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Mesoscale modeling of emulsification in rotor-stator devices Part II: A model framework integrating emulsifier adsorption

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HIGHLIGHTS

- Integrating the two mesoscale issues proves necessary for droplet size prediction.
- First mesoscale deals with emulsifier absorption at interfacial level by CGMD.
- Second mesoscale deals with CFD-PBM for droplet breakage by EMMS.
- Coupling the two mesoscales via surfactant transport equations at interface and bulk.

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ABSTRACT

Precise and rational control of droplet size distribution (DSD) is important in emulsification for target-oriented product design. To develop a complete DSD model, crossing the two mesoscales of two different levels is of great significance, viz., the emulsifier adsorption at interfacial level (Mesoscale 1) and the droplet breakage and coalescence in turbulence in rotor-stator device level (Mesoscale 2). While the first mesoscale can be simulated by coarse-grained molecular dynamic (CGMD), the second has been investigated in computational fluid dynamics and population balance model (CFD-PBM) simulation through the Energy-Minimization Multi-Scale (EMMS) approach in Part I. We then developed a model framework in Part II, coupling CGMD and CFD-PBM simulation through surfactant transport equations in bulk phase and at interface, with source terms taking account of emulsifier adsorption parameters. The parameters including maximal adsorption amount, diffusion coefficient and adsorption/desorption kinetic constants are acquired from CGMD. The coalescence efficiency is then corrected by the interfacial area fraction not occupied by surfactant and fed into the coalescence kernel functions in PBM. Compared to traditional CFD-PBM simulation, the coupled model can greatly improve the simulation of DSD, Sauter mean diameter, median diameter and span for high dispersed phase amount (DPA), and correctly reflect the influence of DPA, surfactant concentration and rotational speed of rotor-stator (RS) devices. While the simulation cases validate and demonstrate the advantage of this new model framework, it is also promising to incorporate different types of surfactant in future.

1. Introduction

Mixing of two or more immiscible liquids to form a stable emulsion is ubiquitous in the manufacture of products such as shampoos, salad dressings, bitumen, pharmaceuticals and others. The process is generally carried out in various high-shear rotor-stator mixing devices (Wu et al., 2014). The droplet size distribution (DSD) of an emulsion is a key property that affects product stability, taste, appearance and rheology. Precise and rational control of DSD is important in target-oriented product design, yet challenging. From a macro-scale perspective, it is not only determined by emulsion formulation, interfacial properties and concentration of dispersed oil and surfactant, but by the processing conditions such as energy input and mixing devices geometry. At the so-called mesoscales, the emulsification process consists of two dynamic

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Notation

N_{break}	breakage energy, m^2/s^3
N_{turb}	energy dissipated in turbulence, m^2/s^3
EMMS	Energy Minimization Multi-Scale
C_{coal}	coalescence efficiency corrector
CMC	critical micelle concentration, mol/m^3
C_{break}	breakage corrector
U_C, U_d	superficial velocities of continuous phase and dispersed phase, m/s
T	torque of rotor walls, N m
N	rotation speed, rps
d_{32}	Sauter mean diameter, m
$d_{i,3}$	cumulative droplet diameter, μm

Greek letters

ν_c	kinematic viscosity, m^2/s
ε	turbulent kinetic energy dissipation rate, m^2/s^3
ρ_c, ρ_d	densities of continuous phase and dispersed phase, kg/m^3
σ	droplet surface tension, N/m
μ_c	viscosity of continuous phase, Pa s
μ	viscosity of fluid particles, Pa s
Γ	adsorption density, mol/m^2

opposite processes, i.e., droplet breakage and coalescence (Luo, 1993; Luo and Svendsen, 1996). Droplets break up or coalesce under the influences of material properties and process parameters. Microscopically droplet breakage or coalescence is pertinent to emulsifier adsorption kinetics, film drainage and complex interaction between turbulence eddies and droplets, as well emulsifier migration at interface. The multiscale phenomena are therefore complex and far from being well understood.

