

On the Vaporization Behavior of Water-in-oil Microemulsions

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INTRODUCTION

Water-in-oil emulsions have been reported to exhibit certain beneficial combustion properties such as reduced NO_x and soot formation, and pool fire resistance behavior (see Ref. 1 for further references). Macroemulsions or generally referred as "emulsions" are immiscible water/oil systems which are largely unstable. The present study concerns microemulsions which are transparent, single phase, thermodynamically stable fluids [2]. The extreme stability of the microemulsions arises from the marked decrease in the size of the water droplet, namely 100–1000 Å as against 0.2–50 μm in macroemulsions [2].

As the liquid fuel has to gasify before combustion can occur in the gas phase, a detailed knowledge of the vaporization behavior of emulsions is essential in understanding the emulsion combustion process [1, 3–5]. Water present in the macroemulsions (or immiscible blends) vaporizes independent of the relative concentration in the liquid phase, as reported by Law [1]. The microemulsions on the other hand represent an interesting multicomponent system whose vaporization behavior is not investigated in detail. Weatherford et al. [6], however, report that the vapor pressure of water in the microemulsions of diesel fuel shows a dependence on concentration of water. The objective of the present study is to develop a basic understanding of the vaporization behavior of microemulsions of *n*-alkanes with widely

varying oil chain lengths, under dynamic heating condition.

EXPERIMENTAL

Water-in-oil microemulsions of various *n*-alkanes from heptane (C_7) to tetradecane (C_{14}) were prepared using a surfactant, Aerosol OT (American Cyanamid Co.). Aerosol OT is sodium bis (2-ethylhexyl) sulfosuccinate. The chemical formula represents a C_8 hydrocarbon chain. The surfactant is soluble both in oil and water. The term "oil" in this report, in a broader sense, refers to hydrocarbon oil or *n*-alkane. The *n*-alkanes used were of analar grade, obtained from Fischer Scientific Co. Distilled water was used in all compositions. The microemulsions contained 10% weight of water. The weight ratio of surfactant/water was varied from 0.5–0.7 from C_7 oil to C_{14} oil. Microemulsions are formed spontaneously upon mixing, with a moderate stirring. The fluids so formed are single phase, transparent and stable. They have been tested for stability up to the boiling point, and are found to be clear and stable.

A dynamic vaporization study was conducted by employing a slow heating rate thermal analyzer. A DuPont 900 Model DTA was employed with a heating rate of 25°C/min and a sample weight ranging 5–10 mg taken in the glass sample holders (tubes of 0.5 mm diameter) in the ambient atmosphere. The principle of DTA is based on the measurement of differential heat liberated (exothermic) or absorbed (endothermic) due to physical or chemical changes occurring as a function of temperature, with respect to an inert sample (Al_2O_3).

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A typical DTA trace (or a thermogram) represents the variation of differential temperature, denoted by $f(\Delta T)$, with the temperature. In the present context, the vaporization behavior (boiling points) of various samples are determined from the endothermic peak temperatures. DTA traces of various samples are highly reproducible ($\pm 2^\circ\text{C}$) at a fixed heating rate and similar sample size. Further confidence was obtained by comparing the results for pure components (water and *n*-alkanes) with the reported data [7]. The data have been found to be in close agreement. However, the endothermic peaks due to surfactant thermal degradation was sensitive to the state of surfactant mass sticking to the sides of the sample tube. More controlled thermal analysis is needed to reproduce the degradation peaks.

RESULTS AND DISCUSSION

The vaporization behavior of water-in-oil microemulsions of C_7 to C_{14} oils is illustrated in Figure 1, in terms of DTA traces showing the endothermic peaks. The DTA traces of macroemulsions which were similar to water and oil mixtures are not shown here for brevity. Referring to heptane microemulsion, the first endothermic peak is seen at 75°C , followed by a peaks at 100, and 280°C . The first endothermic peak temperature is seen to be lower than the boiling points of either water (100°C) or heptane (99°C). Water/*n*-alkane mixtures exhibited similar behavior (dotted curves in Fig. 1). The lowering of boiling point is expected based on the formation of well known water and oil minimum boiling point heteroazeotropes [7]. The first endotherm in the present system is attributed to the minimum boiling point azeotropic composition containing water and heptane [7]. The second endotherm is due to the excess of water or oil, whichever was in excess in the original microemulsion composition. The terminal endotherm is due to thermal degradation of surfactant. DTA traces of microemulsions approximately up to decane show similar behavior. Microemulsions are seen to behave like water and oil mixture in forming well known azeotropes [7], with little or no influence of microstructural features.

