

AFFF Spreading Properties at Elevated Temperatures

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The authors calculated spreading coefficients for aqueous film forming foams and hydrocarbon fuels from surface and interfacial tensions measurements made over a temperature range from 20° C to 90° C.

AQUEOUS FILM forming foams (AFFF) are the most efficient agents in use today for the extinguishment of hydrocarbon fuel fires. These foams have the ability to blanket and cool the burning fuel surface by rapid vaporization of water and also to form a unique aqueous film that spreads on the surface of the less dense hydrocarbon. Because of this aqueous film, the rate of evaporation of the hydrocarbon is greatly reduced, thereby depleting the supply of fuel to the flames. Both of these phenomena are strongly dependent upon the surface tensions of the AFFF and hydrocarbon liquids and upon the properties of the interfacial surface between them.

Theoretically, a liquid will form a film on the surface of a second liquid if the spreading coefficient, as calculated from surface tension measurements, is positive.¹ The spreading coefficient is defined as:

$$S = \gamma_L - \gamma_U - \gamma_{IF}$$

where S = spreading coefficient, γ_L = surface tension of the lower liquid, γ_U = surface tension of the upper liquid, and γ_{IF} = interfacial tension between the liquids. When S is positive, the upper liquid (AFFF) will spread instantly over the surface of the lower liquid (hydrocarbon fuel). If S is zero or negative, the upper higher density AFFF will fall through the fuel surface. The AFFF solution, although it is primarily water, contains a fluorochemical surfactant that reduces the surface tension of water to such an extent that the spreading coefficient is positive with many hydrocarbons.

Since the various tensions are a function of temperature, the spreading ability can vary with temperature. For this reason an AFFF solution

that may form a film on a particular hydrocarbon surface at ambient temperature may not form a film at the higher temperatures encountered when the hydrocarbon is burning. An AFFF, when first applied to a burning surface, cools the surface by the rapid evaporation of water from the AFFF solution. At this time the surface temperature will be in the neighborhood of 100° C, thus facilitating film formation. It was considered worthwhile to determine whether this change in sign of the spreading coefficient does, indeed, occur for several of the more commonly used fuels and AFFFs.

EXPERIMENTAL

MATERIALS

The water used for this work was deionized and then distilled in a simple distillation apparatus.

n-Octane was Aldrich Gold Label, 99+%. Gas chromatographic analysis indicated only a single component.

Four AFFF samples were obtained: FC-206 from 3M Company, St. Paul, MN; Aer-O-Water Plus and Aer-O-Water 6 from National Foam System, Inc., Lionville, PA; Lorcon from Laurentian Concentrates, Ltd., Ottawa, Canada. All of the AFFFs were diluted to 6 percent concentration except Aer-O-Water Plus which was diluted to 3 percent. These are the normal concentrations recommended by the manufacturer when applied to fires.

The aviation fuels — JP-5, JP-4, and aviation gasoline (Av Gas) 115/145 — were obtained from the air facility at this installation. Jet fuel additives AM-1 and FM-9 and the fuel, JET-A, were obtained from Mr. A. San Miguel of this facility who, in turn, obtained them through the Federal Aviation Administration.

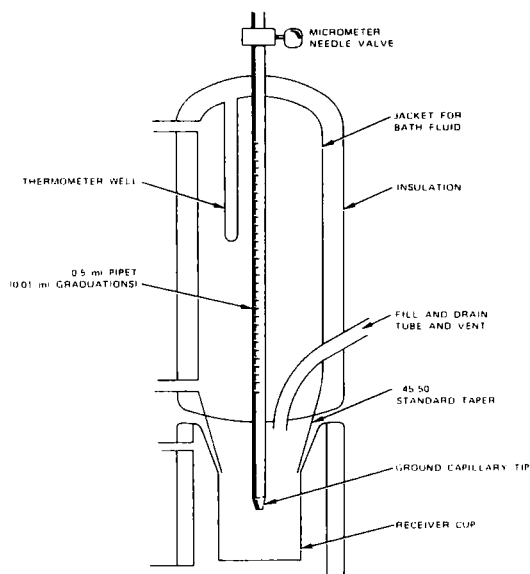
INSTRUMENTS

The surface and interfacial tensions were measured with a drop-volume apparatus.² The volume of a drop of liquid as it falls from the tip of a capillary can be related to the surface tension of the liquid by means of the equation:

