

# Effect of Adsorbed Monomolecular Films on the Evaporation of Volatile Organic Liquids

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## CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	2
Soluble Surfactants	2
Insoluble Surfactant Films	3
Compounds Used	4
EXPERIMENTAL RESULTS	5
Effect of Soluble Surfactants on Rates of Evaporation	5
Effect of Insoluble Adsorbed Films on Rates of Evaporation	9
Relation to Light Water Foams for Extinguishing Hydrocarbon Fuel Fires	11
DISCUSSION	11
REFERENCES	13

## ABSTRACT

An investigation was made of the effect of adsorbed surface-active films on the rate of evaporation of volatile organic liquids. A series of partially fluorinated compounds were studied either as monolayers adsorbed from solution or as insoluble films spread at the liquid/vapor interface. In no instance was the rate of evaporation significantly reduced by the presence of a monomolecular film. Insoluble multimolecular films of polydimethylsiloxanes, however, were found to reduce effectively the rate of evaporation, provided the film thickness was sufficient to decrease the rate of diffusion of the solvent molecules through the film to a value below their rate of diffusion through the saturated, nonturbulent vapor layer overlying the surface. In addition to polydimethylsiloxane polymolecular layers, thin layers of water, containing suitable fluorocarbon spreading agents, were also found to reduce the rate of evaporation of certain volatile organic liquids. These aqueous films are similar to the thin layers of interlamellar water present in aqueous foams used to extinguish gasoline fires, such as the fluorocarbon-containing Light Water foams.

## PROBLEM STATUS

This is an interim report; work on the problem is continuing.

## AUTHORIZATION

NRL Problem C02-10  
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## EFFECT OF ADSORBED MONOMOLECULAR FILMS ON THE EVAPORATION OF VOLATILE ORGANIC LIQUIDS

### INTRODUCTION

The ability of certain insoluble, condensed, monomolecular films to reduce significantly the rate of evaporation of water is well known, and the technique has been successfully applied to problems of water conservation (1,2). By analogy, it may also be possible to retard the rate of evaporation of volatile organic liquids using adsorbed monomolecular films, provided the surface-active compounds meet certain structural requirements. Even with respect to water evaporation, only a limited number of compounds form effective barrier films. The insoluble surface-active compounds that have been observed to retard the evaporation of water all contain n-alkyl chains at least 16 carbon atoms in length and can orient themselves approximately normal to the surface, with the closest possible adlineation between hydrocarbon chains. All other classes of compounds investigated failed to reduce the net evaporation rate of water, even though they formed continuous monomolecular films at the interface.

Langmuir (3) proposed that a layer of relatively quiet, unstirred air will be present above an interface forming a diffusion barrier to the evaporation of a volatile liquid. The rate of transport of molecules from a clean liquid surface to the vapor phase is usually so rapid (4) that the quiet air layer quickly becomes saturated with vapor. The net evaporative loss of solvent will then be determined by the rate of diffusion of the vapor molecules through the saturated, nonturbulent air layer and not by the rate of exchange across the interface. A monolayer will therefore have no apparent effect on evaporation until it can reduce the rate of transport of molecules across the interface to a value less than the rate of diffusion through the quiet air layer. In films that meet this requirement and do form effective barriers to the evaporation of water, the spaces between the long, closely packed hydrocarbon chains must be small compared with the size of the water molecules. This close packing plus the low solubility of water in hydrocarbons present an effective barrier to the movement of water from the liquid to the vapor phase.

To retard the evaporation of a volatile organic liquid, an adsorbed monolayer would likewise have to be closely packed at the interface, with the interstitial spaces being small compared with the size of the molecules of the liquid. A number of fluorocarbon (5-7) and silicone (7-13) derivatives are known to form adsorbed films at organic liquid/air interfaces either as insoluble monolayers or as monolayers adsorbed from solution; none, however, have an orientation and packing similar to the effective-barrier monolayers on water. Fortunately, most volatile organic compounds have molecules significantly larger than water, thus the orientation and packing requirements may be somewhat less stringent for evaporation barrier films on organic liquids.

An earlier study by Blake, Ahlbrecht, and Bryce (14) claimed that several slightly soluble, surface-active fluorinated compounds had reduced the evaporation rate of gasoline as well as of a number of other volatile solvents. Their evaporation studies were carried out in open beakers in a hood where control of evaporation is difficult. The present study was undertaken to establish if adsorbed monomolecular films can have a significant effect on the evaporation rate of various types of volatile organic liquids and, if possible, to determine the orientation and packing that adsorbed molecules must have if their monolayers are to be effective evaporation retardants.

## EXPERIMENTAL PROCEDURE

## Soluble Surfactants

The experimental procedure depended on the use of thermal conductivity detectors to measure the relative rates of evaporation. The apparatus, shown schematically in Fig. 1, was designed to measure differences in the rate of evaporation of a pure solvent and the same solvent containing a slightly soluble surface-active solute. A Carle Model 100 microdetector system in connection with a Varian G-14A recorder was used as the thermal conductivity measuring unit. The thermal conductivity detector consisted of a pair of matched thermistors, each incorporated into the system as one arm of a Wheatstone bridge circuit. Two identical evaporation cells, machined into a brass block, accommodated circular Pyrex sample dishes. Pure solvent, or solvent plus solute, could be added to the dishes as desired by inserting a gastight Hamilton syringe with a 90-degree needle tip through a standard silicone rubber septum (Fig. 2). Helium was used as the carrier gas. Before entering the evaporation cells, the helium gas stream was split, half entering each cell over the center to insure a uniform distribution of gas across the surface. As the helium passed over the liquid surface, it picked up the solvent vapor, carried it to the thermistor detectors and then to flowmeters.

