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Spreading of Aqueous Solutions of a Mixture of Fluoro- and Hydrocarbon Surfactants on Liquid Hydrocarbon Substrates[1]

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We have studied the spreading kinetics of aqueous solutions of a mixture of hydrocarbon and fluorocarbon surfactants on liquid hydrocarbon substrates. A commercial AFFF (aqueous film-forming foam) agent was used as the mixture of the surfactants. An empirical relation was established between the rate of spreading and experimental parameters involved in the spreading, such as the equilibrium and dynamic surface and interfacial tensions, the spreading coefficient, and the concentration of the spreading solution.
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INTRODUCTION

Although many studies have been reported on the spreading of pure liquids on pure liquids (1–3), studies on the spreading of solutions, especially surfactant solutions (4–8), appear to be scarce despite important industrial applications such as the formulation of fire-fighting foams known as aqueous film-forming foams (in short AFFF). This class of fire-fighting foams, as the name implies, has the capability to spread and form a more or less uniform aqueous duplex film (10–30 μm thick) on low-surface-tension organic liquids such as volatile, flammable hydrocarbons and fuels (9). The formation of a spread aqueous layer on the fuel surface provides an effective fuel vapor barrier to the cooling and blanketing effect of the foam. It is also known that the spontaneously spreading aqueous layer augments the fire-extinguishing efficiency of the foam.

AFFFs generally contain mixtures of hydrocarbon and fluorocarbon surfactants as the major components. The spontaneous spreading property of an AFFF is derived mainly from the high surface activity (low surface tension) of the fluorocarbon surfactants at the solution/air interface (15–20 dyn/cm). This low surface tension, coupled with the low interfacial tension (1–5 dyn/cm) at the solution/substrate interface, allows the AFFF solution, as the result of a positive spreading coefficient, to spread spontaneously on many liquid hydrocarbons and fuels (20–30 dyn/cm). The hydrocarbon surfactants preferentially adsorb at the solution/hydrocarbon substrate interface because of the mutual phobicity between the hydrocarbon and fluorocarbon surfactants, and therefore they are largely responsible for the low interfacial tension.

The practical use of the now well-known immiscibility between the fluorocarbon and hydrocarbon surfactants in AFFF formulations predates, as in many other technologies, a full understanding of the fundamental aspects of the mutual interaction between the two classes of surfactants (10).

The spreading of one liquid on another has generally been investigated from two points of view: spreadability and kinetics. The spreadability refers to the thermodynamic spreading conditions or criteria and can be properly determined based on the Harkins spreading coefficient (11) defined as

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22

$$S_{a/o} = \gamma_o - (\gamma_a + \gamma_{a/o})$$

(spreading of liquid a on o), [1]

where γ_a and γ_o are the surface tension of liquids a and o, respectively, and $\gamma_{a/o}$ is the interfacial tension between the two liquids. Spontaneous spreading will occur when $S_{a/o}$ is positive.

The kinetic aspect of the spreading phenomena can also be studied. It obviously involves liquids that spread spontaneously ($S_{a/o} > 0$). In the cases of pure liquids the areal rate of spreading has been shown to be proportional to the spreading coefficients (3). When the spreading liquid (a in Eq. [1]) is a surfactant solution, however, the spreading rate is expected to be a function of time-dependent surface and interfacial tensions and also of the surfactant concentration. The concentration dependence obviously stems from the fact that the spreading front is continuously depleted of surfactant molecules due to their adsorption at the expanding interfaces and therefore should be replenished with those from the bulk phase until spontaneous spreading ceases. The time dependence of the spreading coefficient due to the dynamic response of the surfactant molecules to the expanding interfaces can, in theory, be expressed as

$$S_{a/o}(t) = \gamma_o(t) - [\gamma_a(t) + \gamma_{a/o}(t)]. \quad [2]$$

The same time dependence can also be used to describe the effects of mutual solubility between the spreading liquid and the substrate. In fact, different stages of spreading such as "initial" and "final" spreading and their corresponding spreading coefficients have been conveniently defined and used (11).

