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Oil-in-water microemulsion containing ferrocene: A new fire suppressant

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ABSTRACT

This paper reports the preparation and fire-suppression efficiency of oil-in-water microemulsions containing ferrocene. In this work, oil-in-water emulsions containing 0–1000 ppm ferrocene and four surfactants (Surfynol 465, Olfin E1020, Triton X-100 (TX), and Noigen TDS-80 (NT)) were prepared by homogenizing n-octane solutions of ferrocene and aqueous surfactant solutions at ambient temperature. Four emulsion parameters were then characterized: emulsion stability, oil-droplet size in emulsion, flash point, and capability of extinguishing n-heptane pool fires. Emulsion stability experiments and droplet-size measurements clearly demonstrated that the oil-in-water emulsions containing ferrocene and TX/NT were thermodynamically stable microemulsions. Flash-point measurements confirmed that no oil-in-water microemulsions tested ignited below 93 °C. Suppression trials involving microemulsions containing 0–1000 ppm ferrocene and NT revealed the relationship between their fire suppression efficiency and the concentrations of ferrocene and NT, and also demonstrated that the microemulsions tested in this study have a higher ability to suppress pool fires compared with a conventional wet chemical agent.

1. Introduction

Accidental fires are disaster that can lead to human suffering, property losses, and environmental damage. Thus, they are an important social issue in most countries; for instance, fires in the United States and Japan still claimed the lives of 3275 and 1675 people in 2014, respectively. In many situations, containing and extinguishing a small developing fire with handheld fire extinguishers is of great importance. Developing more effective fire suppressants is, therefore, of considerable help in reducing such fire-related casualties. Nowadays, phosphates and their derivatives are widely used as fire-extinguishing agents [1,2]. As is well known, phosphorus is one of the three major nutrients in crop production. As shown in Fig. 1, owing to recent global problems involving nonrenewable phosphate rock such as future scarcity and dramatically increased costs [3,4], developing not only efficient phosphorus recycling and recovery techniques [5] but also alternatives for phosphorus-based fire suppressants are required at present.

Water-mist technology has received increasing attention because of its low-cost, ubiquity, and environmentally friendly properties. It is known that the major mechanisms through which water mist extinguishes fires involve the removal of heat in the flame zone (or fuel surface), attenuation of thermal radiation, and displacement of oxygen [6]. Additives to water are often required to further enhance its suppression capability and these typically include surfactants [7], antifreezes [8], and metallic compounds. Several transition metals have the ability to catalytically scavenge radicals involved in the gas-phase chain reactions. They exhibit various oxidation states, which means that transition-metal compounds can potentially behave as flame inhibitors. Of all the transition-metal compounds, ferrocene ($FeCp_2$, Fig. 2a), an organo-iron compound, is a novel promising flame inhibitor due to its high radical-trapping capability [9,10]; ferrocene and its derivatives are applied in related areas as smoke suppressants and flame retardants [11–14]. Despite its excellent extinguishing properties, using ferrocene as an additive in water poses two problems: strong fraction-dependency of fire-suppression efficiency and insolubility in water. The former reflects the fact that the ability to suppress a flame dramatically decreases at lower and higher ferrocene fractions, i.e., an optimum amount of ferrocene must be introduced into a flame. The latter means that it is difficult to directly add ferrocene (as-is) in water because of its high

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Abbreviations

ANOVA	Analysis of variance
Bu	Butyl
d	Droplet diameter (nm or μm)
F	F value (also called F statistic; dimensionless)
$FeCp_2$	Ferrocene
HA	Height of an aqueous layer (mm)
HE	Total height of the emulsion (mm)
HMIS	Hazardous Materials Identification System
HO	Height of an oil layer (mm)
Me	Methyl
ME	Microemulsion
ME_{NT} (x, y)	Microemulsion containing NT, x-wt% oil, and y-ppm ferrocene
ME_{TX} (x, y)	Microemulsion containing TX, x-wt% oil, and y-ppm ferrocene
n	Number of droplets (dimensionless)
NFPA	National Fire Prevention Association
NT	Noigen TDS-80
OE	Olfin E1020
O/W	Oil-in-water
p	Probability, p-value (dimensionless)
PS	Phase separation (vol%)
R	Weight ratio of n-octane to surfactant (dimensionless)
SMD	Sauter mean diameter (nm or μm)
SN	Surfynol 465
Soln	Aqueous solution
TX	Triton X-100
USD	U.S. dollar
W	Weight (g)

Greek characters

σ	Standard deviation of extinguishing times (s)
τ	Average extinguishing time (s)

