princen-Lacasse-Mason-Modellen führen kann, die lediglich die Oberflächenenergie als einzige Elastizitätsquelle berücksichtigen. Das neu vorgestellte Modell ermöglicht die Vorhersage neuer Effekte, insbesondere die Möglichkeit einer nichtlinearen Abhängigkeit des Elastizitätsmoduls auf die Tröpfchengröße, und kann zur Diskussion der Elastizitätsquellen von hochkonzentrierten Emulsionen verwendet werden. Im zweiten Teil dieses Artikels wird die ungewöhnliche Elastizität hochkonzentrierter explosiver Emulsionen mithilfe des vorgestellten Modells diskutiert.

## RÉSUMÉ:

Nous présentons un modèle de pression osmotique et un module de rigidité d'émulsions à forte concentration en incluant l'interaction entre gouttelettes en termes de pression de disjonction. Les résultats montrent que même un ajout minime d'interaction entre gouttelettes peut mener à des déviations importantes des modèles classiques Princen-Lacasse-Mason qui ne prennent en considération que l'énergie de surface comme source unique d'élasticité. Le nouveau modèle proposé prévoit de nouveaux effets, en particulier la possibilité de dépendance non linéaire du module d'élasticité de la taille de la goutte, et peut être utilisé pour discuter de la source d'élasticité des émulsions à forte concentration. Dans la deuxième partie de cet article on discute de l'élasticité insolite des émulsions explosives à forte concentration, en utilisant le modèle proposé.

**KEY WORDS:** shear modulus, osmotic pressure, highly concentrated emulsion, Laplace pressure

## 1 INTRODUCTION

An emulsion is a mixture of two immiscible fluids, one of which is dispersed in the continuous phase of the other, typically formed by rupturing droplets down to colloidal sizes through mixing. To inhibit recombination or coalescence, a surfactant that concentrates at the interfaces must be added to create short-ranged interfacial repulsion between droplets [1]. The increase of the dispersed phase concentration beyond close packing of spheres has significant technological

applications in the food and cosmetics industries, as well as "liquid explosives" [2].

Emulsions consisting of highly concentrated droplets, despite comprising fluids only, can possess a striking shear elasticity that is usually characteristic of a solid. Princen [3, 4] attributed this elasticity to the interfacial energy of deformed droplets that is due to the increment of droplet surface area. Lacasse et al. [5, 6] and Mason et al. [7] also predicted the osmotic pressure  $\Pi$  and the static shear modulus  $G$  – by using

surfactant head-group in the surface layer of droplets. Hence, it is reasonable to claim the presence of electrostatic repulsion; its theoretical formulation, however, needs further fundamental studies.

It is known that the diffuse electric double layer (Debye length) of electrostatic forces is decreased by increasing the concentration of electrolytes in the continuous aqueous phase [25]. Therefore it is expected that, increasing the reversed micelle concentration in the studied explosive emulsions will decrease the electrostatic repulsion. This implies that a higher surfactant concentration will result in lower interdroplet interaction and hence, lower shear modulus. The same trend was seen in the shear modulus of the studied explosive emulsions.

## 5 CONCLUSION

A basic model for the elasticity of highly concentrated emulsion has been proposed. This model takes into account the effect of interdroplet interaction as additional to the classical understanding of the elasticity of compressed emulsions. The model includes two components: a usual term reflecting the role of interfacial tension due to the increase of droplet area and a term considering the disjoining pressure which can be introduced by the presented optimisation method. It was shown that the disjoining pressure gives a physically meaningful contribution which results in the deviation of shear modulus to scale with the Laplace pressure. This model predicts the possibility of a nonlinear dependency of elastic modulus on the droplet size. The model was used to discuss the unusual high elasticity of explosive emulsions which is not contributed by Van der Waals, steric and micellar forces, but by electrostatic repulsion enhanced by reversed micelles.

## ACKNOWLEDGEMENT

We thank African Explosive Limited for their financial support of this study, and the Lake International Co. for supporting the surfactants.