Moran *et al.* (4a) and Leonard and Burnett (4b) in their studies on the spreading of surfactant solutions on hydrocarbon liquids investigated the relationships between the film formation and suppression of fuel evaporation from the point of view of spreadability. Woodman *et al.* (5) investigated the spreading properties of some commercial AFFFs, also based strictly on the spreadability. Nicolson and Artman (6) appear to be the first to investigate semiquantitatively the kinetic aspects of the spreading of commercial and experimental AFFFs on various hydrocarbon fuels. Recently, Zhao and Zhu (7) made a study on the spreadabilities of various mixtures of hydrocarbon and fluorocarbon surfactants on kerosene and heptane. In their study only relations between the spreadability and the presence of film formation were investigated.

More recently, Joos and Van Hunsel (8) studied the spreading rates of aqueous solutions of FC-129, a commercial fluorocarbon surfactant, and a mixture of perfluoroammonium caprylate (PFAC) and cetyltrimethylammonium bromide (CTAB), respectively, on CCl_4 and benzene. They established the relationship between the spreading rate and the spreading coefficient. They, however, did not investigate the effect of surfactant concentration.

In this report we have studied the spreading rates of aqueous solutions of a commercial AFFF on liquid hydrocarbons with varying surface tensions in an attempt to determine the quantitative relations between the rate of spreading and the experimental parameters involved in the spreading, such as the spreading coefficient, dynamic surface tension, and concentration. Unlike Joos and Van Hunsel's experiments where a single drop (undefined quantity) of the spreading liquid was placed on the substrate and the "linear" spreading was followed, our experiments involved the measurement of the areal expansion of the spreading film under the conditions of continuous supply of spreading liquid onto the surface of the substrate.

EXPERIMENTAL

Materials

The mixture of fluoro- and hydrocarbon surfactants used in this study was FC-206A, a commercial AFFF concentrate also known as "light water" manufactured by 3M. Solutions

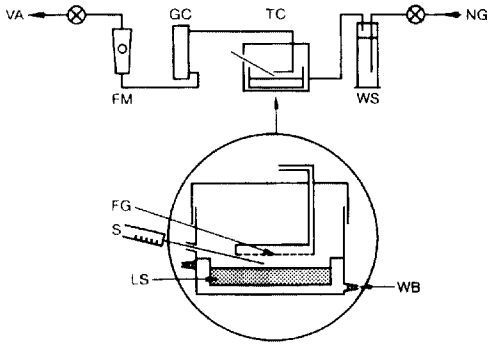

FIG. 1. Schematic diagram of the apparatus: VA, vacuum; FM, flow meter; GC, IR gas cell; TC, test cell; WS, water saturator; NG, nitrogen gas; FS, fritted glass; S, syringe; LS, liquid substrate; WB, water bath.

of this concentrate in artificial sea water[2] were used in the spreading experiments. As substrates, mixtures of *n*-heptane and cyclohexane in various volume proportions were used to generate a range of surface tensions (24.5 to 19.8 dyn/cm at 25°C). Mixtures of *n*-heptane and *n*-hexane were also used to extend further the surface tension range of the substrate (19.8 to 18.6 dyn/cm).

Methods

Determination of spreading rate. The apparatus schematically shown in Fig. 1 was used to determine the spreading speed. It consists mainly of an IR spectrophotometer equipped with a flow-through gas cell (GC) and a test cell (TC). The experimental technique is based on the continuous monitoring by IR of the vapor concentration of the hydrocarbon substrate. Since the vapor concentration in the gas cell is proportional to the area of the aqueous film-free surface of the substrate, the absorbance read directly from the recorder chart paper can be used with a proper calibration to determine the areal spreading rate. A detailed description of the apparatus has been given elsewhere (6).

Briefly the experimental procedure was as follows. The recorder of the IR spectrophotometer was set on a time base to read the absorbance at the wavelength corresponding to the C–H stretch (~2950 cm^{-1}) of the substrate liquid.

The IR was adjusted to read zero absorbance with an empty test cell (6 cm diameter; 27.5 cm^2 open area). The test cell was then filled with 15 ml of substrate and the resulting absorbance was arbitrarily adjusted to read an absorbance of 1.0. This absorbance value corresponds to a surface area of the aqueous film-free substrate.

The test spreading solution was then applied dropwise through a needle (#22G) to the surface of the substrate. The needle was positioned in the center of the test cell in such a way that the gap between the tip of the needle and the surface just allowed a complete droplet to form. At the moment the first drop of the spreading solution touched and started to spread the time-based recording on the IR was turned on. The solution was applied continuously at a flow rate of 0.17 ml/min, which was controlled by a syringe pump, until the surface of the substrate was completely covered with the spread film. This complete coverage was evidenced by the reduction of the absorbance to zero. Figure 2 shows some typical scans.

