**Ferrocene-Containing Emulsion-Based Fire-Extinguishing Agents**

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**ABSTRACT**

This paper proposes a novel fire suppressant: a ferrocene-containing oil-in-water (O/W) emulsion. In this study, oil-in-water emulsions containing a surfactant (triton X-100) and ferrocene (0-500 ppm) were prepared and their stabilities and capabilities to extinguish pool fires were investigated. The resulting O/W emulsions exhibited no phase separation for at least one month. Suppression experiments clearly demonstrated that (1) the ferrocene-containing O/W emulsions have a high suppression capability even if the emulsion contained 1.05-wt% \textit{n}-octane and that (2) the suppression capability is positively correlated with the ferrocene concentration in the 0-500 ppm concentration range.

**Keywords:** Fire Suppression, Ferrocene, Oil-In-Water Emulsion, Extinguishing Time

1. **INTRODUCTION**

Residential fires have emerged as a serious social issue in many countries; for instance, 12,862 fires and 1,115 fire-related deaths were reported in Japan in 2014. The development of high-performance fire suppressants can potentially contribute to limiting the number of such fatalities. Dry chemicals (also known as ABC powder) with ammonium dihydrogen phosphate (NH₄H₂PO₄) as the main active component are globally used as effective fire-extinguishing agents; however, alternatives to these chemicals are currently required owing to the risk of depletion and increasing cost of phosphate ore [1, 2]. Additive-containing water mist is a potential candidate to be used as an alternative fire suppressant [3-5].

Interestingly, despite its flammability, ferrocene (Fe(C₅H₅)₂), illustrated in Figure 1 behaves as a good flame inhibitor at low ferrocene fractions [6,7]; the suggested inhibiting mechanism for iron compounds is based on the ready production of active iron species (e.g., FeO, FeO₂, FeOH, and Fe(OH)₂) in a flame, followed by the catalytic recombination of radicals, including H, O, and OH [8]. Hence, ferrocene can be considered as an iron transporter to the flame. To use lipophilic ferrocene as an additive
in water, Koshiba and co-workers prepared aqueous ferrocene dispersions by adding the ferrocene particles directly into water using dispersion techniques [9, 10]. This previous study demonstrated the high extinguishing capabilities of ferrocene dispersions and the positive relation between their dispersibility and suppression ability. However, they also pointed out the problem of a dramatic decrease in dispersibilities and extinguishing capabilities over a short period of time and the degradation of the organometallic ferrocene due to its reaction with water.

While the use of emulsion (emln.) techniques is an effective approach for solving these problems, few studies have been reported on the extinguishing efficiency of emulsions [11]. In the present study, ferrocene-containing oil-in-water (O/W) emulsions were prepared by dissolving ferrocene in an oil and dispersing the ferrocene-containing oil in water. The main objective of this study was to elucidate the suppression abilities of ferrocene-containing O/W emulsions using pool fires.

2. MATERIALS AND METHODS

2.1 Chemicals

In this study, triton X-100 (TX; purity > 98.0%; illustrated in Figure 2) was used as a nonionic surfactant. Ferrocene (purity > 98.0%) was used as-received without further purification. Water used in this study was deionized (<1 μS/cm). Dry n-octane was chosen as the oil due to its high solvation ability for ferrocene at room temperature (n-hexane: ca. 31 mg/mL, n-octane: ca. 36 mg/mL, n-decane: ca. 35 mg/mL).
2.2 Emulsion Preparation

\( n \)-octane solutions of ferrocene were emulsified into aqueous solutions of TX at 5,000 rpm for 15 min at room temperature by using a homogenizer (T18, IKA, USA). Table 1 presents the samples used in this study. The emulsions contained 1.05-wt% \( n \)-octane and the weight ratio of TX to \( n \)-octane was set to 5:1 [12]; the ferrocene concentrations in this study were 0, 100, and 500 ppm on a mass/mass basis. Hereafter, O/W emulsion containing 0-, 100-, and 500-ppm ferrocene are referred to as Emln. 0, Emln. 100, and Emln. 500, respectively.

| Sample     | TX / wt% | \( n \)-octane / wt% | Ferrocene / ppm |
|------------|----------|----------------------|-----------------|
| Pure water | 0        | 0                    | 0               |
| TX Soln. a | 5.25     | 0                    | 0               |
| Emln. 0    | 5.25     | 1.05                 | 0               |
| Emln. 100  | 5.25     | 1.05                 | 100             |
| Emln. 500  | 5.25     | 1.05                 | 500             |

a: aqueous solution of triton X-100.