Subscripts

m	Mist
ME	Microemulsion
NT	Noigen TDS-80
o	Oil
oct	n-octane
surf	Surfactant
TX	Triton X-100

Superscripts

i	iso
t	tert

lipophilicity. Koshiba and co-workers reported a ferrocene-containing water-based fire suppressant: aqueous ferrocene dispersions having an optimum ferrocene concentration using dispersion techniques [15,16]. The earlier studies clearly demonstrated that (i) aqueous dispersions containing smaller ferrocene particles exhibit higher dispersibilities and that (ii) the fire-extinguishing capabilities of ferrocene dispersions are positively correlated with their dispersibility. However, they also revealed that the dispersibility steeply decreases in a short time, potentially resulting in a decrease in their suppression ability. In addition, directly dispersing organometallic ferrocene powder in water may cause the ferrocene to degrade, so that ferrocene dispersions eventually break down. To solve these issues, Koshiba and co-workers recently proposed a new ferrocene-containing emulsion-based fire suppressant: a ferrocene-containing emulsion [17]. This emulsion technique involves dissolving ferrocene in oil and then dispersing the solution in an aqueous medium using surfactants. Unfortunately, however, this earlier study only reported one emulsion system.

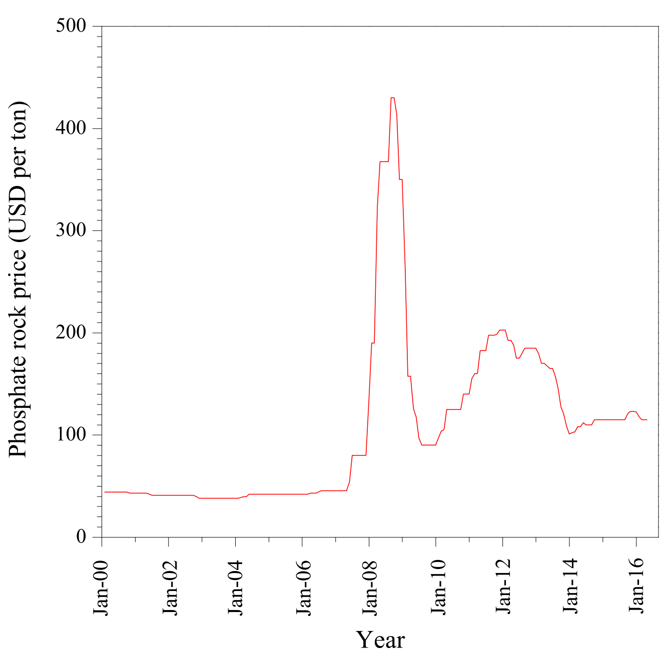

Fig. 1. Trend in market prices of phosphate rock from 2000 to 2016 (adapted from [4]).

By definition, oil-in-water (O/W) “macroemulsions” are heterogeneous, opaque, and thermodynamically unstable systems in which oil droplets will coalesce, eventually leading to phase separation. In contrast, oil-in-water “microemulsions” have nano-sized oil droplets and are macroscopically homogeneous and thermodynamically stable systems; they also have some distinguishing physicochemical properties: optical transparency, isotropy, and low viscosity [18]. The present work focuses on the fire-suppression capability of ferrocene-containing microemulsions. The major advantages of using microemulsion techniques are as follows:

- The dispersibility, which is positively correlated with the suppression capability as stated above, would be dramatically improved if

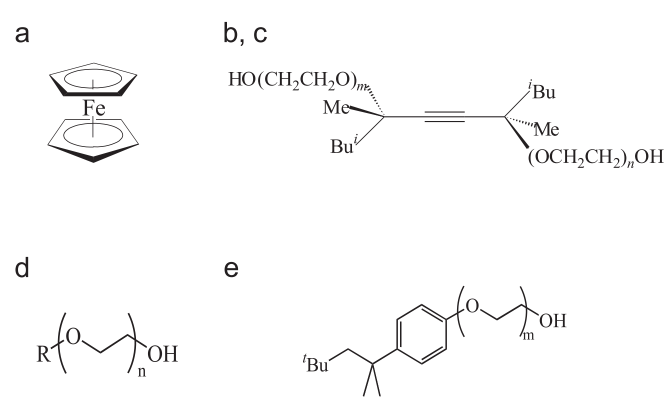

Fig. 2. Chemical structures of (a) ferrocene and the surfactants: (b) Surfynol 465 (SN, $m+n=20$), (c) Olfin E1020 (OE, $m+n=30$), (d) Noigen TDS-80 (NT, $R=CO(CH_2)_{16}CH_3$), and (e) Triton X-100 (TX, $m=10$).

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