To locate on the absorbance scale the 50% coverage point which was used throughout the experiments to define the average spreading speed, a calibration curve was constructed by measuring the absorbance as a function of the film-covered area of the substrate. Glass rings of various diameters with a height slightly greater than the depth of the substrate (cyclohexane) were used to create several film-covered areas: A glass ring was centered in the test cell. The surface of the cyclohexane inside the ring was then completely covered with the spread film thereby creating a fractional surface coverage, and the corresponding absor-

[2] The artificial sea water was prepared using "Sea Salt" (ASTM D1141-52) manufactured by Lake Products Comp., Ballwin, MO.

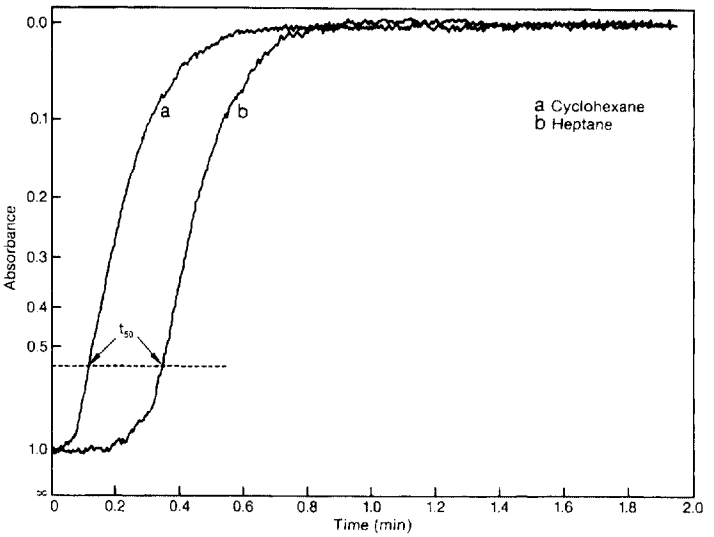

FIG. 2. Typical determinations of the spreading time for 50% coverage (t_{50}) on two substrates.

bance was read. The calibration curve thus obtained is shown in Fig. 3. The absorbance value of 0.56 was used throughout the experiments to determine the 50% coverage. The choice of the 50% coverage was made based on our preliminary observations that up to this coverage the spreading was reasonably radial on most of the substrates.

In this study the spreading speed under the condition of constant application of the spreading liquid is defined as

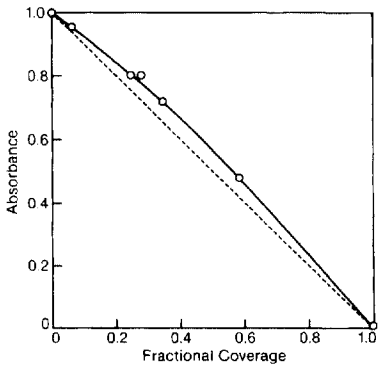

FIG. 3. Calibration curve for the determination of the adsorbance value corresponding to 50% coverage.

$$\bar{V}_A \cdot t_{50} = A/2 \text{ or } \bar{V}_A = 13.75/t_{50}\,[\text{cm}^2/\text{s}]. \quad [3]$$

Here $\bar{V}_A$ is the average areal spreading speed, t_{50} is the time required for the 50% surface coverage, and A is the open area of the substrate surface in the test cell (27.5 cm^2).

The determination of the time for the 50% surface coverage (t_{50}) therefore constitutes the major portion of the experiments of this study.

Measurement of equilibrium and dynamic surface tensions. The surface tensions of the spreading solutions and the substrates were all measured using the Wilhelmy plate technique. The interfacial tensions between the spreading solutions and the substrates were measured by the ring method. The presence of the unavoidable spread films on the surface of the substrate made the Wilhelmy plate method unsuitable for the interfacial tension measurement.

Dynamic surface tensions of the spreading solutions were determined using the dynamic drop weight method developed in our laboratory (12).

All the measurements including those of the spreading speed were performed at 25°C.

25

RESULTS AND DISCUSSION

The experimental results of the measurement of the spreading speed as a function of substrate surface tension (γ_o) are shown in Fig. 4.

The choice of the concentrations of the AFFF concentrate in artificial sea water was not entirely arbitrary, but based on the general usage levels for AFFF concentrates (3 and 6% (v/v)).