Approximately above C_{10} oil, the first endother-

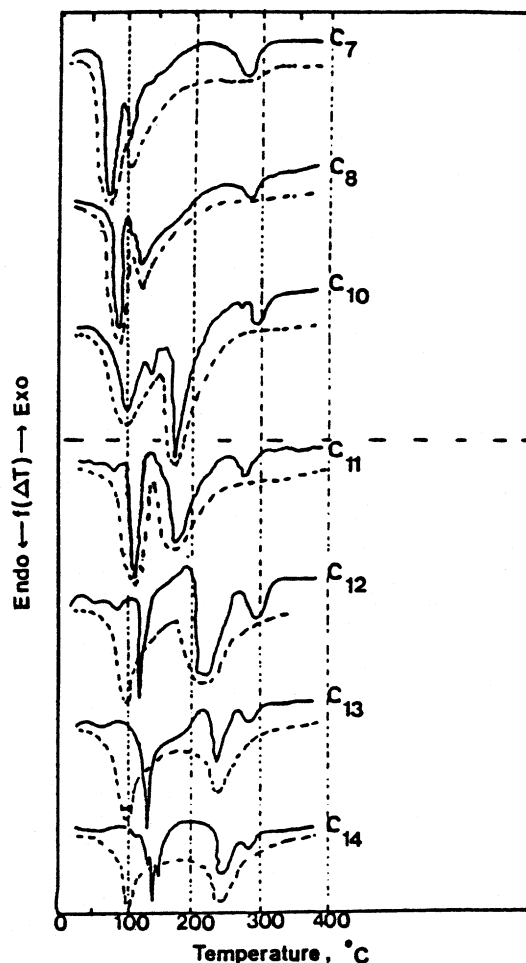


Fig. 1. DTA traces of various water-in-oil microemulsions indicating endothermic peak temperatures corresponding to boiling points. The dotted curves represent DTA traces of water and oil mixture.

mic peak temperatures in the DTA traces are similar or higher than the boiling point of water. The relative elevation of boiling point increased with the oil chain length. The second endotherms correspond to the boiling point of respective pure oils. The terminal peak corresponds to thermal degradation of the surfactant. Water/oil mixtures exhibited independent peaks due to water and oil (dotted DTA traces in Figure 1), and water exhibited boiling point consistent with the free water.

A schematic of the structure of water-in-oil microemulsion, in relation to the orientation of surfactant molecules and the state (environment) of

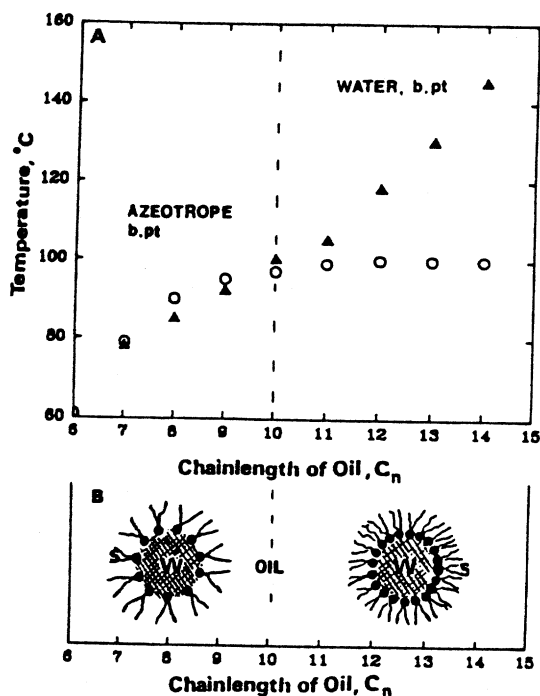


Fig. 2. (a) Boiling points of azeotropes in the region of short chain length oils, and boiling point of water in the region of long chain oils for microemulsions [\blacktriangle] and oil and water mixtures [\circ], as a function of oil chain length. (b) Schematic of water-in-oil microemulsion in relation to orientation of the surfactant molecules and state of water in the oil medium. Two limiting cases of short chain (left hand side structure) and long chain (right hand side structure) hydrocarbon oil environments are depicted. The letters W and S represent water droplet and surfactant molecule respectively.

water, is shown against the chain length of oil, in Figure 2. For short chain oils, water vaporized along with oil with a minimum boiling point (up to C₁₀ or C₁₁). This region is characterized by azeotropic compositions (Fig. 2A). Here, the azeotropic behavior predominates over the influence of microemulsion environment. For higher chain length oils, or region where azeotrope formation is not feasible, microemulsion environment appears to play an important role in the vaporization of water from the emulsion. Here, water vaporized with a boiling point considerably higher than free water. In this region, the penetration of the oil in to the interface is not so much favored

because of the longer oil chains. This allows for a tighter packing of surfactant molecules at the interface (Fig. 2B). Thus, an apparent increase in vaporization temperature is expected in terms of more restricted environment for water to gasify from the oil pool. The postulation is based on the generally observed chain length effect in microemulsion systems [8]. Further work is needed to establish the proposed mechanism.

CONCLUDING REMARKS

This preliminary report provides a conceptual basis for the organization of water and its apparent thermochemical state with respect to vaporization (or gasification) from the microemulsion environment. Scope exists for development of a basic theory of vaporization of microstructured, multicomponent microemulsion fluids. The observed state of water in the long chain hydrocarbon microemulsions provides some clues to the combustion behavior of microemulsified fuels, in terms of physical effects such as microexplosion, the liquid phase cracking of fuel and formation of soot. A detailed study in this area is in progress.

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Received 15 September 1988; revised 11 April 1989