2.3 Emulsion Characterization

Typical methods for evaluating emulsion stability include zeta potential and light scattering techniques [13, 14]. In this study, emulsion stability was determined by the phase separation method [15]: 100 mL of every emulsion was poured into long test tubes having a diameter and length of 35 mm and 125 mm, respectively, and the tubes were capped and maintained at 25 °C.

In general, the droplet size of the suppressants directly affects extinguishing efficiency [16]; thus, the droplet size distribution of the oil in water governs not only the emulsion stability but also their extinguishing abilities. In this study, the droplet size distributions of the emulsions with or without ferrocene were measured at 22 °C using the dynamic light scattering method (ELSZ-2, Otsuka Electronics, Japan).

2.4 Suppression Experiments

The experimental apparatus for the suppression trials enables a simple evaluation of the fire-extinguishing capability and is depicted in Figure 3. An 83-mm diameter pan was placed at 600 mm below a nozzle. For each trial, 80 mL of \( n \)-heptane was poured into the pan. The nozzle was then activated when the preburning had reached a quasi-steady burning rate. The flow rate and spray angle were 300 mL/min and 50°, respectively. The average extinguishing time (\( \tau \)) and its standard deviation (\( \sigma \)) were determined in 10 trials per emulsion sample.
3. RESULTS AND DISCUSSION

3.1 Emulsion Characterization

3.1.1 Appearance of The Ferrocene-Containing Emulsions

Figure 4 shows a digital photograph of the emulsions prepared in this study. As shown in this figure, emulsions 0, 100, and 500 were poured into the left, centeral, and right test tubes, respectively. The O/W emulsions were completely transparent; the coloration of emulsions 100 and 500 is attributed to the yellow ferrocene itself. No phase separation was observed for the resultant emulsions for at least one month. This indicates that the emulsions tested in this study are quite stable and that the emulsion stability is negligibly influenced even when ≤ 500 ppm of ferrocene is dissolved in the oil.
3.1.2 Sauter Mean Diameters and Viscosities of The Ferrocene-Containing Emulsions

As shown in Table 2, the Sauter mean diameters (SMD; Equation 1) of emulsions 0, 100, and 500 were found to be 4.4, 4.6, and 5.3 nm, respectively.

\[
SMD = \frac{\sum N_i D_i^3}{\sum N_i D_i^2}
\]

where \( N_i \) is the measured number of droplets with the diameter \( D_i \). There are no significant differences in the droplet sizes among the emulsions, thereby indicating that the presence of ferrocene does not influence the droplet size for the 0-500-ppm ferrocene concentration range.

The size distribution measurements and stability tests described above imply that the ferrocene-containing emulsions are microemulsions. In addition to the droplet size, viscosities (\( \eta \)) of the emulsions were measured at 17 °C. The viscosity measurements obtained \( \eta \) values of 1.45, 1.46, and 1.48 mPa·s for emulsions 0, 100, and 500, respectively (Table 2). There were no significant differences in their viscosities and droplet sizes, thereby allowing a direct comparison of their suppression efficiency.

| Table 2 | Sauter mean diameter (SMD) and viscosity (\( \eta \)) values of the emulsions. |
|---------|---------------------------------|
| Sample  | SMD / nm | \( \eta \) / mPa·s |
| Emln. 0 | 4.4      | 1.45           |
| Emln. 100 | 4.6      | 1.46           |
| Emln. 500 | 5.3      | 1.48           |

3.2 Suppression Experiments

Prior to the extinguishment trials, we confirmed that pure water was unable to suppress pool fires; furthermore, the SMD values were found to be ca. 50 \( \mu \)m for all sprayed emulsions using the immersion method. The use of this method involves gathering the sprayed droplets with an immiscible liquid, followed by the direct observation of the collected droplets with a microscope (DMI 3000B, Leica, Germany).

We confirmed that no re-ignition was observed during the extinguishing of the pool fire. The suppression experiment also revealed that owing to the surfactant efficiency [17], even an aqueous solution of TX was able to extinguish pool fires (\( \tau = 4.2 \) s and \( \sigma = 1.0 \) s). As seen in Figure 5, upon addition of 1.05-wt% \( n \)-octane to an aqueous solution of TX (i.e., emln. 0), the solution exhibited a longer extinguishing time (\( \tau = 6.2 \) s) and a larger standard deviation (\( \sigma = 2.8 \) s) than the aqueous solution of TX because of the flammability of \( n \)-octane. Interestingly, increasing the ferrocene concentration significantly reduced the extinguishing times and standard deviations (\( \tau = 4.2 \) s and \( \sigma = 1.3 \) s for emln. 100; \( \tau = 2.9 \) s and \( \sigma = 0.5 \) s for emln. 500). For the aqueous 45-wt% potassium carbonate solution, which is a well-known conventional fire suppressant (i.e., Wet chemical), \( \tau \) and \( \sigma \) values of 8.9 s and 3.1 s, respectively, were obtained by the
suppression experiment. Thus, the results obtained in the suppression trials clearly indicated that the emulsions proposed in this study exhibit remarkably shorter extinguishing times than the conventional fire extinguishing agent.

