Droplet size distribution and droplet size correlation of chloroaluminate ionic liquid–heptane dispersion in a stirred vessel

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HIGHLIGHTS

- Ionic liquid–heptane dispersion was studied as model system for ionic liquid alkylation process.
- FBRM and PVM were successfully used to determine the phase inversion and droplet size distribution respectively.
- The phase inversion point was close to the heptane holdup of 0.5.
- Self-similar droplet size distribution of IL-continuous dispersion was found.
- A semi-empirical correlation is proposed to predict the Sauter diameter of the heptane droplets.

GRAPHICAL ABSTRACT
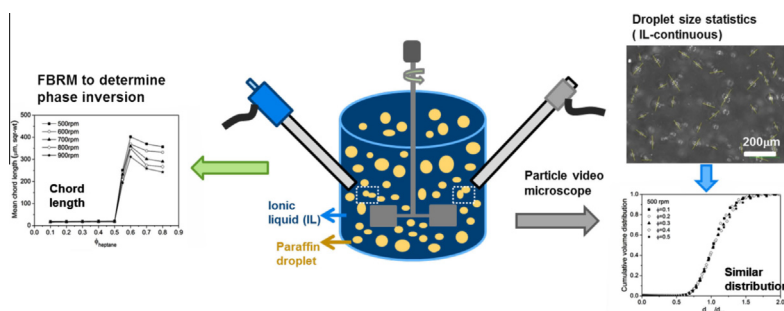
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ABSTRACT

Droplet size distribution (DSD) and mean droplet size of chloroaluminate ionic liquid (IL)–heptane dispersion in a stirred vessel were investigated as a model system for the composite ionic liquid/hydrocarbon system applied in the commercial isobutane alkylation process. Focused beam reflectance measurement was used to identify the phase inversion, and particle video microscope (PVM) was employed to measure the DSD of IL-continuous dispersions. The effects of agitation speed and dispersed phase holdup on the DSD and mean droplet size were investigated. Phase inversion was found at a heptane hold-up of just above 0.5. The observed DSDs could be described well by logarithmic normal distributions in spite of variable operating conditions. The DSDs appeared to be more or less independent of the dispersed phase holdup ($\phi_{\text{heptane}} \geqslant 0.3$) at the same agitation speed. A semi-empirical correlation based on Shinnar theory was proposed to predict the droplet mean size in the impeller region for the IL-continuous dispersion, and the predicted value agreed well with the experimental data. This work will be a good basis to predict the dispersion behavior under process conditions.

1. Introduction

Alkylation of isobutane with light olefins is an important process in petroleum industry to produce high-quality gasoline. Concentrated sulfuric acid (H_2SO_4) and hydrofluoric acid (HF) are the commercial catalysts. However, these liquid catalysts exhibit disadvantages such as severe corrosion, safety and environmental

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Nomenclature

$\bar{a}$	specific interfacial area (m^2)		$\bar{X}$	median of the logarithmic normal function (m)
b_0, b_1, b_2	constant values in the correlation of d_{32} (-)		We_{imp}	impeller Weber number, (= $\rho_c N^2 D^3/\gamma$), (-)
C	impeller clearance off the tank bottom (m)			
C_1, C_2, C_3, C_4	empirical constants in population balance equation (-)		*Greek letters*	
			γ	interfacial tension (N/m)
d, d'	diameter of a droplet (m)		ε	energy dissipation rate (m^2/s^3)
d_{32}	Sauter mean diameter (m)		$\bar{\varepsilon}$	average energy dissipation rate (m^2/s^3)
d_{99}	diameter related to the cumulative percentage of 99% in DSD (m)		ε_{imp}	energy dissipation rate at impeller region (m^2/s^3)
D	diameter of impeller (m)		σ	standard deviation of distribution function (m)
$g(d)$	breakage frequency of droplet (1/s)		$\zeta\,(d, d')$	coalescence rate between droplets with diameter d and d' (1/s)
$h(d, d')$	collision between droplets with diameter d and d' (1/s)		$\lambda\,(d, d')$	coalescence efficiency between droplets with diameter d and d' (1/s)
L_k	Kolmogoroff length (m)		ρ_c, ρ_d	densities of the continuous and dispersed phases (kg/m^3)
$n(d)$, $n(d')$	number of droplets with d or d' (-)		ρ_m	average density of the dispersion (kg/m^3)
N	agitation speed (rpm, 1/min)		μ_c	viscosity of the continuous phase (Pa s)
N_p	power number of impeller (-)		ϕ	holdup (volume fraction) of the dispersed phase (-)
P	power input of impeller, (W)			
Re_{imp}	impeller Reynolds number, (= $\rho_c N D^2/\mu_c$), (-)			
T	internal diameter of vessel (m)			
X	independent variable in logarithmic normal function (m)			

issues, hard disposal of spent catalyst and high operating cost. Acidic ionic liquids (ILs) are promising substitutes for H$_2$SO$_4$ and HF as alkylation catalysts because of their safer operation, low consumption and good catalytic performance [1,2]. The composite ionic liquid developed by China University of Petroleum shows a high selectivity to high octane alkylate and has been demonstrated in industrial application [3].

