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A new FCCS-CFD coupled method for understanding the influence of molecular structure of ionic liquid on bubble behaviors

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ABSTRACT

The complex interaction between cations and anions as well as the molecular structure makes the ionic liquids (ILs) different from organic solutions. Thus, the conventional hydrodynamic models, which are suitable for water and organic solutions, are not able to predict bubble behaviors in ILs accurately. In this work, a new FCCS (Fragment Contribution Corresponding State)-CFD(CFD) coupled method is proposed, so that the influence of molecular structure of ILs can be revealed. A source term which represents the electrostatic interaction between cations and anions of ILs is introduced into the momentum equation, which makes the model reflect strictly the inner feature of ionic liquids. The simulation results show that the relative error of aspect ratio is only 0.06%, much lower than 3.73% which is calculated by the conventional method, indicating the new method is more accurate. Furthermore, the bubble behaviors, i.e. the bubble shape and velocity, in 30 ILs are simulated. As a result, the relationship between molecular structures of ILs and bubble behaviors, as well as the bubble flow regime is obtained.

1. Introduction

As potential green solvents, ionic liquids (ILs) present unique opportunities for industrial applications. For instance, ILs are widely studied to be potential solvents for gas separations, such as CO_2 capture [1], SO_2 absorption [2–4], NH_3 absorption [5,6] and biogas upgrading [7]. As for these gas-liquid processes, one important issue for engineering scale-up is understanding the fluid dynamics of IL systems, in which the bubble behavior is one of the key properties [8] For now, empirical and theoretical models have been developed to predict the bubble behaviors in gas-liquid systems [9,10]. However, the complex interaction between cations and anions in ILs [11,12] and discrepancy in their physicochemical properties [13] make modeling the bubble behaviors strictly in such liquids much difficult. The conventional hydrodynamic models, which are suitable for water [14] and organic solutions [15], are not able to predict bubble behaviors in ILs accurately [16].

Moreover, the physicochemical properties of IL systems determined by the molecular structure of ILs play an important role for predicting bubble behaviors. But how does the molecular structure influence the bubble behaviors of ILs is not deeply understood, which becomes a bottleneck for IL design based on fluid dynamics. From another point of view, the diverse structures (such as designable cations, anions and groups) and properties of ILs provide a good opportunity for developing new method to reveal the relationship between the molecular structure and bubble behaviors. Therefore, in this work, a new FCCS-CFD coupled method is proposed to solve these problems. In the new method, the fragment contribution corresponding states (FCCS) method [17] is applied for calculating the physicochemical properties of ILs, and the computational fluid dynamics (CFD) method is used to describe the gas-liquid flow and bubble behaviors.

Bubble behaviors in ILs have been an emerging research area in the last decade. Due to the unique properties of ILs, such as the electrostatic interaction between ions, the bubble behaviors in ILs are different from those in molecular solvents [16]. In our previous works [8,16,18–21], the bubble behavior parameters, such as bubble diameter, velocity and aspect ratio, have been investigated experimentally and computationally. For example, CFD method and empirical correlations suitable for IL systems have been established to predict accurately the bubble behaviors. Besides, Kaji et al. [22] studied the interaction of [Emim][$EtSO_4$] and air in bubble column by using high-speed video, and proposed an empirical correlation between gas holdup and

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Nomenclature

Symbols

D	Self-diffusion coefficient ($m^2 s^{-1}$)
d_{eq}	Area equivalent bubble diameter (mm)
d_h	Horizontal bubble diameter (mm)
d_v	Vertical bubble diameter (mm)
$\overrightarrow{F_e}$	Electrostatic interaction source term ($N m^{-3}$)
$\overrightarrow{F_{sf}}$	Surface tension source term ($N m^{-3}$)
$\vec{g}$	Gravitational acceleration ($m s^{-2}$)
I	Unit tensor
M	Molecular weight ($g mol^{-1}$)
P	Pressure (Pa)
P_b	Normal boiling pressure (1.01325 bar)
P_c	Critical pressure (bar)
p_b	Perimeter (mm)
Q	Electric charge (C)
$\vec{r}$	Position vector (m)
T	Temperature (K)
T_b	Normal boiling temperature (K)
T_{br}	Reduced temperature at normal boiling point
T_c	Critical temperature (K)
T_r	Reduced temperature
t	Time (s)
V_c	Critical volume ($cm^3 mol^{-1}$)
$\vec{v}$	Velocity vector ($m s^{-1}$)
Y	Mass fraction