![Figure 5 Extinguishing times of emulsions. 0, 100, and 500. Error bars indicate standard deviations.](image)

To check whether there are significant differences in the extinguishing times among the suppressants, one-way analyses of variance (ANOVA) and post hoc comparisons (Tukey’s honest significant differences tests) were performed. Prior to ANOVA tests, the homoscedasticity and normality were confirmed by using the Levene’s and Kolmogorov-Smirnov tests. Consequently, the extinguishing times were significantly different ($F = 7.98$, $df = 3$, $p < .01$). The post hoc tests revealed significant differences in the extinguishing times between emln. 0 and emln. 100, and emln. 0 and emln. 500, which means that ferrocene acts as a good flame inhibitor.

As described above, ferrocene readily yields in the flame inhibiting iron species such as FeO, FeOH, and Fe(OH)$_2$ that effectively act as H, O, and OH radical scavengers [7]. The catalytic radical recombination significantly varies depending on the concentrations of iron inhibiting species, i.e., the reaction is effective at excess of their super-equilibrium concentrations [8]. However, it is known that higher ferrocene fractions decrease the suppression efficiency [18]. For instance, Linteris et al. numerically and experimentally demonstrated that the extinguishing efficiency dramatically decreases at high iron fractions, which is owing to the agglomeration and condensation of the active iron species [7]. Similarly, Koshiba et al. clearly demonstrated that for aqueous dispersions containing ferrocene particles, the ability to suppress a pool fire is maximized with a ferrocene concentration of ca. 100 ppm. At higher ferrocene concentrations of 100 ppm, the extinguishing efficiency significantly decreases [10]. Note that the experimental conditions in the present study differ slightly from those in the
previous study; nevertheless, emulsions containing ferrocene and flammable oil exhibited somewhat higher optimum ferrocene concentration compared with aqueous ferrocene dispersions without oils.

Unfortunately, due to the solubility of ferrocene in \(n\)-octane, O/W emulsions containing more than 500-ppm ferrocene could not be prepared. It should be noted that while higher ferrocene fractions decrease the extinguishing efficiency [18], the experimental results obtained in this study imply that high-performance O/W emulsions containing higher amounts of 500-ppm ferrocene can be produced by increasing the amount of \(n\)-octane, as the extinguishing capability of ferrocene exceeds its flammability.

3.3 Limitations

The present study investigated the emulsion properties (i.e., phase separation behavior, oil droplet sizes in O/W emulsions, and viscosity), spray properties, and the ability to suppress heptane pool fires. In general, the extinguishing efficiency strongly depends on the fire source condition (e.g., the type of fuel and fire pan size) as well as the spray properties such as the droplet size distribution, spray flow rate and spraying location [19]. For instance, Cong and Liao experimentally demonstrated that the extinguishing efficiency strongly depends on the type of fuel, like gasoline, diesel, or ethanol [20]. Heskestad reported that the water flux required to suppress a pool fire with water spray is proportional the characteristic length to the power of 2 (i.e., the pan diameter) [21]. The present study clearly briefly demonstrated the high suppression capability of ferrocene-containing emulsions. However, unfortunately, only one fuel type and pan size were examined. Hence, further works should be conducted to systematically investigate the suppression efficiency of the new ferrocene-containing emulsion fire suppressant.

4. CONCLUSIONS

In the present work, the stability and fire-extinguishing capability of ferrocene-containing O/W emulsions (0-500 ppm) were experimentally investigated. The obtained ferrocene-containing O/W emulsions were highly stable for at least one month at 25 °C. No significant differences in their Sauter mean diameters and viscosities were observed among the O/W emulsions containing ferrocene in the 0-500 ppm concentration range, thereby enabling the direct comparison of their extinguishing capabilities.

Suppression experiments using pool fires clearly demonstrated that the extinguishing capability is enhanced with increasing ferrocene concentrations in the O/W emulsion (emln. 0: \(\tau = 6.2\) s and \(\sigma = 2.8\) s, emln. 100: \(\tau = 4.2\) s and \(\sigma = 1.3\) s, and emln. 500: \(\tau = 2.9\) s and \(\sigma = 0.5\) s); furthermore, the ferrocene-containing O/W emulsions exhibit higher extinguishing capabilities than a conventional fire-extinguishing agent (Wet Chemical, \(\tau = 8.9\) s). Hence, the experimental results obtained in this study can provide an indication for a promising approach toward the development of a novel emulsion-based fire suppressant.
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