



Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp

Short communication

Extinguishing pool fires with aqueous ferrocene dispersions containing gemini surfactants

Yusuke Koshiba ^{a, *}, Hideo Ohtani ^b^a Department of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan^b Department of Safety Management, Faculty of Environmental and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan

ARTICLE INFO

Article history:

Received 8 May 2015

Received in revised form

27 November 2015

Accepted 29 November 2015

Available online 8 December 2015

Keywords:

Ferrocene

Fire extinguishing agent

Aqueous dispersion

Water mist

Gemini surfactant

Additive

ABSTRACT

The objective of the present study was to explore the relationship between the dispersibility and fire-extinguishing capability of aqueous ferrocene dispersions containing gemini surfactants belonging to the same series, namely, olfin E1020, olfin PD 201, and surfynol 465. In this study, the dispersibility and ability to suppress pool fires were characterized by turbidity and extinguishing time, respectively. Ultrasonication enabled easy preparation of the aqueous dispersions of ferrocene powder containing the gemini surfactants. Visual observations and turbidity measurements clearly demonstrated that the order of dispersibility was as follows: ferrocene dispersion containing surfynol 465 \geq ferrocene dispersion containing olfin E1020 > ferrocene dispersion containing olfin PD201. Fire suppression experiments indicated that the ferrocene diameter, in the ferrocene diameter range of 10.4–21.5 μm , negligibly influenced the extinguishing time. Furthermore, for the same ferrocene samples as were used for the turbidity measurements, the order of extinguishing ability was as follows: ferrocene dispersion containing surfynol 465 > ferrocene dispersion containing olfin E1020 > ferrocene dispersion containing olfin PD201; thus, the extinguishing ability was identical to the dispersibility order.

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1. Introduction

Over the past two decades in Japan, the number of fires in industrial facilities storing and handling dangerous goods (e.g., flammable liquids) has gradually increased, despite a decrease in the number of such facilities over the same period (FDMA, 2014). Accidental fires can cause deaths and injuries as well as severe economic loss; for instance, in 2013, 188 fires in industrial facilities were reported in Japan, causing 10 deaths, 60 injuries, and property loss of approximately 4.4 hundred million yen. Therefore, an effective fire-extinguishing agent for Class B fires is needed. A number of studies have been reported on such agents, including dry chemicals (Kuang et al., 2008), foam (Wang, 2014), pure water mist (Jenft et al., 2014), and water mist with additive(s). The additives have included surfactants and inorganic or transition metal compounds (Joseph et al., 2013). Of the transition metal

compounds, commercially available ferrocene (FeCp_2) shown in Fig. 1a is expected to become a new flame inhibitor, based on recent studies (Koshiba et al., 2015a). Linteris et al. (2000) first reported that 200-ppm ferrocene vapor significantly reduces the burning velocity of premixed methane/air flames. Furthermore, Koshiba et al. (2012) clearly demonstrated that even a low ferrocene fraction can extinguish a filter paper fire. However, these earlier studies also highlighted the issue of fire-suppression efficiency, which was found to decrease dramatically at high ferrocene fractions.

One approach to solve this issue is to employ an aqueous dispersion of ferrocene powder as a suppressant. The benefit of this method lies in the ease of preparation of dispersions with optimum ferrocene concentrations using surfactants. In addition, aqueous dispersions offer the combined benefit of the suppression efficiencies of both water and ferrocene. In our previous study, the aqueous dispersions of ferrocene powder were prepared with a gemini surfactant (Koshiba et al., 2015b), which demonstrated that ferrocene dispersions have high suppression abilities; however, only one gemini surfactant was examined.

The main objectives of the present study were to experimentally elucidate the fire extinguishing ability of ferrocene dispersions

* Corresponding author. 79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan.

E-mail address: ykoshiba@ynu.ac.jp (Y. Koshiba).

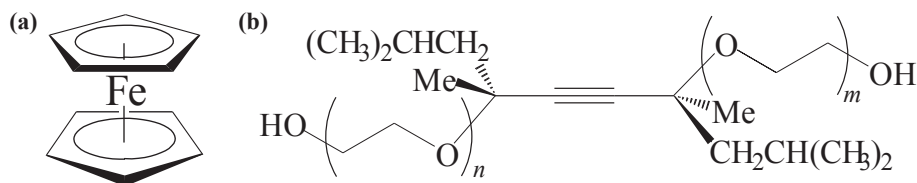


Fig. 1. Chemical structures of (a) ferrocene, (b) olfin E1020 ($m + n = 30$) and surfynol 465 ($m + n = 20$).

containing gemini surfactants and to explore the relationship between the dispersibility and extinguishing capability for three gemini surfactants from the same series: olfin E1020, olfin PD 201, and surfynol 465 (see Fig. 1b). Their dispersibilities were characterized by both visual observations and turbidity measurements, whereas their fire suppression abilities were evaluated based on their fire extinguishing times for n-heptane pool fires. Aqueous ferrocene dispersions are also advantageous as they are phosphorus free and pose low environmental risks. The former characteristic is beneficial owing to the increasing cost and depletion risk of phosphate rock (Cordell and Neset, 2014), whereas the latter is a result of the halogen-free natures and low toxicities of these dispersions; ferrocene itself poses almost no environmental risk, as its toxicity is low and the primary products of the inhibition reaction are likely to be iron oxides. Surfynol 465 complies with Food and Drug Administration and Environmental Protection Agency regulations.