Some researchers have taken account of emulsifier adsorption effects on droplet coalescence in physical modeling or analyzing experimental results. Maindarkar et al. (2015) extended a population balance equation (PBE) by modeling the coalescence frequency to be a function of the surfactant coverage and adding a surfactant mass balance, including the effects of free surfactant concentration on interfacial tension and surface coverage of droplets. The models contained six adjustable parameters estimated by nonlinear optimization to minimize a least-squares objective function for the error between the predicted and measured drop volume distribution. Hall et al. (2011) reported that the limited impact of dispersed phase volume fraction and viscosity on droplet size was attributed to the presence of excess surfactant aiding the prevention of coalescence. Hakansson et al. (2009a) developed a dynamic modelling approach for emulsion formation in a high-pressure homogenizer. The rate of adsorption of macromolecular emulsifier to droplet interface was modeled as the sum of adsorption rates due to Brownian motion and turbulent forces. The coalescence frequency and efficiency was then assumed to be proportional to the percentage of surface free of emulsifier and correlated with transient adsorption amount. Hakansson et al. (2013) developed bivariate population balance equations to study the transport of surfactants between droplets of different sizes due to the breakage and coalescence based on their previous work (Hakansson et al. 2009a, 2009b).

Actually, interfacial tension has been incorporated in most of current kernel function models of droplet breakage and coalescence, and the various kernel function models have been reviewed by Liao and Lucas (2009, 2010). However, the inhibition of droplet coalescence due to emulsifier adsorption could not be reflected only by incorporating interfacial tension in these kernel models, as will be demonstrated in this study.

To achieve a complete description of coalescence and breakage in CFD-PBM simulation, one needs to consider the two mesoscale physical constraints, i.e., the physics at the interfacial level (smaller than a single droplet) and the physics at the device level (larger than a single droplet). The former refers to the emulsifier adsorption at droplet interface, and the latter is relevant to the turbulence stress due to hydrodynamic interactions. This work is intended to integrate the two mesoscale problems by combining the CFD-PBM simulation with the coarse-grained molecular dynamic (CGMD) simulation. To isolate the two mesoscale problems, surfactant-free oil-in-water systems in a rotor-stator device were simulated by CFD-PBM simulation in Part I (Chen et al., in press) of this work. We have developed the Energy-Minimization Multi-Scale (EMMS) approach for liquid-liquid flow to deal with the mesoscale problem in the rotor-stator device level (Qin et al., 2016). A mesoscale energy dissipation for droplet breakage was derived to close population balance equations through a breakage rate corrector. Part I aims only to deal with the mesoscale constraint at the device level to improve the CFD-PBM simulation for surfactant-free systems.

This paper (Part II) aims to integrate the two mesoscale problems. We proposed the transport equations of emulsifier concentration of bulk phase and interface in which there are source terms taking account of both emulsifiers adsorption and turbulence effects on droplet breakage and coalescence. The droplet coalescence frequency was then corrected by the interfacial area fraction not occupied by surfactant. The relevant model parameters in the source terms, i.e., maximal adsorption density, diffusion coefficient and adsorption/desorption kinetic constants, were acquired from the CGMD simulation. Finally, all the models were coupled within a unified framework.

2. Emulsification experiments

The experiments of droplet dispersion in a Megatron rotor-stator (RS) device have been described in Part I for surfactant-free MCT-oil/water systems, and the experimental circuit is illustrated in Fig. 1. In this paper, the oil droplet was dispersed with the emulsifier Agnique® TSP 16 (Tris(1-phenylethyl) phenol, ethoxylated, Agnique® TSP 16, BASF, referred as TSP for short) in water. The MCT-oil/water system contains 1 wt% or 30 wt% MCT-oil with viscosity 27 mPa s and interfacial tension 25 mN/m (Table 1). 0.1 and 3 wt% of the emulsifier were dissolved in water forming the aqueous phase of the emulsions. To neglect the effect of the disperse phase content on the size of the pre-emulsions we actually started preparing 10 L of a 30 wt% pre-emulsion within our mixing tank. After 1 min of stirring, we took 3 L of this sample from the mixing tank (for subsequent experiments). The remaining 7 L were directly emulsified via the Megatron.

When the experiment of the 30 wt% MCT-oil/water system was finished, then, the experiment of the 1 wt% MCT-oil/water system was carried on. To get a 1 wt% pre-emulsion, the remaining 3 L of the 30 wt% sample was diluted with an adequate amount of the aqueous phase (water + emulsifier). Hereby, only gentle stirring was applied to ensure that further breakup of the pre-emulsion droplets won't take place within the mixing tank. In the next step, the 1 wt% sample was also emulsified via the Megatron. After-