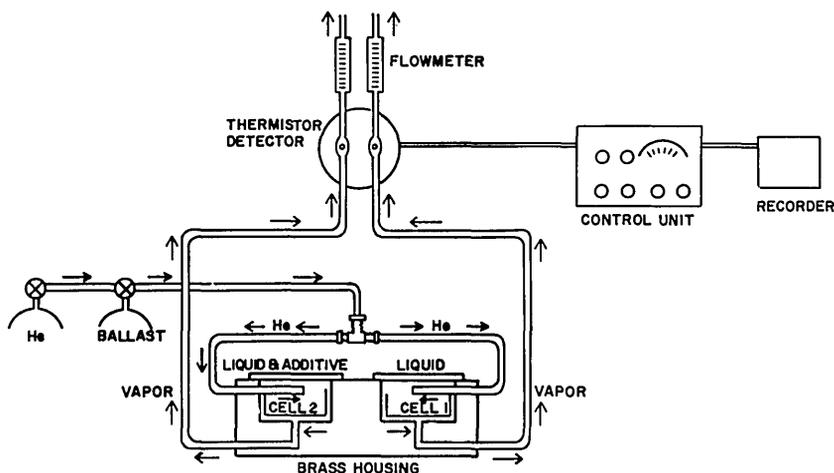


Fig. 1 - Dual-cell thermal conductivity apparatus for measuring relative rates of evaporation

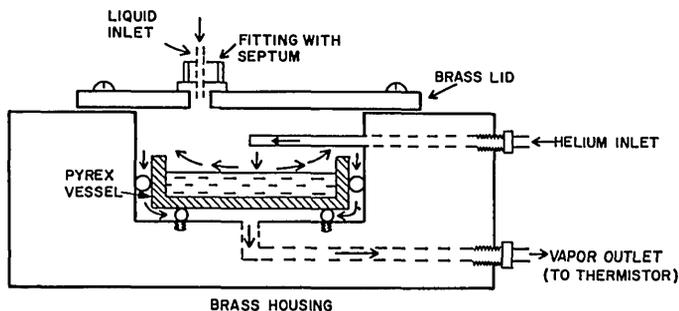


Fig. 2 - Evaporation cell in detail

When pure solvent was placed in both cells, each detector gave approximately the same signal; the small potential difference between them was registered on the recorder and was used as the zero baseline for the evaporation reduction studies. Any reduction in the evaporation rate in one cell with respect to the other would cause a change in the recorded potential; the magnitude of the potential change could be related quantitatively to the change in rate of evaporation by measuring the volume or weight loss of solvent in the dish with time.

The 3.2-cm-diameter Pyrex sample dishes were first placed in the cells, and the covers bolted on, using Buna-N O-rings to insure a gastight fit. The helium stream was then adjusted to the desired flow rate (either 156 or 236 cc/min, depending on the solvent used), and the two thermistors were balanced in pure helium, using a bridge current of 18 mA. Solvent was then added to one sample dish, and solvent plus solute was added to the other. Unless otherwise stated, 1.0 ml of liquid was introduced into each cell. Since the two evaporation cells were identical, it was immaterial which contained the additive solution; only the sign of the resulting signal would be changed. All measurements were made at  $23.0 \pm 1.0^\circ\text{C}$ . Best results were obtained when the thermistor detector block was carefully insulated to insure a constant  $60^\circ\text{C}$  temperature throughout a run.

In addition to measuring differences in the rate of evaporation, the surface tension of each substrate liquid containing a soluble additive was determined. Surface tensions of these solutions were determined with a Cenco-duNuoy interfacial tensiometer using the correction tables of Harkins and Jordan (15).

### Insoluble Surfactant Films

Those surface-active compounds which showed measurable solubility in the various solvents could easily be studied by the technique described above, the surface concentration of solute being estimated from surface tension measurements. Several prospective barrier compounds, however, were either insoluble or had sufficiently low solubility in the solvents studied to give relatively persistent films when spread at the organic liquid/air interfaces. Since it is of great interest to know the spreading behavior as well as the solubility of the various surfactants, a simple spreading test was devised to determine which of these additives spread on the various organic liquids, which ones formed stable insoluble films, and also to what extent they reduced the surface tensions of the liquid substrates.

The volatile solvent to be investigated was placed in a shallow Teflon dish, and a clean, roughened platinum Wilhelmy plate, which was 3.95 cm long and 0.01 cm thick, was arranged so that it just touched the liquid surface. The pull that the liquid exerted on the plate, and thus its surface tension, was measured with a Statham UC 2 strain gage in conjunction with a Statham UR 5 transducer readout and a Varian G-11A recorder. Changes in surface tension could be measured to  $\pm 0.02$  dyne/cm. Spreading compounds that formed stable, insoluble, surface-active films caused significant decreases in the substrate surface tension when spread on that surface, with little subsequent change in surface tension with time. If the spread film was soluble, the surface tension of the substrate would increase with time as the surfactant dissolved. From these experiments it was also possible to determine which surfactant compounds spread as uniform multi-molecular layers and which spread as monomolecular films in equilibrium with floating lenses of bulk material. This could be done by observing whether the spreading liquid produced interference colors, indicative of thick films, or whether that liquid contracted into small lenses at the interface in equilibrium with a spread monolayer. The initial spreading could be detected using Teflon powder as a floating indicator on the substrate liquid.