$$\gamma = \frac{V(\Delta d)g}{r} F$$

in which γ is the surface tension, V is the drop volume, Δd is the density difference between the dropping liquid and surrounding medium, g is the local acceleration of gravity, r is the capillary radius, and F is a correction factor which is a function of $r/V^{1/3}$. The apparatus shown in Figure 1 was used for the measurements. The drop volume was determined by means of a 0.5-ml pipet, which has 0.01-ml graduations; the tip was carefully ground from Tru-Bore tubing. A micrometer needle valve on top of the pipet was used to adjust the flow rate. Each determination was the

Figure 1. Drop-volume apparatus for measuring surface and interfacial tensions.



average of five to ten drops usually. Temperature control was achieved by circulating bath oil through the jackets around the pipet and receiver cup. The pipet was filled by drawing up the liquid from the receiver, which in turn was filled by means of a syringe fitted with a long Teflon needle. When making interfacial tension measurements, hydrocarbon was added to the receiver until the level was above the ground tip.

The performance of the instrument was checked with water and *n*-octane. On comparing the experimental results with the literature values, shown in Table 1, it can be seen that the octane values agree very well,³ but the water surface tensions are slightly low at all temperatures.⁴ The differences are probably due to the purity of the water used.

TABLE 1. Surface Tensions of Water and *n*-Octane

| Temperature (°C) | Water ($mN m^{-1}$) | | <i>n</i> -Octane ($mN m^{-1}$) | |
|---------------------|-----------------------|--------------|----------------------------------|--------------|
| | literature* | experimental | literature† | experimental |
| 20 | 73.36 | 72.24 | 21.62 | 21.64 |
| 30 | 71.82 | 70.94 | 20.67 | 20.74 |
| 45 | 69.40 | 68.97 | 19.24 | 19.25 |
| 60 | 66.84 | 66.15 | 17.81 | 17.85 |
| 75 | 64.14 | 63.53 | 16.39 | 16.53 |
| 90 | 61.30 | 60.83 | 14.96 | 15.18 |

* Reference 4

† Reference 3

Density measurements for the liquids used were made with a 10-ml pycnometer at 30° C. The density-temperature relationships were then determined with a Bingham-type pycnometer,⁵ which had been calibrated with mercury. A cathetometer reading to 0.05 mm was used to read the liquid level at each temperature.

RESULTS AND DISCUSSION

Results of measurements of surface tensions as a function of temperature for four samples of AFFF and four commonly used aviation fuels are shown in Figures 2 and 3, respectively. It can be seen that the surface tensions of all liquids but one vary linearly with temperature. Measurements made with Av Gas 115/145 were not made above 70° C because of the lower boiling point of this fuel. Moran et al.⁶ found a decrease of about 0.07 mN m⁻¹ to 0.12 mN m⁻¹ per degree Celsius increase in temperature over the range of 10° C to 50° C for the hydrocarbons they investigated. The range found for the fuels in this study was about 0.08 mN m⁻¹ °C⁻¹ to 0.09 mN m⁻¹ °C⁻¹. For the surfactant solutions, the decrease in this study ranged from 0.03 mN m⁻¹ °C⁻¹ to 0.05 mN m⁻¹ °C⁻¹ compared to 0.05 mN m⁻¹ °C⁻¹ to 0.06 mN m⁻¹ °C⁻¹ in Moran's report. The surfactant solutions were not the same in each case, however.