The values of the spreading speed presented in Fig. 4 are averages of at least three measurements. The vertical bars on the data points indicate the standard deviation of the mean value.

The spreading speed appears to be a linear function of the substrate surface tension, γ_o. Relatively large experimental uncertainties and scatter of the data points are observed on the 6% solution. These are believed to be caused by the marked irregularities in the spreading pattern of the films of this highly concentrated solution on high-surface-tension substrates. The spreading pattern of these fast-spreading (high spreading coefficients) films was found to be considerably less radial than those of the slow-spreading cases. Some parts of the spreading film showed "fingering." It is also observed that the spreading speed of the 6% solution of the high-surface-tension substrates ($\gamma_o > 23$ dyn/cm) deviates from the straight line and appears to reach a plateau; thus, the spreading speed becomes practically independent of the surface tension of the substrates. The cause of this limiting spreading behavior will be further examined later in connection with the discussion of the dynamic-surface-tension aspect of the spreading phenomena (Fig. 5b).

All three spreading speed vs γ_o curves except the plateau region on the 6% solution can be represented as straight lines in the following form:

$$\bar{V}_A = k_1\gamma_o + k_2 = k_1(\gamma_o + k_2/k_1). \quad [4]$$

Since no spreading occurs ($\bar{V}_A = 0$) when $S_{a/o}$ ($t = \infty$) = 0 it can be shown from Eqs. [2] and [4], and on the assumption that the surface tension of the substrate is independent of time due to the lack of mutual solubility in the time frame of this spreading experiment, that

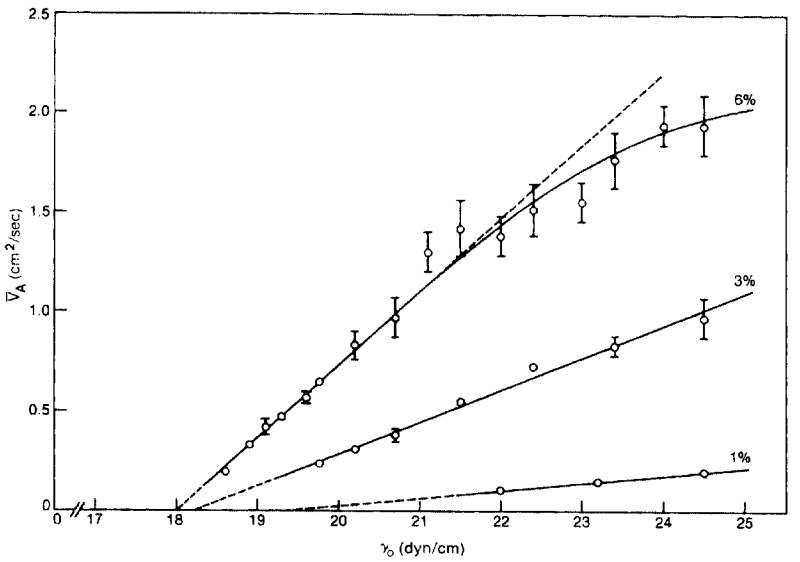

FIG. 4. Average spreading speed as a function of the surface tension of the substrate.

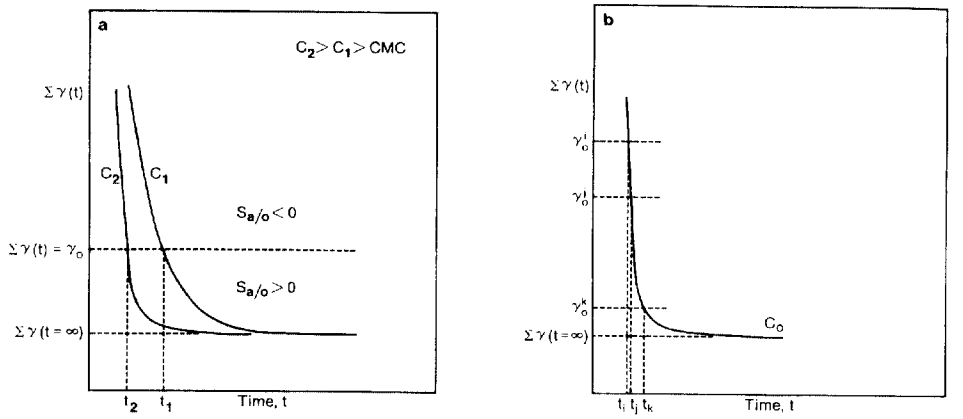

FIG. 5a. Sum of the surface and interfacial tensions of a surfactant system at two concentrations above the CMC as a function of time; an illustration.