To study more conveniently the effect of insoluble films on evaporation rates, a second experimental apparatus, similar to the evaporometer probe described by Walker (16), was constructed as shown in Fig. 3. The probe consisted essentially of three concentric cylinders, the largest being 5-1/2 in. long and having an outer diameter of 1 in. The probe was closed at the bottom except for a 1-mm annular space between the two outer cylinders and a 1-mm I.D. center tube. Connectors at the top of the tube allowed for the movement of helium to and from the probe. The incoming helium flowed down the annular space near the edge of the probe and out over the surface. About 90% of the helium gas flowed away from the probe, preventing air from entering the system. The remaining helium, at a flow rate of 200 cc/min, was drawn across the surface and up through the central tube. This helium stream was then introduced into a thermal conductivity cell to determine the amount of vapor picked up from the surface. Pure helium, also at a flow rate of 200 cc/min, was introduced into the matching thermal conductivity cell. By comparing the potential signals from the two detectors it was possible to measure changes in the rates of evaporation. This evaporometer probe had the advantage that it was portable and could be lowered over any liquid surface, such as a Langmuir film balance.

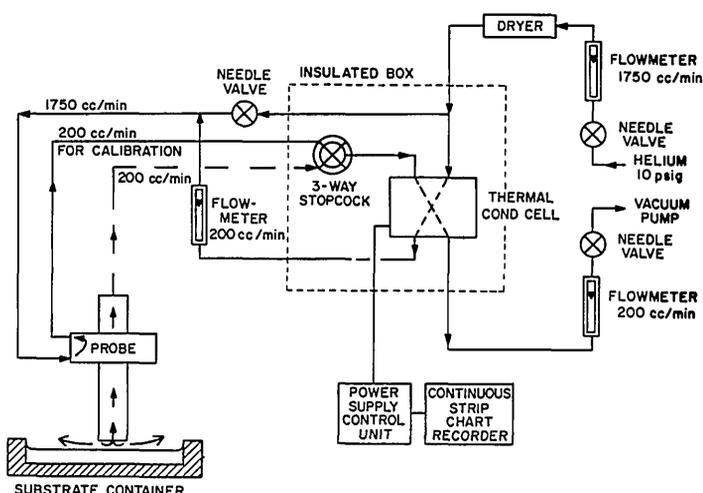


Fig. 3 - Evaporometer probe apparatus as described by Walker (16)

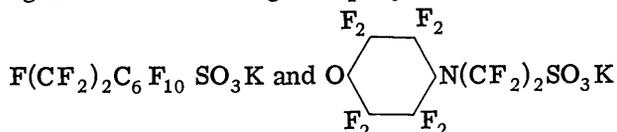
The apparatus contained a Gow-Mac thermal conductivity cell 9680 with a matched pair of 8,000-ohm (at 25°C) thermistors and a model 40-05D power supply and control unit. The control unit was connected to a G-11A stripchart recorder. The bridge current was usually between 5.5 and 6.5 mA, but it and the sensitivity setting were changed with each organic liquid substrate studied, being adjusted in each case to give a full-scale, or a 100%, reading for evaporation from a clean surface. Reductions in evaporation could then be read directly from the chart paper as percent decrease. The total helium flow rate was normally maintained at 1750 cc/min with 200 cc/min being diverted through the thermal conductivity detectors. The thermistor detector block was carefully maintained at 60°C ± 0.1°C. Other details of the apparatus and of the experimental technique are essentially as described by Walker (16).

#### Compounds Used

The volatile organic liquids used in this investigation were pure toluene (bp 110.6°C), 2,2,4-trimethylpentane (bp 99.3°C), and nitromethane (bp 101°C). These liquids were

obtained from the Fisher Scientific Co., Phillips Petroleum Co., and Eastman Organic Chemicals Co., respectively, and their boiling points are in excellent agreement with the best literature values. Apart from volatility these liquids were selected because of their differences in molecular structure. A number of high-purity, partially fluorinated compounds used as additives in this study were prepared at NRL by J.G. O'Rear and P.J. Sniegoski and have been previously reported. These compounds are 1,2,3-trimethylolpropane tris(heptafluorobutyrate) (5), tris(1H,1H-pentadecafluorooctyl)tricarallylate (6), bis(1H,1H-pentadecafluorooctyl)4-chlorophthalate (17), and bis(1H,1H-pentadecafluorooctyl)n-octylsuccinate (6).

Several solid fluorochemical derivatives were kindly provided by Dr. J.D. LaZerte of the Minnesota Mining and Manufacturing Company:



were reported to be free of inorganics and by analysis were at least 98% pure;  $F(CF_2)_8SO_2N(C_2H_5)CH_2COOH$  was reported to be 98.8% pure with a small amount of branched chain  $C_8F_{17}$  present;  $[F(CF_2)_8SO_2NH(CH_2)_3N(CH_3)_3]I$  contained no free base, the iodine analysis was near quantitative, and isomers were removed by recrystallization;  $F(CF_2)_8SO_2N(C_2H_5)(CH_2)_2OP(O)(OH)_2$  was said to be better than 95% pure. The trimethyl end-blocked polydimethylsiloxanes, DC 200 (7-cs viscosity) and L-45 (50-cs viscosity), were obtained from the Dow Corning Corporation and the Union Carbide Corporation. The methyl ester  $CF_3(CF_2)_7(CH_2)_{10}COOCH_3$  was prepared by P.J. Sniegoski of NRL from the partially fluorinated acid synthesized by N.O. Brace (18) of the E.I. duPont de Nemours and Company and made available to us for earlier studies (19,20). Chromatographic analysis showed the methyl ester to be at least 99.8% pure. A sample of the so-called Light Water mixture developed as an extinguishing foam for hydrocarbon fires by Tuve and Jablonski (21) was also investigated. The sample was the commercial product of the Minnesota Mining and Manufacturing Company and was used as received.

