Rheology of Highly Concentrated Emulsions – Concentration and Droplet Size Dependencies

Irina Masalova[1], Alexander Ya. Malkin[2]

[1] Cape Peninsula University of Technology, Faculty of Engineering, Department of Civil Engineering, P.O. Box 652, Cape Town 8000, Republic of South Africa

[2] Permanent address: Profsoyuznaya ul., 98, korp. 5, kv. 92, 117485 Moscow, Russia

E-mail: masalovai@ctech.ac.za
Fax: x27.21.4603990

Received: 8.12.2006, Final version: 4.1.2007

Abstract:
The concentration and size dependencies of elastic properties of highly concentrated w/o emulsions were studied. The range of weight concentration of the disperse phase was 90 - 96%, the range of the average droplet size was 16 - 20 μm, and the droplet size distribution remained unchanged. The disperse phase consists of droplets of overcooled concentrated aqueous solutions of inorganic salts. The concentration range being studied lies above the limit of maximal close packing, $\varphi > \varphi_m$. The droplet size distribution is fairly wide and the shape of droplets is polygonal. These factors alone determine possible new rheological effects, such as the elasticity and visco-plastic behaviour of emulsions, as well as the observed form of concentration and size dependencies of rheological properties of emulsions. The complete flow curves were measured for these fairly new emulsion systems. It emerged that they were similar to the entire concentration and droplet size ranges being studied. The concentration dependencies of the yield stress and storage modules corresponded to the Princen-Kiss theory with critical volume concentration approximately 0.71 - 0.74. However, this theory describes the size dependence of elastic modules incorrectly. A new model is proposed, which correctly describes the dependencies of elastic modules on both determining parameters - those of concentration and droplet size.

Zusammenfassung:
Studiert wurden die Konzentrations- und Größenabhängigkeiten elastischer Eigenschaften bei hochkonzentrierten W/O-Emulsionen. Der Bereich der Gewichtskonzentration der dispersen (inneren) Phase betrug 90–96%, der Bereich der mittleren Tröpfchengröße betrug 16 – 20 μm, wobei die Tröpfchengrößenverteilung unverändert blieb. Die disperse Phase besteht aus Tröpfchen überkühlter konzentrierter wässriger Lösungen anorganischer Salze. Der studierte Konzentrationsbereich liegt über der Obergrenze der dichtesten Packung, $\varphi > \varphi_m$. Die Tröpfchengrößenverteilung ist recht breit und die Form der Tröpfchen polygonal. Diese Faktoren allein bestimmen mögliche neue rheologische Effekte, wie etwa die Elastizität und das viskoplastische Verhalten von Emulsionen, sowie die beobachtete Form der Konzentrations- und Größenabhängigkeiten rheologischer Eigenschaften von Emulsionen. Für diese recht neuen Emulsionssysteme wurden die gesamten Fließkurven gemessen. Wie sich herausstellte, ähneln sie allen studierten Konzentrations- und Tröpfchengrößenbereichen. Die Konzentrationsabhängigkeiten der Fließspannung und Speichermodule entsprechen der Princen-Kiss-Theorie mit einer kritischen Volumenkonzentration von ca. 0,71-0,74. Diese Theorie beschreibt die Größenabhängigkeit elastischer Module allerdings inkorrekt. Es wird ein neues Modell vorgeschlagen, das die Größenabhängigkeit elastischer Module bei beiden entscheidenden Parametern – jene der Konzentration und der Tröpfchengröße – richtig beschreibt.

Résumé:
Les dépendances entre la concentration et la taille des propriétés élastiques très concentrées sans émulsion ont été étudiées. La fourchette de concentration du poids de la phase de dispersion était de 90 à 96 %, la fourchette de la taille moyenne d'une gouttelette était de 16 à 20 μm, et la distribution de la taille de la gouttelette ne change pas. La phase de dispersion se compose de gouttelettes de solutions aqueuses très refroidies de sels non organiques. La fourchette de concentration étudiée se situe au-dessus de la limite maximale d'étanchéité, $\varphi > \varphi_m$. La distribution de la taille de la gouttelette est assez étendue et la forme des gouttelettes est polygonale. Ces facteurs déterminent à eux seuls les éventuels nouveaux effets rhéologiques, comme le comportement élastique et plastico-visqueux des émulsions ainsi que la forme observée des dépendances entre la concentration et la taille des propriétés rhéologiques des émulsions. Les courbes entières de flux ont été mesurées pour ces systèmes d'émulsion assez récents. il en est ressorti qu'elles étaient semblables aux fourchettes de concentration totale et de taille de la gouttelette qui sont étudiées. Les dépendances de concentration des modules de pression et de stockage correspondaient à la théorie de Princen-Kiss avec une concentration d'un volume important d'environ 0.71 à 0.74. Cependant, cette théorie décrit la dépendance de la taille des modules élastiques de façon incorrecte. Un nouveau modèle est propose afin de décrire correctement les dépendances des modules élastiques en fonction des deux paramètres déterminants : ceux de la concentration et de la taille de la gouttelette.