FIG. 5b. Sum of the surface and interfacial tensions of a rapidly equilibrating surfactant solution as a function of time; an illustration.

$$\bar{V}_A = k_1\{\gamma_o - [\gamma_a(t=\infty) + \gamma_{a/o}(t=\infty)]\}$$
$$= k_1[\gamma_o - \sum\gamma(t=\infty)]$$
$$= k_1 S_{a/o}(t=\infty). \quad [5]$$

The explicit expression of the time dependence of the tensions ($t = \infty$) in the above equations is intended to indicate not the mutual solubility effects but the dynamic surface and interfacial aspects. Therefore the tensions at infinite time should be taken as equilibrium or static values. The results of linear regression analyses of the spreading speed data are summarized in Table I. Also included in Table I are the measured surface (γ_a) and the interfacial tensions ($\gamma_{a/o}$) and the sum ($\sum\gamma$ ($t = \infty$)) of the two values.

TABLE I

Results of Linear Regression Analyses of $\bar{V}_A$ vs γ_o Curves (Fig. 4)

C_o (%, v/v)	k_1	k_2	$\gamma_o(\bar{V}_A = 0)$ (dyn/cm)	$\Sigma\gamma$ ($t = \infty$)[a] (dyn/cm)
1	0.0392	−0.756	19.3	18.7 (16.0 + 2.7)
3	0.1600	−2.914	18.2	18.5 (15.9 + 2.6)
6	0.3709	−6.687	18.0	18.3 (15.7 + 2.6)

[a] Sum of the measured equilibrium surface (first value in parentheses) and interfacial tension.

Equation [5] shows that the average spreading speed is directly proportional to the equilibrium ($t = \infty$) spreading coefficient. However, it also contains a parameter, k_1, which is evidently a function of the surfactant concentration, thereby manifesting the dependence of the spreading phenomena on the dynamic response of the surfactant molecules to the expanding interfaces.

At this point, it is instructive to examine how the dynamic surface behavior of the surfactant molecules comes into play with the spreading phenomena. Figure 5a shows as an illustration the sums of the time-dependent (dynamic) surface ($\gamma_a(t)$) and interfacial tensions ($\gamma_{a/o}(t)$) of two solutions of a given surfactant plotted as a function of time. Two concentrations, C_1 and C_2, above the critical micelle concentration are compared. When the sum of the two tensions of a surfactant solution placed on the surface of a substrate reaches the surface tension of the substrate (γ_o) the spreading coefficient becomes positive, i.e., $S_{a/o} = \gamma_o - \Sigma\gamma(t) > 0$, and spontaneous spreading takes place. The time required for the attainment of this spontaneous spreading

condition, therefore, becomes the rate-controlling factor for spreading. Once this condition is attained, spontaneous spreading will continue until the replenishment of the surfactant molecules from the bulk solution to the expanding interfaces becomes insufficient to maintain the positive spreading coefficient.

In the example given in Fig. 5a the solution C_2 is expected to spread faster than $C_1(t_2 < t_1)$ despite the fact that both solutions have the same equilibrium spreading coefficients. In this respect, the important parameter that determines the relative spreading speed on a given substrate of different surfactant solutions appears to be their rate of surface and interfacial tension reduction (RSTR). In later analyses of our dynamic-surface-tension data, quantification of the RSTR, and their empirical relation with the spreading rate of the test solutions will be established.

Figure 5b illustrates the dynamic-surface- and interfacial-tension behavior of a solution exhibiting a high RSTR; at short times the sum of the tensions, $\sum\gamma(t)$, drops precipitously. This figure can be used to describe the relative spreading rates of the solution on substrates that have varying surface tensions ($\gamma_o^k \cdots \gamma_o^i$). As the surface tension of the substrate increases, the time necessary to attain the spontaneous spreading conditions gets shorter ($t_k \cdots t_i$). As a consequence one would expect the spreading rate to increase with the surface tension of the substrate, as already shown in Fig. 4. The increase in the spreading rate will, however, become progressively smaller when the substrate surface tension gets higher beyond the value that reaches the precipitously descending portion of the curve, such as γ_o^i in Fig. 5b. On such substrates the spreading rate will become practically independent of the substrate surface tension because the difference in the time required to attain the spontaneously spreading conditions gets negligibly small compared with the time scale of spreading.