All glassware used in these experiments was cleaned in a hot 1:4 nitric acid-sulfuric acid bath and rinsed copiously with distilled water. The nonpolar organic liquids were percolated through adsorption columns containing activated Florisil to remove any polar impurities.

## EXPERIMENTAL RESULTS

### Effect of Soluble Surfactants on Rates of Evaporation

The optimum sensitivity and reproducibility for evaporation rate studies of toluene were obtained using the dual-cell evaporometer shown in Fig. 1 with a bridge current of 18 mA and a helium flow rate of 156 cc/min; a somewhat higher helium flow rate, 236 cc/min, was used for studies of 2,2,4-trimethylpentane and nitromethane. When 1.0 ml of pure toluene was added only to the Pyrex dish in cell 1, with a helium flow rate of 156 cc/min through each cell, a difference in potential of  $670 \pm 10$  mV was recorded. When pure toluene was added only to cell 2, the signal was  $-700 \pm 10$  mV. The difference in magnitudes of the two signals indicates that the two cells and/or thermistors in the system were not perfectly balanced. Repeating the experiment and reversing the positions of the evaporometer cells with respect to the thermistors did not change the recorded potentials, demonstrating that the imbalance was in the thermistor detectors and not in the geometry of the cells. Addition of toluene to both dishes would be expected to give a resulting signal midway between 670 and -700 mV, or about -15 mV. The actual measured potential difference with pure toluene in each dish was  $-17 \pm 4$  mV, which could then be used as a baseline  $\Delta V_0$  for studies of evaporation retardation. Any reduction in the rate of evaporation of toluene in either dish would result in a change in this baseline potential.

Similarly, potentials of 875 and -905 mV were recorded for 2,2,4-trimethylpentane at 18 mA and 236-cc/min helium flow, with the baseline potential  $\Delta V_0$  being  $-22 \pm 5$  mV for 1.0-cc samples. For nitromethane, also at 18 mA and 236-cc/min helium flow, potentials of 600 and -622 mV were recorded, with the baseline value  $\Delta V_0$  being determined as  $-16 \text{ mV} \pm 5 \text{ mV}$ . Assuming the thermistors respond in a linear fashion to changes in vapor concentration, one would expect that even a 1% change in evaporation rate would give a significant change in potential. A 1% decrease in evaporation would correspond to about 7 mV for toluene, 9 mV for 2,2,4-trimethylpentane, and 6 mV for nitromethane.

The partially fluorinated compounds used as soluble additives in toluene are listed in Table 1, along with the concentrations and surface tensions of the solutions studied. These compounds were selected for this investigation because previous studies had shown them to be unusually surface active in a number of organic liquids. The slightly soluble compound tris(1H,1H-pentadecafluorooctyl)tricarallylate gave a saturated solution at the concentration listed. The other solutions were 0.1 mole/l or less depending on their solubility in toluene. If the surfactant did not dissolve completely at this concentration, sufficient solvent was added to bring the remaining material into solution. A concentration of 0.1 mole/l was the largest initial concentration studied. As solvent evaporation proceeded during the experiments, the solutions became increasingly more concentrated, and in effect the influence of solution concentration on evaporation rate was observed.

Table 1  
Effect of Surfactants on the Rate of Evaporation of Toluene as Indicated by  
the Difference in Detector Potential\*

Surfactant		Solution			
Compound	Density† (g/cc)	Concentration (g/cc)	Surface Tension‡ (dynes/cm)	Potential $\Delta V$ (mV)	Potential Difference $\Delta V - \Delta V_0$ (mV)
1,2,3-Trimethylolpropane tris(heptafluorobutyrate)	1.614	$7.22 \times 10^{-2}$	23.5	$-13 \pm 4$	$4 \pm 4$
Tris(1H,1H-pentadecafluorooctyl) tricarallylate	Solid	$< 5 \times 10^{-5}$	25.6	-9	8
Bis(1H,1H-pentadecafluorooctyl) 4-chlorophthalate	Solid	$6.35 \times 10^{-3}$	28.2	-17	0
Bis(1H,1H-pentadecafluorooctyl) n-octyl succinate	1.483	$3.62 \times 10^{-2}$	25.1	-21	-4
$\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{10}\text{COOCH}_3$	Solid	$5.83 \times 10^{-3}$	28.4	-21	-4
$(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_2]_{7.5}\text{OSi}(\text{CH}_3)_3$	0.920	$7.78 \times 10^{-2}$	26.1	-13	4

\*Experimental conditions: helium flow rate = 156 cc/min, bridge current = 18 mA, liquid volume = 1cc, temperature = 23° C, and baseline potential for pure toluene =  $-17 \pm 4$  mV.

†Density of pure toluene = 0.867 g/cc.

‡Surface tension of pure toluene = 28.5 dynes/cm.

The first compound in Table 1, 1,2,3-trimethylolpropane tris(heptafluorobutyrate) was the most surface active of the additives in toluene; it reduced the surface tension from 28.5 to 23.5 dynes/cm, which is close to the surface tension of the additive itself, 21.2 dynes/cm. This low surface tension was indicative of a high concentration of the fluorocarbon additive at the interface, sufficient to form a nearly continuous monomolecular film (5,6).