Liquid acid catalyzed isobutane alkylation is a heterogeneous system wherein the reactions occur in or near the interface between the catalyst and hydrocarbon phases [4]. The intrinsic reaction rate is extremely fast, which is explained by the highly reactive carbonium intermediate in the generally accepted mechanism [5]. In H$_2$SO$_4$-catalyzed isobutane alkylation, the alkylate quality can be enhanced with increased mixing intensity [6]. Mixing largely determines the interfacial mass transfer and reaction performance [7]. The interfacial mass transfer rate is proportional to the interfacial area. In practice, the interfacial area is controlled by the mixing intensity, geometry of mixer and reactor, dispersed phase holdup and physicochemical properties of fluid phases [8–10].

In industrial isobutane alkylation, liquid H$_2$SO$_4$ or HF is applied in more than 50 vol% to form the acid-continuous dispersion in the reactor. As reported by Am Ende [11], the interfacial area reached a maximum at the dispersed isooctane holdup of 0.25. The interfacial area increased furthermore with increasing acid soluble oil content, which was attributed to the decreased interfacial tension. Liquid HF has lower viscosity and density compared to H$_2$SO$_4$, and continuous HF dispersion is found to have much larger interfacial area under vigorous agitation, resulting in a faster reaction rate. On the other hand, continuous HF dispersion produces more undesirable by-products in case of too long contact times [12]. Thus, hydrodynamics influences the selectivity in the current systems.

In the actual ILA process, the IL catalyst is expected to be the continuous phase in the reactor, comparable to the isobutane alkylation processes using liquid H$_2$SO$_4$ or HF. The physical properties of the recently developed IL-catalyzed alkylation (ILA) are different from those of liquid H$_2$SO$_4$ and HF-catalyzed systems, and the interfacial area being one of the controlling factors in

determining the apparent reaction rate is still unknown. In a recent study of the intrinsic kinetics of ILA, the reaction rate was found to be extremely fast and consequently the reaction was found to be limited by mass transfer of light olefins to the IL phase [13]. Similar finding was reported by Schilder et al. [14] who demonstrated that the apparent reaction rate of ILA increased pronouncedly with a decrease in IL droplet size, and the reaction was predicted to be completed in approximately 0.1 s when the IL mean droplet size decreased to 10 μm. In addition, ILA experiments at a short contact time by our research group showed that an IL/hydrocarbon volume ratio of ⩾1 and sufficient mixing were critical to obtain a high-quality alkylate [15]. Thus, like in the current systems, mass transfer affects reaction selectivity in ILA. Determining the effect of hydrodynamics (mixing conditions and geometry) and phase volume ratio on the interfacial area generated in the IL/hydrocarbon system is desirable for the design of the ILA reactor. Therefore, quantifying the local interfacial area to understand the mass transfer is crucial.

The local interfacial area ($\bar{a}$) can be derived from the Sauter diameter (d_{32}) and the holdup (volume fraction) of the dispersed phase (ϕ), using Eq. (1) [16]:

$$\bar{a} = 6\phi/d_{32} \tag{1}$$

wherein d_{32} is determined as defined in Eq. (2) [17]:

$$d_{32} = \frac{\int_{d_{min}}^{d_{max}} d^3 p(d)\,\mathrm{d}d}{\int_{d_{min}}^{d_{max}} d^2 p(d)\,\mathrm{d}d} \tag{2}$$

wherein d_{max} and d_{min} denote the maximum and the minimum droplet size, respectively, and $p(d)$ is the probability density function of the droplet size. The local interfacial area and how to be influenced can be determined by measuring the droplet distribution and hold-up at different operating conditions.

Dispersion behavior and the corresponding DSD are dynamically controlled by the breakage and coalescence events [18–20]. To date, liquid–liquid mixing and dispersion behaviors are still not thoroughly understood because of the highly complex phenomena of drop breakage and coalescence [21–23]. The main factors influencing liquid–liquid dispersion include local flow