In this respect it is interesting to observe that a surfactant solution that equilibrates rapidly would nearly be expected to spread on a high-surface-tension substrate as a pure liquid because the rate of spreading is not controlled by the time-dependent spreading coefficient.

The previously mentioned limiting spreading behavior observed of the 6% solution (Fig. 4) can now be readily understood on the basis of the above explanation.

Both figures 5a and 5b essentially present parametrically the same relationship between the tensions and time as that in Fig. 3 because the spreading speed ($\bar{V}_A$) is inversely related to time (t_{50}) (Eq. [3]). They also can be used to compare the spreading rates of two different surfactants at a given concentration.

Table I shows that the surface tensions of the substrates on which $S_{a/o} = 0$ ($\bar{V}_A = 0$) predicted from the spreading experiments agree well with the measured values of the sum of the equilibrium surface and interfacial tensions. The interfacial tensions of both 6 and 3%, and 1% solution were measured against *n*-hexane and *n*-heptane, respectively. It should be noted that FC-206A as a surfactant mixture has the CMC of 0.1% (v/v) in the artificial sea water. The CMC was determined from the γ vs ln C curve (not shown). Therefore all three solutions used for the spreading study are above the CMC and show virtually the same equilibrium surface and interfacial tensions.

Since the parameter k_1 in Eq. [5] represents the concentration dependence of the spreading speed it is expected to be related to the dynamic surface and interfacial tensions as illustrated in Figs. 5a and 5b. Consequently, the time dependence of the spreading coefficient (Eq. [2]) may be replaced by the concentration dependence of the surface and interfacial tensions that constitute the spreading coefficient.

Figure 6 presents the results of the dynamic-surface-tension measurements. Because of the lack of a suitable method for the dynamic-interfacial-tension measurement, we only investigated the dynamic-surface-tension aspect of the spreading phenomena. It is assumed that either the adsorption kinetics at the solution/substrate interface is similar to that at the so-

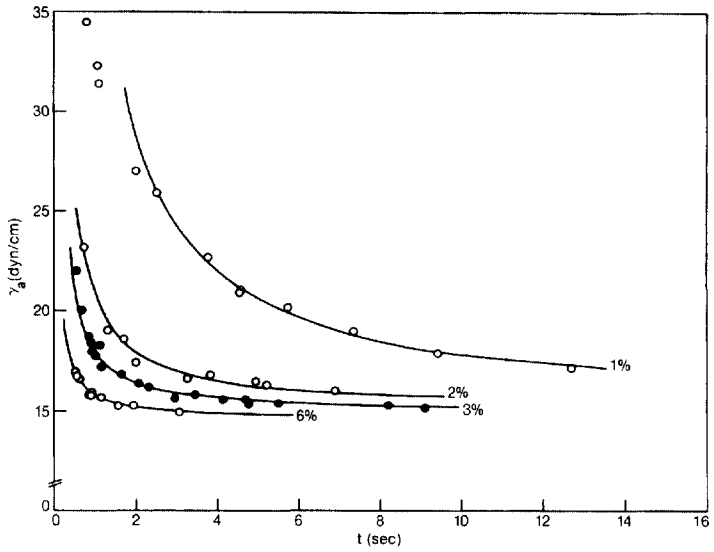

FIG. 6. Dynamic surface tensions of the test solutions: the curves are the best fits obtained for the linear relation between γ_a and t^{-1} (shown in Fig. 7).

lution/air interface, or that the rate of the preferential adsorption of hydrocarbon surfactants at the solution/substrate interface is higher than the adsorption rate of fluorocarbon surfactants at the solution/air interface. In other words, the interfacial tension equilibration is practically independent of time in the time frame of dynamic-drop-weight measurement (>0.5 s) and consequently contributes a constant value to $\Sigma\gamma(t)$.

The dynamic-surface-tension data presented in Fig. 6 appear to conform, as shown in Fig. 7, to what is known as the long-time approximation of the Ward and Todai equation for micellar solutions according to which the following can be shown (13),

$$\gamma_a(t) = \gamma_a(t = \infty) + k_3 t^{-1}, \qquad [6]$$

where $k_3 = RT(\Gamma^\infty)^2/(Dk)^{1/2}C_o$. Here Γ^∞ is the saturation adsorption, D is the apparent diffusion coefficient, and k is the rate constant for demicellization.