The interfacial tensions of FC-206 with the various hydrocarbon fuels and *n*-octane are shown in Figure 4. They are all about the same, ranging from about 3 mN m⁻¹ to 5 mN m⁻¹ at 20° C. The decrease in interfacial tensions with increase in temperature ranges from 0.01 mN m⁻¹ °C⁻¹ to 0.03 mN m⁻¹ °C⁻¹; this is considerably less than those reported by Moran et al.,⁶ who found the temperature dependence to be about the same as that of the hydrocarbon surface tensions.

Even though the surface tensions of the AFFFs are all about equal and the interfacial tensions between AFFF and hydrocarbons are all about the same, only small differences in these can make a large difference in *S* and, consequently, in whether a film of AFFF will form on the hydro-

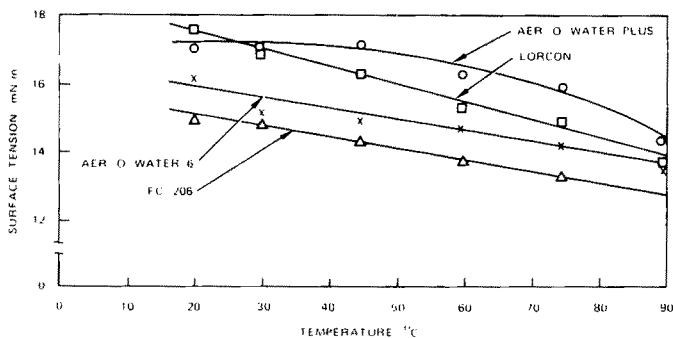


Figure 2. Surface tension as a function of temperature for AFFF solutions.

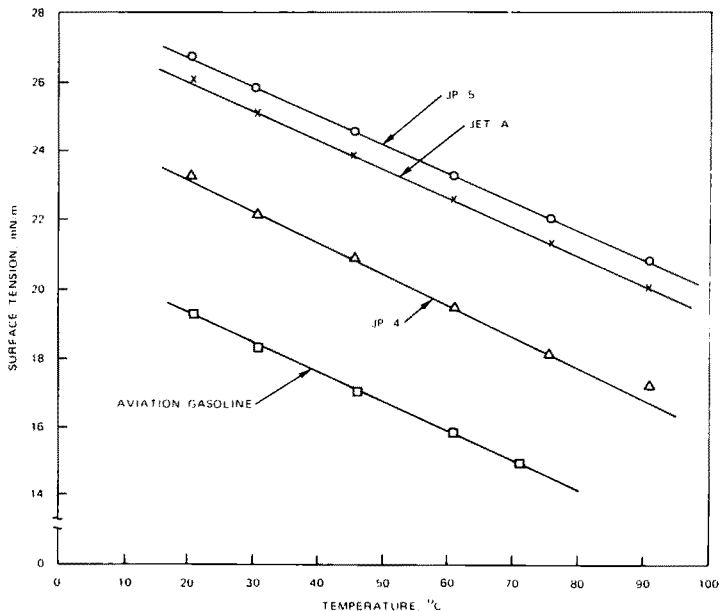


Figure 3. Surface tension as a function of temperature for hydrocarbon fuels.

carbon. Unfortunately, time limitations prevented the interfacial measurements of all four AFFFs with all of the hydrocarbons. However, the conclusions reached with FC-206 will probably hold for the others also.

Figure 5 shows the spreading coefficients for FC-206 with the various fuels and *n*-octane. The coefficients became negative for Av Gas 115/145 and *n*-octane at about 60° C and 95° C, respectively. Thus films of FC-206 will not form on these liquids above these temperatures. This correlates

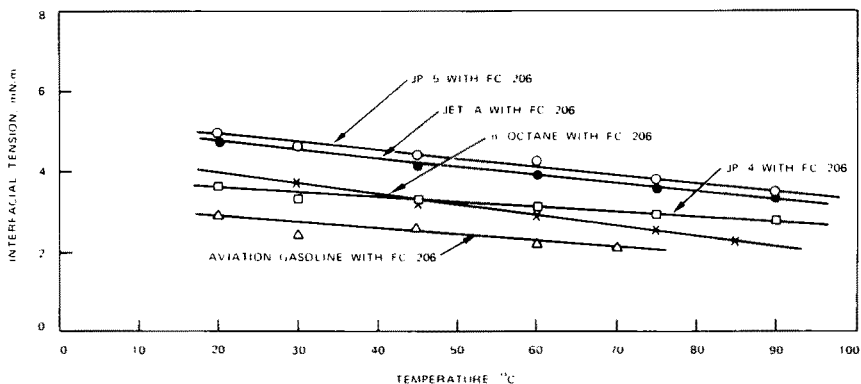


Figure 4. Interfacial tension as a function of temperature for FC-206 with hydrocarbon fuels.