2. Material and methods

2.1. Chemicals

Ferrocene was of reagent grade (>98.0%, Wako Pure Chem. Ind. Ltd., Japan). n-Heptane (>99.9%, Kanto Chem. Co. Inc., Japan) was passed through molecular sieves to remove residual water. Deionized water (<1 $\mu\text{S}/\text{cm}$) was used. The three surfactants (i.e., olfin E1020, olfin PD 201, and surfynol 465) were purchased from Nissin Chem. Ind. Co. Ltd., Japan and were used as received.

As described above, olfin E1020, olfin PD201, and surfynol 465 are gemini surfactants, which can be viewed as bis-surfactants, where two amphiphilic molecules are connected by a short spacer (Holmberg et al., 2003). In general, gemini surfactants are highly efficient in lowering the critical micelle concentration (CMC) (Páhi et al., 2009). Olfin E1020 ($m + n = 30$) and surfynol 465 ($m + n = 20$) are 2,4,7,9-tetramethyl-5-decyne-4 and 7-diol-di(polyoxyethylene) ether, respectively, while olfin PD201 is a mixture consisting primarily of the ether and propylene glycol.

2.2. Preparation

2.2.1. Ferrocene milling procedures

Three ferrocene samples (S1–S3) were prepared to investigate the effects of ferrocene particle size on dispersibility and extinguishing time. Micron-sized ferrocene particles (yellow powder) were prepared by wet-milling as-received ferrocene particles (light orange powder) in a planetary mill (Pulverisette 7, Fritsch, Germany) with ϕ 2 mm ZrO_2 balls. The particle size distributions of the ferrocene samples were determined by laser diffraction spectroscopy (SALD 7000, Shimadzu, Japan). The median diameters (d_{50}) of S1, S2, and S3 were determined to be 10.4, 11.4, and 21.5 μm , respectively.

2.2.2. Preparation of aqueous ferrocene dispersion

Milled ferrocene powder was added to an aqueous solution of the surfactant, whose surfactant concentration was set to twice the

CMC value determined by the du Noüy ring method (du Noüy, 1925). Aqueous dispersions of ferrocene particles were prepared by ultrasonication (43 kHz) for 20 min at 323 K. A temperature of 323 K is below the cloud point of the surfactants, which is the temperature at which phase separation occurs (ASTM D2024, 2013).

2.3. Characterization

2.3.1. Dispersibility

Visual observations and nephelometric measurements were conducted to gain insight into the dispersibilities of the aqueous ferrocene dispersions. Dispersibility is typically characterized as a function of the turbidity of the dispersion (Itami and Fujitani, 2005), where higher turbidity indicates better dispersibility. The ferrocene concentration was set to 100 ppm on a mass/mass basis in these experiments, which was the same as that used in our previous study (Koshiba et al., 2015b). In the present study, the turbidity measurements (NTU for formazine) were conducted by a turbidimeter (2100Q, Hach Co., USA) at room temperature. Prior to performing the turbidity measurements, the turbidimeter was calibrated using 20, 100, and 800 NTU StabCal standards (Hach Co., USA). To negate the ferrocene color, the turbidity was determined from the ratio of the 90° scattered light signals to transmitted light signals.

2.3.2. Suppression experiments

The experimental setup for the suppression experiments, depicted in Fig. 2a, was the same as that used for a preceding study (Koshiba et al., 2015b). The experimental apparatus was built to simply investigate the effect of dispersibility on suppression capability. An 83-mm-diameter pan was used with a nozzle placed 600 mm above it, which was connected to an electric high-pressure pump. For each trial, 80 mL of n-heptane was poured into the pan and a free burn was conducted until a quasi-steady burning rate was achieved. After preburning, the nozzle was activated at a flow rate of 250 mL/min. The average extinguishing times (τ) were determined in 10 fire-suppression trials per ferrocene sample.

Prior to the suppression experiments, the full cone spray pattern properties were assessed. The spray is typically characterized by water-flux distribution and droplet properties, namely, the droplet size, viscosity, specific gravity, temperature, and pressure (Santangelo et al., 2014). The temperature and pressure were kept constant in the present study. The viscosity and specific gravity were expected to have minimal impacts on the droplet properties owing to the very low content of ferrocene (100 ppm) and surfactant (0.2–0.4 wt%) in the aqueous ferrocene dispersions. The droplets from the nozzle were directly collected in 73 jars (23 mm in diameter \times 55 mm in height) to determine the volume flux distribution. The vessels were arranged in a radial pattern on the floor under the nozzle (see Fig. 2b). The average volume flux ($\text{L}/\text{m}^2 \cdot \text{min}$) decreased gradually with distance from the center (D , see Fig. 2c). The immersion method (Hurlburt and Hanratty, 2002) using silicone oil provided values for the Sauter mean diameter d_{32} ,

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