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Possible effects of complex internal structures on the apparent viscosity of multiple emulsions

Jingtao Wang [a,b,*], Hefeng Jing [a], Yan Wang [a]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China
[b] State Key Laboratory of Chemical Engineering, Tianjin University, PR China

HIGHLIGHTS

- Asymmetrical deformation of multiple emulsions is studied in 2D rotational device.
- Deformation connects internal structures and viscosity of multiple emulsions.
- As for small deformations, viscosities increase with the deformation of globules.
- Inner droplet has suppressing and enhancing effects on the deformation of globule.

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ABSTRACT

Through a two-dimensional (2D) boundary element method, this paper investigates the asymmetrical deformations of multiple emulsions with different internal structures under rotational shear flows induced by the rotation of the inner cylinder in a two-concentric-cylinder microfluidic system like a rotational viscometer. As the total shear stress (including components and interfacial contribution) of simple emulsions in a shear flow is severely affected by the deformation of the droplets, the deformation parameter D is chosen as the bridge to connect the internal structures of multiple emulsions with their apparent viscosity. Thus, the relations among the internal structures, the deformation of the globule, the torque of the inner cylinder and the apparent viscosity of multiple emulsions are discussed qualitatively in order to disclose the effects of the internal structure on the apparent viscosity. As for the small deformation of multiple emulsions, the inner droplets have both suppressing and enhancing effects on the deformation of the globule, and they will rotate along with the inner circulation which is like a big vortex. Generally speaking, the larger the deformation is, the larger the torque is, which means that the apparent viscosity of multiple emulsions increases along with the increase of the deformation of the globule. As for the large deformation (without breakup) of multiple emulsions, the situations are much more complicated and depend on the complex interaction between the inner droplets and the outermost interface of the globule.

1. Introduction

Emulsions have been widely used in many fields including food (Garti, 1997), petroleum (Sjoblom et al., 2003), pharmaceutical (Okochi and Nakano, 2000) and cosmetics industries (Lee et al., 2001). In the past decades, emulsions industries have been developed rapidly. Based on simple emulsions, multiple emulsions with complex internal structures have been fabricated recently. Simple emulsions, such as water-in-oil (W/O) and oil-in-water (O/W) emulsions, are generated when the second immiscible liquid phase (the disperse phase, DP) is dispersed in the continuous phase (CP). As for the multiple emulsion, it is a kind of nested liquid system which has a highly ordered inner structure consisting of many smaller engulfed droplets (Wang et al., 2011). Owing to their great potentials in microreactors (Shum et al., 2009), targeted drugs deliveries (Lawrence and Rees, 2000) and the synthesis of polymer particles (Gong et al., 2009; Shum et al., 2011; Chen et al., 2009), multiple emulsions have attracted much attention all over the world. Due to the structural complexity, the preparation of multiple emulsions with monodispersity is difficult. However, the rapid development of microfluidics has offered a great platform to prepare

* Corresponding author at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China.
E-mail address: wjingtao928@tju.edu.cn (J. Wang).

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such complicated soft particles (Nisisako, 2008; Chu et al., 2007; Abate and Weitz, 2009; Kim and Weitz, 2011; Deng et al., 2011). As shown in Fig. 1, multiple emulsions with extremely diverse inner structures have been generated.

In processes involving emulsions, the viscosity of the fluid system is an important physical property which will affect severely the process control, quality and stability of the final products (Kita et al., 1977; Barylko-Pikielna et al., 1994; Dormandy, 1970; Cheng et al., 2013; Wang et al., 2013). Early in 1977, Kita et al. (1977) employed viscometric method to estimate the stability of multiple emulsions. In the food industry, Barylko-Pikielna et al. (1994) employed viscosity as a variable to evaluate the perception of taste intensity in food emulsions. In clinical iatrology (Dormandy, 1970), the monitoring and the assessment of the blood viscosity in patients are of great significance in predicting various diseases. Cheng et al. (2013) found that the viscosity of disperse phase has an influence on the macro-mixing process by simulating the macro-mixing of emulsions system through computational fluid dynamics (CFD) approaches. Similarly, Wang et al. (2013) concluded that the mixing process of the oil–water phase would be affected by the viscosity of continuous phase.

Due to various applications of the viscous properties of emulsions, the measurement and prediction of the viscosity of emulsions are of significant importance. For the measurement of the viscosity, the commonly used viscometers are capillary viscometer, falling ball viscometer, cone plate viscometer, rotational viscometer, etc. As for the prediction of the emulsion viscosity, many numerical calculations have been done. The surfactant effects on the viscosity of emulsions during the start-up of shear flows were investigated by Skartlien et al. (2012) through a 3-dimensional lattice Boltzmann model. Tran-Duc et al. (2013) employed the dissipative particle dynamics (DPD) method to study the relative viscosity of bubble suspensions by using a hard-core DPD particle to model the gas bubble. Pan et al. (2014) simulated the rheology of droplet suspensions through the DPD method and disclosed the increment of the relative viscosity of the suspension due to droplet deformation. By using the Front-tracking method, Sarkar and coworkers (Li and Sarkar, 2005; Singh and Sarkar, 2011) have investigated the effects of inertia on the rheology of dilute emulsion of drops in shear flows.