By applying the Gibbs adsorption equation

$$\Gamma = - \frac{c}{RT} \left( \frac{\partial \gamma}{\partial c} \right) \quad (1)$$

to the surface tension-vs-concentration data for this solute, the actual surface concentration of a 0.1-mole/l solution was calculated to be  $6.70 \times 10^{13}$  molecules/cm<sup>2</sup>, which corresponds to 150 Å<sup>2</sup>/molecule in the interface. In Eq. 1,  $\Gamma$  is the surface excess of adsorbed material,  $c$  is solute activity (or concentration in dilute solutions),  $R$  is the gas constant, and  $\gamma$  is the solution surface tension. From measurements on Stuart-Briegleb ball models, the smallest possible area that a fluorinated trimethylolpropane molecule could occupy at an interface would be approximately 90 Å<sup>2</sup>, which corresponds to the three adjacent fluorocarbon groups on the molecules being oriented perpendicular to the surface and in closest possible packing. Since the fluorocarbon chains were only four carbon atoms long, the intermolecular forces of attraction between adjacent molecules would not be expected to be sufficient to maintain the adsorbed molecules in such a closely packed configuration at the interface. This conclusion was reflected in the calculated area per molecule (150 Å<sup>2</sup>), which indicated that even though the fluorocarbon groups were necessarily oriented outermost and in close proximity at the surface, they were probably not perpendicular to it. Also they were sufficiently separated to allow for molecular motion and for penetration of the film by solvent molecules. The remaining additive solutions, with smaller surface tension depressions, would be expected to have lower concentrations of additive molecules at the interface. In the case of bis(1H,1H-pentadecafluorooctyl)4-chlorophthalate and  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{10}\text{COOCH}_3$  there is apparently very little solute adsorption.

Table 1 also shows the effect of the dissolved surfactants on the rate of evaporation of toluene. It is apparent that none of the solutes were able to reduce significantly the rate of evaporation, whether they formed a continuous monomolecular film or not. In only one instance was the potential change greater than the experimental uncertainty; that was for the saturated solution of tris(1H,1H-pentadecafluorooctyl)tricarallylate, which gave a  $\Delta V - \Delta V_0$  of  $8 \pm 4$  mV, indicating at most a 1% decrease in the rate of evaporation. The potential differences reported were normally taken after evaporation had proceeded for several minutes and had reached a steady-state value. For all solutions this steady-state potential difference  $\Delta V - \Delta V_0$  remained constant, often to the point where the solvent no longer completely covered the bottoms of the sample dishes. Inasmuch as the solutions became increasingly more concentrated and finally saturated as evaporation proceeded, it is apparent that these additives, at all concentrations, did not significantly impede the evaporation of toluene under the experimental conditions used.

Results of the evaporation rate studies with 2,2,4-trimethylpentane are given in Table 2. Because of the low surface tension of 2,2,4-trimethylpentane (19.3 dynes/cm), the solutes studied caused changes in the surface tension which were too small to permit reliable use of the Gibbs' equation. One would not expect these adsorbed solutes to form closely packed monomolecular films at the solution/vapor interfaces. The results show that the evaporation rate of this solvent is essentially unaffected by the presence of the soluble surfactants. With 1.0-ml samples in the evaporometer cells, a 1% reduction in evaporation would result in a potential change of 9 mV. The largest potential difference recorded for any solution was  $9 \pm 4$  mV, indicating at most a 1% decrease in evaporation rate. In two instances 2.0-ml solution samples were used, causing a small shift in the baseline to  $-30 \pm 4$  mV; otherwise, the results were the same.

Only two compounds were investigated as soluble surfactants in nitromethane. In Table 3 the additives, initial solution concentrations, and surface tensions are given along with the potentials recorded during the evaporation studies. The small  $\Delta V - \Delta V_0$  values recorded were much less than 6 mV, which corresponds to a 1% reduction in evaporation, indicating no detectable change in evaporation rate of nitromethane, even though the surface tension had been reduced 10 to 12 dynes/cm. In Ref. 5 the Gibbs adsorption equation was applied to surface tension-vs-concentration data for 1,2,3-trimethylolpropane tris-(heptafluorobutyrate) in nitromethane. The surfactant was found to occupy an area of approximately 80 Å<sup>2</sup>/molecule in the interface at a solution concentration equivalent to

Table 2  
Effect of Surfactants on the Rate of Evaporation of 2,2,4-Trimethylpentane  
as Indicated by the Difference in Detector Potential\*

Surfactant		Solution			
Compound	Density <sup>†</sup> (g/cc)	Concentration (g/cc)	Surface Tension <sup>‡</sup> (dynes/cm)	Potential $\Delta V$ (mV)	Potential Difference $\Delta V - \Delta V_0$ (mV)
1,2,3-Trimethylolpropane tris(heptafluorobutyrate)	1.614	$8.07 \times 10^{-3}$	18.6	$-23 \pm 4$	$-1 \pm 4$
Tris(1H,1H-pentadecafluorooctyl) tricarallylate	Solid	$< 5 \times 10^{-5}$	19.0	-21 (2 ml)	9
Bis(1H,1H-pentadecafluorooctyl) 4-chlorophthalate	Solid	$6.02 \times 10^{-3}$	18.8	-14	8
Bis(1H,1H-pentadecafluorooctyl) 3-methylglutarate	1.689	$2.43 \times 10^{-2}$	18.9	-16	6
$(CH_3)_3Si[OSi(CH_3)_2]_{10.2}OSi(CH_3)_3$	0.930	$3.86 \times 10^{-2}$	18.6	-32 (2 ml)	-2

\*Experimental conditions: helium flow rate = 236 cc/min, bridge current = 18 mA, temperature = 23°C, baseline potential for pure 2,2,4-trimethylpentane:  $\Delta V_0 = -22 \pm 4$  mV for 1-ml samples and  $\Delta V_0 = -30 \pm 4$  mV for 2-ml samples.