According to Eq. [6] the $\gamma_a(t)$ vs t^{-1} plot would show a straight line with the inversely concentration-dependent slope, k_3. The slopes of the straight lines in Fig. 7 can best be fitted through linear regression analyses to a relation, $k_3 = (k_4C_o + k_5)^{-1}$, with $k_4 = 0.1583$ and $k_5 = -0.1327$, instead of $k_3 = k_6C_o$ as required by Eq. [6]. However, when $k_4C_o \gg k_5$, in other words, when $\Delta\gamma_a = \gamma_a(t) - \gamma_a(t = \infty)$ is small for which case Eq. [6] is theoretically valid, both expressions become identical. As indicated in the discussion of Fig. 5 the values of k_3 in Eq. [6] are a quantitative measure of the rate of surface tension reduction (RSTR): a lower k_3 represent a higher RSTR, and hence a faster spreading.

The quantitative relationship between the RSTR and the rate of spreading represented by k_1 is shown in Fig. 8. Here the concentration dependence of k_1 is $k_1 = 0.0667C_o - 0.0322$.

It is interesting to compare our experimental results with those of Joos and Van Hunsel (8). They have recently shown that the spreading rate of an immiscible liquid on another liquid can be expressed theoretically as

$$V_1 = dl/dt = KS^{1/2}t^{-1/4}, \qquad [7]$$

where l is the distance traveled by the spreading liquid, S is the spreading coefficient, and K is

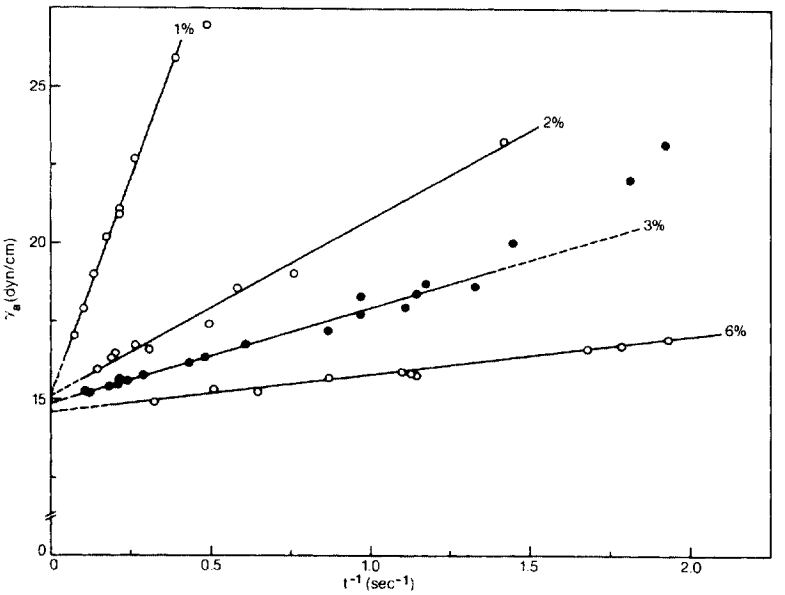

FIG. 7. Dynamic surface tensions (same as in Fig. 6) plotted as a function of reciprocal of time.

a constant containing the density and viscosity of the substrate. In terms of the areal spreading this expression becomes

$$V_A = dA/dt = K'St^{1/2}. \quad [8]$$

The same rate expression, except for the numerical constant, was also derived by Cochran and Scott in their study of the spreading of oil slicks on water (14).

Joos and Van Hunsel demonstrated that the spreading of a FC-129 solution on CCl_4 was well predicted by Eq. [7], whereas a mixture of PFAC and CTAB on benzene was not. Considering the fact that Eq. [7] is strictly valid only for pure liquids it is surprising that the equation was also proved to be valid for the former surfactant system. For the spreading of the mixed system, however, they obtained an empirical expression showing that the exponent of time t is not $-\frac{1}{4}$ as required by theory, but rather close to $-\frac{1}{2}$ (actual value -0.425). They correctly attributed the disagreement between theory and experiment to the fact that the spreading coefficient depends on time. If one uses the empirical exponent $-\frac{1}{2}$ in Eq. [7] the time dependency of the areal spreading rate V_A (Eq. [8]) would vanish and the expression for V_A would become identical to Eq. [5].