Besides numerical works, numerous theoretical works have been done to predict the viscosity of emulsions. Einstein's viscosity equation, which presents the relative viscosity of the suspensions is related to the volume fraction of solid spheres, is probably the first equation to describe the viscosity of an infinitely dilute suspension of rigid spheres. Assuming that the drops remain nearly spherical because of the great enough surface tension, Taylor (1932) extended Einstein's viscosity equation to make it available to dilute emulsions by replacing the solid spheres with fluid droplets. However, the interaction between the two droplets was ignored in Taylor's viscosity expression. Mooney (1951) obtained the functional equation to express the viscosity of concentrated suspensions by considering the first-order interaction between the spheres in concentrated suspensions based on Einstein's viscosity equation. Oldroyd (1953) calculated the elastic properties of dilute emulsions and concluded three parameters affecting the viscosity of emulsions: the droplet size, the interfacial tension and the concentration of disperse phase. Similarly, Pal (1996a) talked about the effect of droplet size on the viscosity of concentrated emulsions. The conclusion in the paper (Pal, 1996a) is that the viscosity of emulsions increases with the decrease of the droplet size and the viscosity of emulsions containing fine droplets will be greater than that of emulsions containing coarse droplets. In 1989, Pal and Rhodes (1989) developed an empirical correlation which correlates the relative viscosities of Newtonian and non-Newtonian emulsions and also proposed a viscosity/concentration equation for the non-Newtonian emulsions by employing theoretical analysis. Then Pal (1996b) studied the viscosity of multiple emulsions through modified Mooney equation and discussed the effect of aging on viscosity of multiple emulsions. He found that the multiple emulsions, whose viscosity could be divided into three flow regions – lower Newtonian region, shear-thinning region and upper Newtonian region – behave as non-Newtonian. Assuming the double emulsions containing many inner droplets as concentric double emulsions, Pal (2007) derived four viscosity equations to predict the viscosity of concentrated core-shell emulsions through differential effective medium approach (DEMA). Recently, Pal (2008) studied the viscosity of both dilute and concentrated double emulsions containing many inner droplets and developed new equations to describe the viscosity of that.

In the previous studies of our group (Tao et al., 2013; Wang et al., 2013a, 2013b, 2014), it was found that the complex internal structures affected the deformation of the droplet, and predicted that the deformation of the droplet would probably have an influence on the apparent viscosity of multiple emulsions. In this paper, we compare and analyze the relations among the internal structures, the deformation of the globule, the torque suffered by the inner cylinder, and the apparent viscosity of the multiple emulsions by simulating the rotation of the inner cylinder in a two-concentric-cylinder system filled with liquids through a two-dimensional boundary element method. As a qualitative relation between the deformation of the globule and the apparent viscosity of the multiple emulsions is clearly presented, it could be concluded the internal

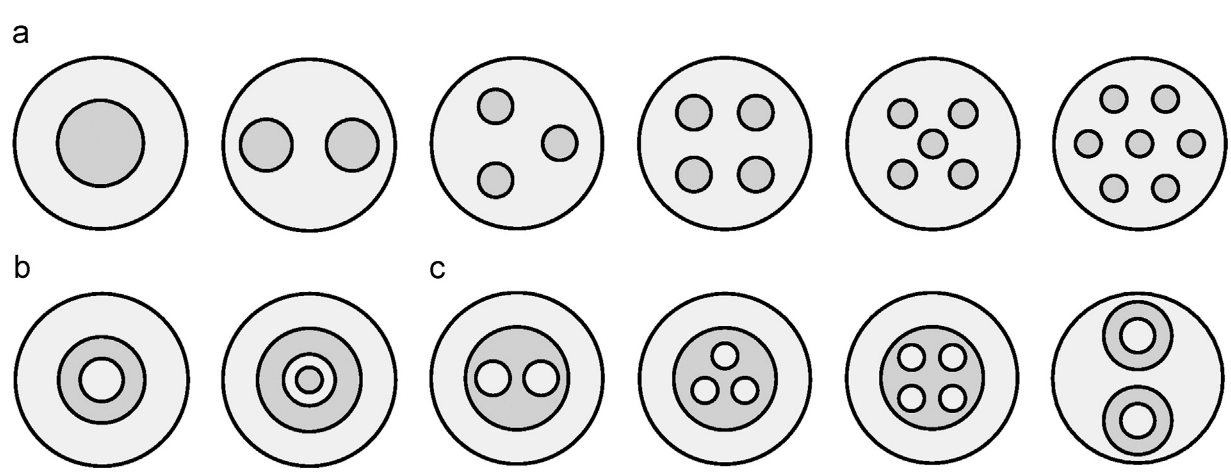

Fig. 1. Illustration of types of multiple emulsions. (a) Double emulsions with inner droplets of different numbers. (b) Concentric multiple emulsions with layers more than two. (c) Multiple emulsions with more complex internal structures.