## REFERENCES

- [1] Becher P: Emulsions: Theory and Practice, Reinhold, New York, (1965); F. Sebba, Foams and Biliqid Foams-Aphrons, Wiley, Chichester (1987).
- [2] Bampfield HA, Cooper J: Emulsion explosives.
- [3] Encyclopedia of Emulsion Technology, Marcel Dekker, New York. 7 (1985) 281-306.
- [4] Princen HM: Highly concentrated emulsions. I. cylindrical systems, *J. Colloid Interface Sci.* 71 (1979) 55-66.
- [5] Princen HM: Osmotic pressure of foams and highly concentrated emulsions. I. Theoretical consideration, *Langmuir* 2 (1986) 519-524.
- [6] Lacasse M-D, Grest GS, Levine D: Deformation of small compressed droplets, *Phys. Rev. E* 54 (1996) 5436-5446.
- [7] Lacasse M-D, Grest GS, Levine D, Mason TG, Weitz DA: Model for the Elasticity of Compressed Emulsions, *Phys. Rev. Lett.* 76 (1996) 3448-3451.
- [8] 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.
- [9] Seth JR, Cloitre M, Bonnecaze RT: Elastic properties of soft particle pastes, *J. Rheol.* 50 (2006) 353-376.
- [10] Pons R, Solans C, Stébé MJ, Erra P, Ravey JC: Stability and rheological properties of gel emulsions, *Prog. Colloid Polym. Sci.* 89 (1992) 110-113.
- [11] Pons R, Solans C, Tadros TF: Rheological Behavior of Highly Concentrated Oil-in-Water (o/w) Emulsions, *Langmuir* 11 (1995) 1966-1971.
- [12] Otsubo Y, Prud'homme RK: Effect of drop size distribution on the flow behavior of oil-in-water emulsions, *Rheol Acta* 33 (1994) 303-306.
- [13] Dimitrova TD, Leal-Calderon F: Rheological properties of highly concentrated protein-stabilized emulsion, *Adv. Colloid Interface Sci.* 108-109 (2004) 49-61.
- [14] Malkin A Ya, Masalova I, Slatter P, Wilson K: Effect of droplet sizes on the rheological properties of highly concentrated w/o emulsions, *Rheol. Acta* 43 (2004) 584-591.
- [15] Masalova I, Malkin A Ya, 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.
- [16] Bengoechea C, Cordobés F, Guerrero A: Rheology and microstructure of gluten and soya-based o/w emulsions, *Rheol Acta* 46 (2006) 13-21.
- [17] Mougel J, Alvarez O, Baravian C, Caton F, Marchal P, Stébé MJ: Aging of an unstable w/o emulsion with nonionic surfactant, *Rheol. Acta* 45 (2006) 555-560.
- [18] Masalova I, Malkin A Ya: Rheology of Highly Concentrated Emulsions – Concentration and Droplet Size Dependencies, *Appl. Rheol.* 17 (2007) 42250.
- [19] Romero A, Cordobés F, Puppo MC, Guerrero A, Bengoechea C: Rheology and droplet size distribution of emulsions stabilized by crayfish flour, *Food Hydrocolloids* 22 (2008) 1033-1043.

- [19] Rusanov AI, Krotov VV: Manifestation of Gibbs Elasticity in Thin Films, *Colloid Journal* 66 (2004) 204-207.
- [20] Danov KD, Petsev DN, Denkov ND, Borwankar R: Pair Interactions between Deformable Drops and Bubbles, *J. Chem. Phys.* 99 (1993) 7179-7189.
- [21] Buzzia DMA, Cates ME: Osmotic Pressure of Dense Emulsion Systems: The Role of Double-Layer Forces, *Langmuir* 9 (1993) 2264-2269.
- [22] Denkov ND, Tcholakova S, Golemanov K, Ananthapadmanabhan KP, Lips A: Viscous Friction in Foams and Concentrated Emulsions under Steady Shear, *Phys. Rev. Lett.* 100 (2008) 138301.
- [23] Brakke K: The surface evolver, *Exp. Math.* 1 (1992) 141-165.
- [24] Derjaguin BV: Theory of Stability of Colloids and Thin Liquid Films, Plenum Press, Consultants Bureau, New York (1989).
- [25] Israelachvili J N: Intermolecular and Surface Forces. Academic Press, London (1992).
- [26] Kralchevsky PA, Danov KD, Denkov ND: Chapter 5 in *Handbook of Colloid and Surface Chemistry*, Bridi KS (Ed.) CRC Press (2003).
- [27] Buzzia DMA, Cates ME: Uniaxial elastic modulus of concentrated emulsions, *Langmuir* 10 (1994) 4503-4508.
- [28] Dimitrova TD, Leal-Calderon F, Gurkov TD, Campbell B: Disjoining pressure vs thickness isotherms of thin emulsion films stabilized by proteins bulk elasticity of concentrated protein-stabilized emulsions, *Langmuir* 17 (2001) 8069-8077.
- [29] Masalova I, Taylor M, Kharatiyan E, Malkin A Ya: Rheopexy in highly concentrated emulsions, *J. Rheol.* 49 (2005) 839-849.
- [30] Lifshitz EM: The theory of molecular attractive forces between solids, *Soviet Phys. JETP (Engl. Transl.)* 2 (1956) 73-83.
- [31] De Gennes PG: Polymer at interface: A simplified view, *Adv. Colloid Interface Sci.* 27 (1987) 189-209.
- [32] Kralchevsky PA, Denkov ND: Analytical expression for the oscillatory structural surface force, *Chem. Phys. Lett.*, 240, 385-392 (1995); *Prog. Colloid Polym. Sci.* 98 (1995) 18.
- [33] Reynolds PA, Gilbert EP, White JW: High Internal Phase Water-in-Oil Emulsions Studied by Small-Angle Neutron Scattering, *J. Phys. Chem. B* 104 (2000) 7012-7022.
- [34] Reynolds PA, Gilbert EP, White JW: High Internal Phase Water-in-Oil Emulsions and Related Microemulsions Studied by Small Angle Neutron Scattering. 2. The Distribution of Surfactant, *J. Phys. Chem. B* 105 (2001) 6925-6932.
- [35] Hsu MF, Dufresne ER, Weitz DA: Charge Stabilization in Nonpolar Solvents, *Langmuir* 21 (2005) 4881-4887.
- [36] Ganguly S, Krishna Mohan V, Bhasu VCJ, Mathews E, Adiseshaiah KS, Kumar AS: Surfactant-electrolyte interactions in concentrated water-in-oil emulsions: FT-IR spectroscopic and low-temperature differential scanning calorimetric studies, *Colloid and Surfaces* 65 (1992) 243-256.



This is an extract of the complete reprint-pdf, available at the Applied Rheology website  
<http://www.appliedrheology.org>