Abbreviations

AR	Aspect ratio
CFD	Computational fluid dynamics
FCCS	Fragment contribution corresponding state
IL	Ionic liquid
SF	Shape factor

Greek letters

α	Volume fraction
ε	Electric permittivity ($F m^{-1}$)
μ	Viscosity (Pa s)
ρ	Density ($kg m^{-3}$)
ρ_F	Electric charge density ($C m^{-3}$)
σ	Surface tension ($N m^{-1}$)
ω	Acentric factor

Subscripts

g	Gas
l	Liquid

dimensionless conductivity. Recently, Gotz et al. [23] reported the bubble behaviors in a slurry bubble column at elevated temperature and pressure, and found that larger bubbles are generated in ILs compared with organic solvents. As for CFD simulations, Carvajal et al. [24] studied the behaviors of single bubble in ILs using the level set method, and the calculated results agreed well with experimental data for Reynolds number lower than 5. However, these previous works are mainly based on empirical correlations, and the molecular structures of ILs were not considered, which limited the understanding of the flow dynamics in ionic liquids. Therefore, a theoretical method considering molecular structure for predicting bubble behavior in ILs is imperative.

The molecular thermodynamics method is effectively applied for predicting the physicochemical properties, such as density, viscosity and surface tension, which plays a critical role in bubble behaviors. Among the various molecular thermodynamics methods, the group contribution method is widely used for physicochemical property prediction of ILs [25–28]. Moreover, due to its accuracy and efficiency, the group contribution method is suitable to be combined with CFD method. In our previous work [17], the FCCS method was proposed to predict the thermodynamic properties of ILs, such as density and surface tension. Compared with the conventional group contribution method [26,29], the ILs are divided into cation fragment, anion fragment, and substituent fragment attached to the cation or anion in the FCCS method. Besides, Gardas et al. [30] developed the group contribution method for ILs viscosity prediction. Then, Gharagheizi et al. [31] extended the database, and developed the method for viscosity prediction in a wider range of ILs. In these methods, the ILs are also divided into three types of fragments, which is similar with the FCCS method. Therefore, an extended FCCS method based on the above definition of fragments is employed in this work.

Comparing with the conventional CFD method, the new FCCS-CFD coupled method is able to predict bubble behaviors and reveal the relationship between molecular structure and bubble behaviors in ILs. In the method, the IL is considered to be composed of cation and anion, which is accordant with the reality. The FCCS method is employed to calculate the physicochemical properties of ILs, and the CFD method is applied to simulate the gas-liquid flow. A source term which represents the electrostatic interaction between cation and anion is introduced into the CFD method. The bubble behaviors, i.e. the bubble shape and velocity, in 30 ILs are simulated. The role of electrostatic interaction in bubble behaviors is revealed by the simulation results. The influence of molecular structure of IL on bubble shape and bubble velocity is investigated in this work.

2. Methodology

In this work, simulations on the bubble behaviors in ILs are performed by using a new FCCS-CFD coupled method. The fragment contribution equations and the state corresponding equations in FCCS method, the continuity and momentum equations, the VOF equation and the ion transport equation in CFD method are solved in this procedure. The simulation framework of the FCCS-CFD coupled method is shown in Fig. 1.

2.1. FCCS method

In the FCCS method, the IL is divided into several fragments. Then, five inherent properties, normal boiling temperature, critical temperature, critical pressure, critical volume, and acentric factor, are calculated by the fragment contribution method, which are expressed as follows

$$T_b = 198.2 + \Sigma_i n_i \Delta T_{b,i} \tag{1}$$

$$T_c = \frac{T_b}{0.5703 + 1.0121 \sum_i n_i \Delta T_{c,i} - \left(\sum_i n_i \Delta T_{c,i}\right)^2} \tag{2}$$

$$P_c = \frac{M}{\left(0.34 + \sum_i n_i \Delta P_{c,i}\right)^2} \tag{3}$$

$$V_c = 28.8946 + 14.7525 \Sigma_i n_i \Delta V_{c,i} + \frac{6.0385}{\sum_i n_i \Delta V_{c,i}} \tag{4}$$