<sup>†</sup>Density of pure 2,2,4-trimethylpentane = 0.692 g/cc.

<sup>‡</sup>Surface tension of pure 2,2,4-trimethylpentane = 19.3 dynes/cm.

Table 3  
Effect of Surfactants on the Rate of Evaporation of Nitromethane as Indicated  
by the Difference in Detector Potential\*

Surfactant		Solution			
Compound	Density <sup>†</sup> (g/cc)	Concentration (g/cc)	Surface Tension <sup>‡</sup> (dynes/cm)	Potential $\Delta V$ (mV)	Potential Difference $\Delta V - \Delta V_0$ (mV)
1,2,3-Trimethylolpropane tris(heptafluorobutyrate)	1.614	$8.07 \times 10^{-3}$	25.6	$-14 \pm 5$	$2 \pm 5$
Bis(1H,1H-pentadecafluorooctyl) 4-chlorophthalate	Solid	Saturated	23.8	-19	-3

\*Experimental Conditions: helium flow rate = 236 cc/min, bridge current = 18 mA, liquid volume = 1.0 cc, temperature = 23°C, and baseline potential for pure nitromethane  $\Delta V_0 = -16 \pm 5$  mV.

<sup>†</sup>Density of pure nitromethane = 1.130 g/cc.

<sup>‡</sup>Surface tension of pure nitromethane = 35.9 dynes/cm.

that reported in Table 3. Since  $80 \text{ \AA}^2/\text{molecule}$  is greater than the cross-sectional area of two fluorocarbon chains but less than three, Jarvis and Zisman (5) suggested that they adsorbed at the interface with two fluorocarbon chains directed toward the vapor phase and the other remaining in solution. The calculated area suggests the molecules are not arranged in the closest possible packing but that there is ample room for molecular motion and for coadsorption of solvent molecules at the surface. The same situation is undoubtedly true for other fluorocarbon compounds of similar composition adsorbing from solution at an organic liquid/vapor interface.

In Fig. 4 the total volumes of pure toluene, 2,2,4-trimethylpentane, and nitromethane lost by evaporation are plotted against time and as a function of helium flow rate. During each series of experiments the volume of pure solvent remaining in the evaporometer cell after a given time was determined by extracting it from the cell with a calibrated syringe. It is apparent that following the first several minutes of an experiment, after which the system had reached an equilibrium temperature and evaporation rate, the experimental points plotted in a straight line. The amount of surfactant solution remaining after each experiment was the same as the remaining pure solvent, within the limits of error of the measuring technique used. When the volume-decrease data for the surfactant solutions are also plotted in Fig. 4, they fall on the same line as the data for the

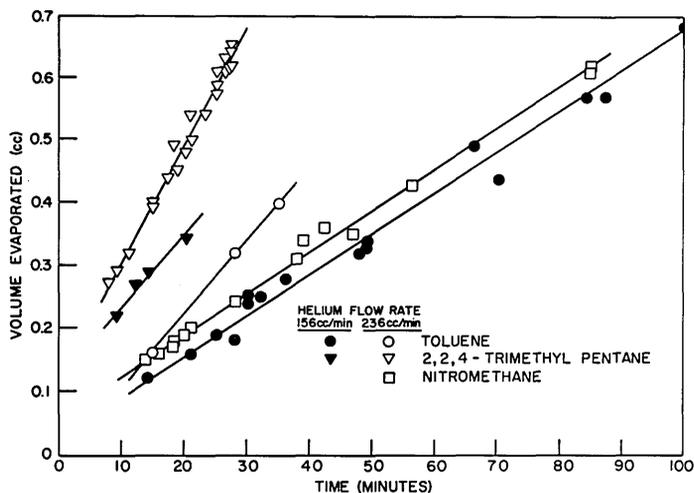
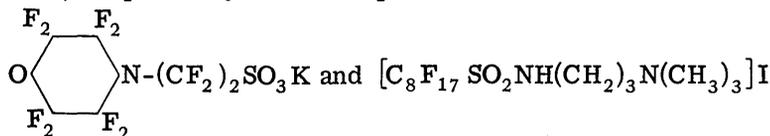


Fig. 4 - Evaporative loss of a volatile solvent as a function of time and helium flow rate

pure liquids. This is additional evidence that the soluble surfactants did not significantly retard the evaporation rate of any of the volatile liquids investigated.

#### Effect of Insoluble Adsorbed Films on Rates of Evaporation

Very few of the available surface-active compounds were capable of spreading to form insoluble monomolecular films on any low-molecular-weight, low-surface-tension, volatile liquid, such as toluene, or 2,2,4-trimethylpentane. In the many spreading experiments tried, a number of fluorocarbon derivatives exhibited positive spreading pressures on toluene, but even the most insoluble and nonvolatile compound slowly lost film pressure with time. If excess bulk fluorocarbon remained on the surface as floating disks of liquid surrounded by spread monomolecular film, the molecules lost from the monolayer to the solution were quickly replaced by additional molecules spreading from the disks of bulk phase material. In this way the film pressure and monolayer coverage were maintained until the bulk phase disappeared. The fluorocarbons  $F(CF_2)_8SO_2N(C_2H_5)CH_2COOH$ ,  $F(CF_2)_2C_6F_{10}SO_3K$ , and tris(1H,1H-pentadecafluorooctyl)tricarallylate spread on toluene to give film pressures, or surface tension depressions, of from 1 to 2 dynes/cm, 2 dynes/cm, and 6 dynes/cm, respectively. The compounds



failed to give detectable spreading pressures.