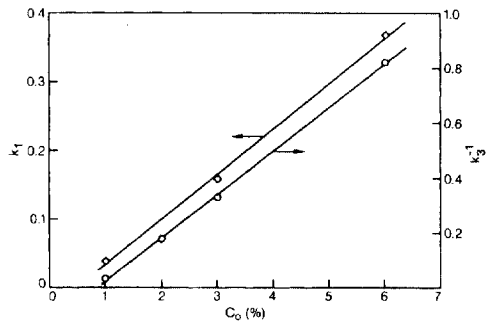

FIG. 8. Concentration dependencies of the spreading speed (k_1, Eq. [6]) and dynamic surface tension (k_3, Eq. [7]) of the test solutions.

The good agreement between their experiment and the theory, Eq. [7], in the case of FC-129/CCl_4 appears to indicate that this fluorinated surfactant at a relatively high concentration (0.5% actives) may indeed have a high rate of surface and interfacial tension reduction and that it behaves as a pure, low-surface-tension liquid on a high-surface-ten-

sion substrate, CCl_4, as already discussed (Fig. 5b).

Equation [5] which describes our experimental concentration dependence arises, as demonstrated in this study, from the dynamic adsorption behavior of the surfactant molecules at the interfaces and therefore can be properly understood in terms of the dynamic surface and interfacial tension of the spreading solution.

It is also interesting to note that despite vastly different experimental conditions used in Joos and Van Hunsel's study and in our investigation the same dependence of the areal spreading rate on the spreading coefficient was empirically observed. The fact that both results can be described by the same equation may indicate that the initial inertia that exists under our experimental condition of constant application of the spreading solution was small compared to the major driving force of spreading, the spreading coefficient.

It should be noted in summary that the conventional spreading coefficient based on the equilibrium surface and interfacial tension (Eq. [1]) is not sufficiently useful to predict the relative spreading speed of surfactant solutions on a given substrate. In fact, erroneous predictions can be made based solely on the values of the equilibrium spreading coefficient as already illustrated in Fig. 5a. However, the spreading rate of a given surfactant system on various substrates can be predicted, and it is a linear function of the equilibrium spreading coefficient as shown in this study.

ACKNOWLEDGMENT

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REFERENCES

1. Davies, J. T., and Rideal, E. K., "Interfacial Phenomena," p. 172. Academic press, New York, 1963.
2. Pomerantz, P., Clinton, W. C., and Zisman, W. A., *J. Colloid Interface Sci.* **24,** 16 (1967).
3. Joos, P., and Pintens, J., *J. Colloid Interface Sci.* **60,** 507 (1977), and references therein.
4. (a) Moran, H. E., Burnett, J. C., and Leonard, J. T., NRL Report 7247, Naval Research Laboratory, Washington, DC, 1971, (b) Leonard, J. T., and Burnett, J. C., NRL Report 7842, Naval Research Laboratory, Washington, DC, 1974.
5. Woodman, A. L., Richter, H. P., Adicoff, A., and Gordon, A. S., *Fire Technol.* **14,** 265 (1978).
6. Nicolson, P. C., and Artman, D. D., *Fire Technol.* **13,** 13, 247 (1977).
7. Zhao, Guo-Xi, and Zhu, Bu-Yao, *Colloid Polym. Sci.* **261,** 89 (1983).
8. Joos, P., and Van Hunsel, J., *J. Colloid Interface Sci.* **106,** 161 (1985).
9. Tuve, R. L., "Principle of Fire Protection Chemistry," National Fire Protection Association, 1976. p. 168.
10. Shinoda, K., and Nomura, T., *J. Phys. Chem.* **84,** 365 (1980) and references therein; Patent literature abounds with AFFF formulations. See, for example, Falk, R. A., US Patent 4,090,967 (1978).
11. Harkins, W. D., and Feldman, A., *J. Amer. Chem. Soc.* **44,** 2665 (1922).
12. (a) Jho, C., and Burke, R., *J. Colloid Interface Sci.* **95,** 61 (1983). (b) Jho, C., and Carreras, M., *J. Colloid Interface Sci.* **99,** 543 (1984).
13. Rillaerts, E., and Joos, P., *J. Phys. Chem.* **86,** 3471 (1982).
14. Cochran, R. A., and Scott, P. R., *J. Pet. Technol.* **781** (July, 1971).