Key words: highly concentrated emulsions, elasticity, storage modules, concentration dependence, size dependence, rheopexy, yield stress

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

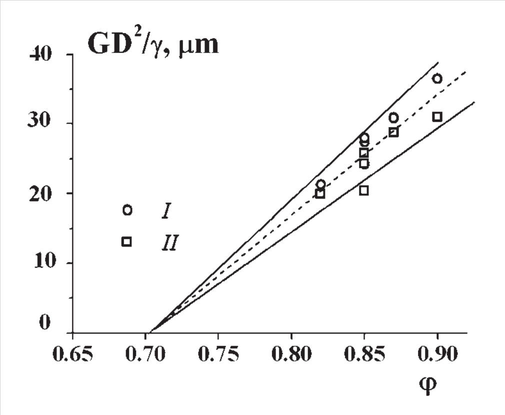

Figure 7: Presentation of experimental data in the coordinates of Eq. 13 (I and II – two surfactants).

where, again, we have an uncertain front-factor k. The scaling factors m and n are also not known beforehand.

It is clear that Eq. 15 is more general than Eq. 13, although they are similar. It is evident that both approaches – energetic and dimensional – lead to analogous equations. For the sake of simplicity, it is reasonable to assume than $m = 1$ and $n = 1$, as the first approximation. Eqs 13 and 15 are equivalent in this case. It is important that any of these equations show that G should be proportional to D^{-2} and includes d as a necessary factor. The form of the concentration dependence (Eq. 15) is different from Eq. 5, because Eq. 5 does not contain the $\varphi^{1/3}$ factor. Elastic modules in Eq. 5 is proportional to D^{-2} instead of D^{-1}.

As seen from formal arguments, the presentation of G (as well as σ_Y) as functions of D^{-2} is possible only if another factor with a dimension of length is introduced. We do not see another structure parameter other than the width of the elastically active surface of a stabilizing layer in emulsions. Our experimental data obtained for two different surfactants are collected in Figure 7 in co-ordinates GD^2/γ versus φ. The boundary lines correspond with ± 15% divergence from the average that is the limits of possible experimental errors. It is clear that Eq. 13 (or Eq. 15 with $m = 1$ and $n = 1$) correctly describes all the experimental data in the experimental ranges of concentration and droplet size. These ranges might not be wide but they correspond with the possible limits of existence of highly concentrated emulsions. The φ^* value obtained from Figure 7 is equal to 0.71, which is rather close to the φ^* value in Fig. 5. The difference is immaterial and we can presume that 0.71 - 0.73 is the real limit of close packing for the systems in this study. However, this value might depend on the details of droplet size distribution. The other set of experimental data related to samples obtained in the different technological regime, presents a dependence quite similar to Figure 7. But the value φ^* is close to 0.75. It might be considered that the share of very small particles in the latter case is larger, which is the reason why the closest packing is reached at a higher concentration threshold. The slope of the straight lines in Figure 7 is the product $k\delta$. The value of $k\delta$ in Figure 7 equals $1.73 \cdot 10^{-4}$ m. Both factors cannot be separated in the product $k\delta$. However, if the value of δ is expected to be in the order of several microns, the front-factor should be in the order of 100.

4 CONCLUSIONS

Rheological properties of highly concentrated w/o emulsions (in the range up to 96 w. %) were studied. This concentration range lies beyond the limit of maximal close packing, $\varphi > \varphi_m$. Droplet size distribution is rather wide, but similar for all samples. The shape of droplets is polygonal. Only these factors determine a possibility of special rheological effects, such as the elasticity and plasticity of emulsions. All these emulsions are rheopectic materials in the whole concentration range. The complete flow curves in steady regimes of deformation include the transition to the yield stress and inflection at the middle part of the flow curves. The elastic (storage) modules are practically constant in the wide frequency range. The concentration dependencies of storage modules and the yield stress are similar. If the Princen-Kiss theory is applied to the concentration dependence of elastic modules, the value of the critical volume concentration (corresponding to the close packing of droplets) equals 0.71. At the same time this theory provides incorrect predictions about the dependence of elastic modules on the droplet size. The new model, based on either geometrical or dimensional arguments, predicts that elastic modules should be proportional to the concentration of a dispersed phase and squared reciprocal size of droplets. This model includes the width of an elastic layer as an additional geometrical factor. Experimental data confirms the reliability of this model.