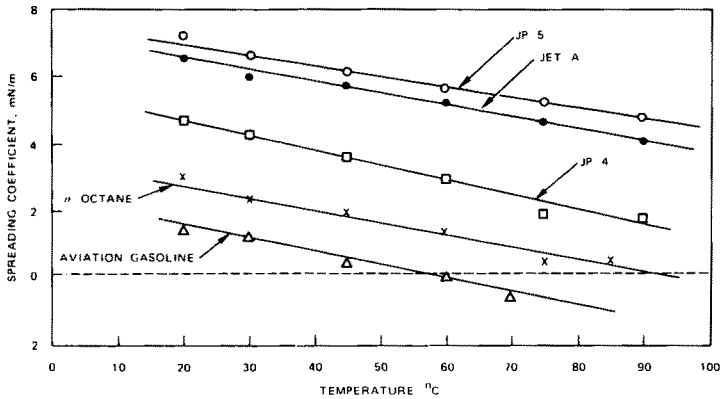


Figure 5. Spreading coefficient as a function of temperature for FC-206 with hydrocarbon fuels.

very well with the knowledge that AFFF agents are not as effective in reducing evaporation rates of the more volatile fuels such as Av Gas.⁷ It can therefore be concluded that it would be more difficult to extinguish fires and to prevent reflashing of these fuels.

Since one of the requirements of an AFFF for Navy use is that it be equally as effective when diluted with sea water as with fresh water, the effects of sea water on the surface tensions and spreading coefficients were determined. Figure 6 shows the surface tensions, which are only slightly higher than those for the AFFF in distilled water. The interfacial tensions and spreading coefficients are shown in Figure 7 for FC-206 with JP-5. It can be seen that the interfacial tensions for the sea water solution are about 1 mN m^{-1} to 2.5 mN m^{-1} higher, which results in a slight 1.5 mN m^{-1} increase in spreading coefficient. This would seem to indicate that the film forming capability of FC-206 is enhanced slightly when mixed with sea water.

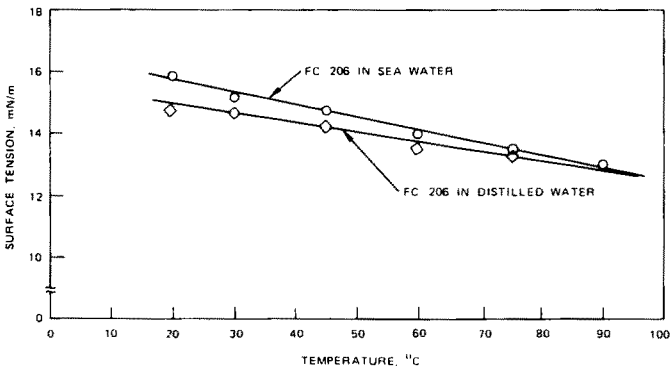


Figure 6. Surface tension as a function of temperature for FC-206 in distilled water and in sea water.

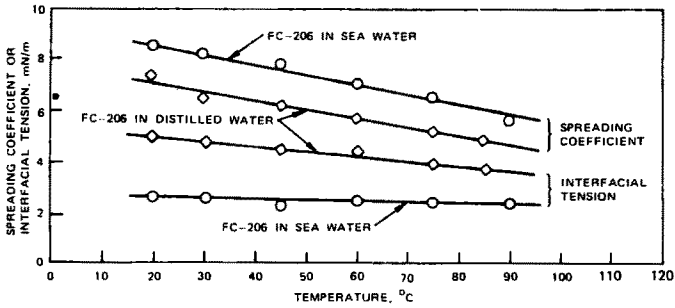


Figure 7. Interfacial tension and spreading coefficient as a function of temperature for JP-5 with FC-206 in distilled water and in sea water.