By keeping excess compound at the interface, monomolecular films of the three compounds that spread could be maintained on toluene for a short period of time, and their effects on the rates of evaporation could be studied. Using the evaporometer probe method it was relatively simple to maintain an excess of bulk fluorocarbon at the interface while determining changes in the rate of evaporation of the solvent. The sensitivity of the evaporometer probe was first checked using water as the substrate. An adsorbed film of hexadecanol at its equilibrium spreading pressure decreased the rate of water

evaporation by 62%, which was in good agreement with the previous work of Walker (16). When the experiments were repeated using toluene as the substrate liquid, no significant change in the rate of evaporation was observed with any of the three above-mentioned fluorochemical compounds that spread at the interface. From the results of these experiments it is doubtful that even a completely insoluble monolayer of any fluorocarbon derivative similar to those studied would be able to retard significantly the evaporation rate of a volatile organic solvent. In conclusion, none of the fluorocarbon compounds investigated were observed to form films more than a monolayer deep when spread at the solvent/vapor interface; rather, they appeared to spread as monolayers in equilibrium with bulk liquid phase.

Films of polydimethylsiloxanes of two different viscosities, however, were found to spread as stable polymolecular films on nitromethane as evidenced by the interference colors exhibited as the polymer spread. Therefore, by varying the amount of silicone added to the surface, it was possible to control the film thickness. A study was then made of the effect of silicone film thickness on the rate of evaporation of nitromethane, using the evaporometer probe as well as the dual evaporation cell apparatus. The results using the two techniques were essentially the same. Thin layers of silicone up to 30 or 40 $\mu$  thick did not significantly reduce the evaporation rate; however, when the silicone film thickness was increased to 0.05 mm or more, the evaporation rate was measurably reduced. The data in Table 4 show that a linear reduction in the rate of evaporation with film thickness occurred in the range of film thickness of 0.075 to 0.311 mm. Earlier work by Gilby and Heymann (22) demonstrated that polymolecular films of hydrocarbon oils containing surface-active spreading agents failed to reduce the rate of evaporation of water until the film thickness was of the same order as observed here. These multimolecular films become effective barriers to evaporation only when the rate of diffusion of the solvent molecules through the film becomes less than their rate of movement away from the saturated, unstirred vapor layer above the surface.

Table 4  
Effect of Bulk Silicone  $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_2]_{10.2}\text{OSi}(\text{CH}_3)_3$   
Layer at Nitromethane/Air Interface as Indicated by the Difference  
in Detector Potential\*

Thickness of Silicone Layer		Potential Difference $\Delta V - \Delta V_0$		Evaporation Rate Reduction (%) after 20 Min
Millimeters	Molecular Layers (approx.)	Initial	After 20 Min	
0.075	10,000	36	18	3
0.124	17,500	75	58	10
0.187	26,000	134	95	16
0.249	35,000	150	137	23
0.311	43,500	180	170	28

\*Experimental conditions: helium flow rate = 236 cc/min, bridge current = 18 mA, volume of nitromethane = 1.0 cc, and temperature = 23°C.

## Relation to Light Water Foams for Extinguishing Hydrocarbon Fuel Fires

In addition to the polymolecular layers of pure liquids, one would expect that a sufficiently thick, uniform foam of a suitable solution could also be an effective barrier to the transport of molecules from the liquid to the vapor state. The effective system recently developed at NRL for extinguishing hydrocarbon fires depends on the use of what the inventors named Light Water. Essentially Tuve and Jablonski (21) made a stable foam from an aqueous solution of one or two suitable fluorocarbon surfactants containing approximately 0.50% polyethylene oxide. This foam could then be sprayed on the burning fuel. The surface-active compounds that are effective in Light Water foams are commercial products of the Minnesota Mining and Manufacturing Company; two such compounds are  $[C_8F_{17}SO_2NH(CH_2)_3N(CH_3)_3]I$  and  $C_7F_{15}CONH(CH_2)_3N(CH_3)_2CH_2CH_2COO^-$ . Additional fluorocarbon-containing compounds, such as the other previously mentioned pure research samples generously made available to us for this investigation by the 3M Company, may also be effective foaming agents in aqueous solution. Each of these compounds, however, failed to form evaporation barriers when spread in our apparatus as monomolecular films on volatile organic solvents. An obvious possibility is that the layers of water trapped in the lamellas of the foam, and not the fluorocarbon surface-active agents adsorbed at the hydrocarbon fuel/vapor interface, act as the barrier to evaporation of fuel through a layer of foam.

In addition to acting as foam stabilizing agents, these fluorocarbon surface-active compounds also act as powerful spreading agents which cause the foam to spread rapidly over many liquid or solid hydrocarbon surfaces (7,23,24) and to respread over a surface if it should be disturbed. Our spreading experiments revealed that the fluorocarbon additives in commercial Light Water caused the liquid solution (with a surface tension of 17.9 dynes/cm) to spread spontaneously on toluene, n-octane, and nitromethane but not on 2,2,4-trimethylpentane, probably because the fluorocarbon surfactants do not sufficiently reduce the 2,2,4-trimethylpentane/water interfacial tension. The presence of interference colors when the aqueous solutions spread on the organic liquids other than trimethylpentane indicated that the spread films of Light Water were not of constant uniform thickness.