ACKNOWLEDGEMENTS

The authors are grateful to M. Taylor from AEL for providing components of highly concentrated emulsions, to Dr. E. Kharatuyan for her assistance in carrying out the experimental part of the work, and to Dr. A. Andrianov (Mosow State University, Russia) for his help in the computer processing of experimental data.

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

REFERENCES

[1] Taylor GI: The viscosity of a fluid containing small droplets of another liquid, Proc. Royal Soc. London, Ser A 138 (1932) 41-48.

[2] Pal R: Novel viscosity equations for emulsions of two immiscible liquids, J. Rheol. 45 (2001) 509-520.

[3] Chanamai R, McClements DJ: Dependence of creaming and rheology of monodisperse oil-in-water emulsions on droplet size and concentration. Colloids and Surface A 172 (2000) 79-86.

[4] Portal P, Guerrero A, Berjano M, Gallegos C: Influence of concentration and temperature on the flow behavior of oil-in-water emulsions stabilized by sucrose palmitate, J. Amer Oil Chem Soc. 74 (1997) 1203-1212.

[5] Jager-Lezer N, Tranchant JF, Alard CV, Tchoreloff PC, Grossiord JL: Rheological analysis of highly concentrated w/o emulsions, Rheol. Acta 37 (1998) 129-138.

[6] Langenfeld A, Schmitt V, Stébé M-J: Rheological behavior of fluorinated highly concentrated reverse emulsions with temperature, J Colloid Interface Sci. 218 (1999) 522-528.

[7] Rocca S, Stébé M-J: Mixed concentrated water-oil emulsions (fluorinated/hydrogenated): formulation, properties, and structural studies, J. Phys. Chem. B 104 (2000) 10490-10497.

[8] Ponton A, Clément P, Grossiord JL: Corroboration of Princen's theory to cosmetic concentrated water-in-oil emulsions, J. Rheol. 45 (2001) 521-526.

[9] Babak VG, Lengfield A, Fa N, Stébé M-J: Rheological properties of highly concentrated fluorinated water-in-oil emulsions. Progr. Colloid Polymer Sci. 118 (2001) 216-220.

[10] Mason TG, Bibette J, Weitz DA: Elasticity of compressed emulsions, Phys. Rev. Lett. 75 (1995) 2051-2054.

[11] Mason TG, Bibette J, Weitz DA: Yielding and flow of monodisperse emulsions, J. Colloid Interface Sci. 179 (1996) 439-448.

[12] 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.

[13] 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.

[14] Malkin AYa, Masalova I, Slatter P, Wilson K: Effect of droplet size on the rheological properties of highly-concentrated w/o emulsions, Rheol. Acta 43 (2004) 584-591.

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

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

[17] Princen HM: Rheology of foams and highly concentrated emulsions. I Elastic properties and yield stress of a cylindrical model system, J. Colloid Interface Sci. 91 (1983) 160-174.

[18] Princen HM: Rheology of foams and highly concentrated emulsions. II Experimental study of the shear viscosity and yield stress of concentrated oil-in-water emulsions, J. Colloid Interface Sci. 105 (1985) 150-171.

[19] Princen HM, Kiss AD: Rheology of foams and highly concentrated emulsions. III Static shear modulus, J. Colloid Interface Sci. 112 (1986) 427-432.

[20] Princen HM: Rheology of foams and highly concentrated emulsions. IV An experimental study of the yield stress and wall effects for concentrated oil-in-water emulsions, J. Colloid Interface Sci. 128 (1989) 176-187

[21] Malvern Instruments Ltd, http://www.malvern.co.uk

[22] 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.

[23] Malkin AYa, Masalova I: Shear and normal stresses in flow of highly concentrated emulsions J. Non-Newton. Fluid Mech., accepted for publication.

[24] Weber RM: Relation between Laplace pressure and the rheology of high internal phase emulsions. Presented for the Spring AIChE Meeting, Houston, USA (1999) T6005.

[25] Pal R: Novel shear modulus equation for concentrated emulsions of two immiscible elastic liquids with interfacial tension. J. Non-Newton. Fluid Mech. 105 (2002) 21-33.

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