The Federal Aviation Administration is investigating the use of anti-misting agents as additives to hydrocarbon fuels in order to reduce the hazard of accidental ignition.⁸ Surface tensions of two agents were studied to determine if the additives had a significant effect on AFFF spreading coefficients. As is shown in Figure 8, the addition of 0.3 percent FM-9 to JET-A had very little effect on the surface tension of the fuel. The interfacial tensions could not be measured because the AFFF solution would not wet the capillary tip properly in the presence of the FM-9 solution. However, estimates of interfacial tension from the extremely small drops

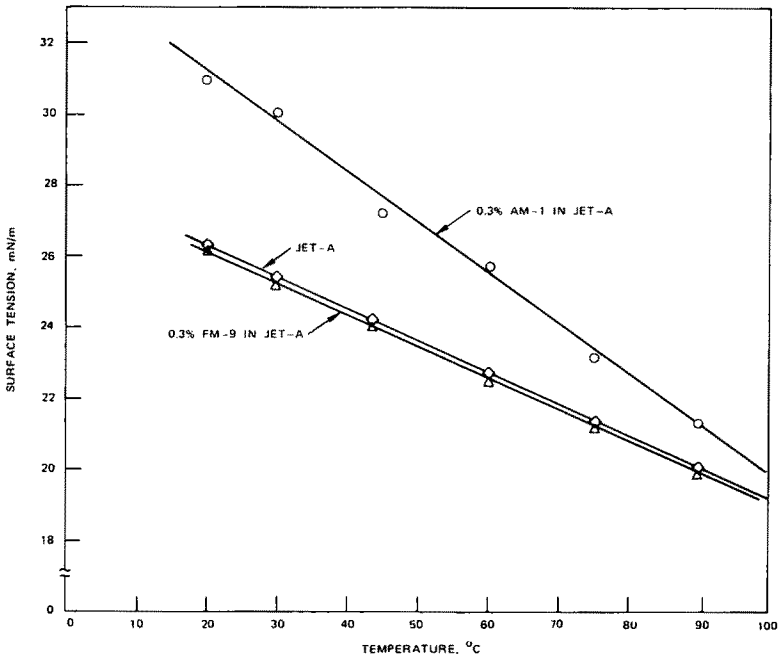


Figure 8. Surface tension as a function of temperature for antimisting agents in JET-A.

that did form were essentially the same as those for the neat JET-A. Thus, little change would be expected in the efficiency of AFFF in extinguishing FM-9 safety fuel fires.

The other additive, AM-1, resulted in a large increase in the surface tensions at lower temperature but only a slight increase at 90° C. However, these results may be in error because the stringy nature of the AM-1 solution leads to drops that do not break cleanly from the tip but leave long strings of solution attached. As the temperature increased, this problem became less severe, as evidenced by the better agreement in surface tensions at the higher temperature. Another means of measuring surface tension needs to be used with this material.

CONCLUSIONS

The following conclusions can be drawn from these measurements:

(a) The surface tensions of the four commercial AFFF agents studied are essentially the same, ranging from 15 mN m⁻¹ to 17 mN m⁻¹ at ambient temperature.

(b) Spreading coefficients for AFFF solutions with some lower boiling hydrocarbon fuels became negative at temperatures below 100° C; this correlates with a marked decrease in the efficiency of AFFF to reduce evaporation rates of these hydrocarbons, and consequently larger quantities of AFFF are required in order to extinguish fires and to prevent re-flashing of these fuels.

(c) Dilution of at least one AFFF concentrate with sea water instead of fresh water will slightly increase its efficiency in forming films on fuels.

(d) Antimisting agents in the fuels will probably not have any noticeable effect on an AFFF agent's fire extinguishing efficiency.

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