It was difficult to determine changes in the evaporation rates of the organic solvents in the presence of thin films of Light Water, because the thermal conductivity cells are sensitive to the presence of water vapor as well as to the organic solvent. This problem could be roughly compensated for by bubbling the helium through a water tower. Using the water-saturated helium, the evaporimeter probe was calibrated with the organic solvents, and changes in the evaporation rate were determined, although with less precision than with pure helium. The rates of evaporation of toluene and n-octane appeared to be reduced 40 to 50% simply by spreading 0.01 ml of Light Water over the liquid surface to form a film about  $5\mu$  deep; however, the change in evaporation rate was very erratic, perhaps due to the observed lack of uniform thickness of the Light Water film. Increasing the thickness of the Light Water layer on the organic liquids further reduced their rates of evaporation, but the rates remained erratic. In the case of 2,2,4-trimethylpentane, on which the Light Water did not spread, the addition of up to 0.10 ml of solution did not measurably change the equilibrium evaporation rate. The evaporation rate of nitromethane also was not reduced by the presence of up to 0.10 ml of Light Water, perhaps because of the solubility of water in nitromethane.

## DISCUSSION

It is apparent from the data presented that adsorbed monomolecular films of each of the soluble fluorinated compounds studied as additives in solution had essentially no effect

on the rates of evaporation of the organic solvents, even though in several instances it was demonstrated that the adsorbed molecules formed essentially continuous films at the surface. In every case the rate of transport of solvent molecules through the adsorbed film was sufficient to maintain a saturated vapor layer above the surface. The rate-determining barrier to evaporation under these conditions continued to be the rate of diffusion through the unstirred saturated layer. This conclusion is not surprising considering that even on water only those adsorbed monolayers that meet stringent molecular close-packing and chain-adlineation requirements are able to retard evaporation. Inasmuch as the organic solvent molecules investigated here are much larger than water molecules, evaporation retardation might be expected to be achieved with adsorbed films whose interstitial spaces are somewhat larger than is required of films that serve as evaporation barriers for water. However, the various types of surfactants used in this study to form barrier films were obviously not sufficiently close packed, or condensed, to be effective.

The partially fluorinated, slightly soluble surfactants that spread spontaneously on the organic solvents to form continuous monomolecular films in equilibrium with bulk phase material at the interface also failed to retard evaporation of the various organic solvents studied. Monomolecular films formed in this manner can generally be maintained as long as bulk spreading material remains at the surface to replace those film molecules that slowly evaporate or else are dissolved by the substrate. Rates of evaporation of the organic liquids appeared to be reduced only by relatively thick polymolecular films, such as those formed by the polydimethylsiloxanes on nitromethane. Under such conditions, a film approximately 0.30 mm deep reduced the evaporation rate by some 28%.

The surface-active hydrocarbon derivatives whose adsorbed monolayers form effective barriers to the evaporation of water all contain long, unbranched, aliphatic chains attached to a polar hydrophilic group whose cross-sectional area is no greater than that of the hydrocarbon chain. Similarly oriented hydrocarbon chains can be held tightly together in a closely packed, adlineated array by the van der Waals forces of cohesion between them. The van der Waals force of attraction between adjacent fluorocarbon chains, however, is considerably less than for hydrocarbons (25). In addition, the normal aliphatic fluorocarbon chains of the compounds used in this study contained at most eight carbon atoms, as compared to the 16-carbon-atom hydrocarbon chains necessary to form effective barrier films on water. It is most unlikely therefore that any of the fluorocarbon additives presently available will give rise to sufficiently coherent, closely packed monomolecular films to form effective evaporation barrier films on organic liquids.

Even though monomolecular films of the fluorocarbon derivatives do not form evaporation barriers, the fluorocarbons can act as powerful wetting and spreading agents as well as foaming agents in aqueous solutions, such as the Light Water fire-fighting mixtures. Many fluorocarbon surface-active agents are capable of lowering the water surface tension sufficiently to permit water solutions, or water-rich foams, to spread spontaneously on many low-surface-tension organic liquids, such as toluene, nitromethane, and n-octane. The commercial Light Water sample spread on all substrates studied except 2,2,4-trimethylpentane. Our experimental methods have proved that thin layers of water, containing suitable spreading agents, will be effective barriers to the evaporation of organic liquids. By analogy one would expect that thin layers of water trapped in the lamellas of an aqueous foam would also impede the evaporation of organic liquids. It is concluded that the water contained in the Light Water foams is actually the effective barrier, decreasing the evaporation of fuel and hence preventing ignition over the foam-covered surface. It would appear from this investigation that foams too poor in water content (i.e., with lamellas that are too thin) may be undesirable for use as fire-fighting foams. It is also apparent that a low surface tension for the Light Water is essential in order that it be able to spread spontaneously on as many types of volatile organic liquids as possible. It may be desirable that surface tension and water content, in addition to foam stability, be considered in future specifications for such materials.

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13. ABSTRACT  An investigation was made of the effect of adsorbed surface-active films on the rate of evaporation of volatile organic liquids. A series of partially fluorinated compounds were studied either as monolayers adsorbed from solution or as insoluble films spread at the liquid/vapor interface. In no instance was the rate of evaporation significantly reduced by the presence of a monomolecular film. Insoluble multi-molecular films of polydimethylsiloxanes, however, were found to reduce effectively the rate of evaporation, provided the film thickness was sufficient to decrease the rate of diffusion of the solvent molecules through the film to a value below their rate of diffusion through the saturated, nonturbulent vapor layer overlying the surface. In addition to polydimethylsiloxane polymolecular layers, thin layers of water, containing suitable fluorocarbon spreading agents, were also found to reduce the rate of evaporation of certain volatile organic liquids. These aqueous films are similar to the thin layers of interlamellar water present in aqueous foams used to extinguish gasoline fires, such as the fluorocarbon-containing Light Water foams.			

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