

Riyaz A. Fazal
Jerome H. Milgram

MIT-T-79-009

C. 2

The Effects of Surface Phenomena on the Spreading of Oil on Water



MIT Sea Grant
College Program

Massachusetts
Institute of Technology
Cambridge
Massachusetts 02139

Report No. MITSG 79-31
November 1979

LOAN COPY ONLY

The Effects of Surface Phenomena on
the Spreading of Oil on Water

by

Riyaz A. Fazal
Jerome H. Milgram

Sea Grant College Program
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Report No. MITSG 79-31
Index No. 78-331-Nom
November 1979

ABSTRACT

An oil spill in the ocean does not spread from its source evenly. Some components thin out into fine films, while others coagulate into thick patches. Most predictive models at present incorporate information on the bulk properties, but they do not account for this actual uneven fractionation.

The oils are composites made up of many compounds which have different chemical and surface properties. This report describes studies of the spreading of four kinds of crude extracted from around the world, as well as the spreading of a mixture of pure hydrocarbons and of diesel fuel. It concludes that spreading effects are not wholly determined by bulk properties, but are also affected by the properties of the individual components in the oil. It recommends that further studies must be undertaken of the various physical and chemical properties of hydrocarbons if oil spill modelling is to be made more accurate.

ACKNOWLEDGEMENTS

This work was supported by the Office of Sea Grant, National Oceanic and Atmospheric Administration, under grant number 04-7-158-44074.

RELATED REPORTS

- Chrysostomidis, Marjorie. OFFSHORE PETROLEUM ENGINEERING: A BIBLIOGRAPHIC GUIDE TO PUBLICATIONS AND INFORMATION SOURCES. MITSG 78-5 New York: Nichols Publishing Company, 1978. 366 pp. \$45.00
- Yeung, Ronald W. DOCUMENTATION OF FOUR OCEAN-RELATED COMPUTER PROGRAM MODULES. MITSG 76-18. NTIS: PB- 264 146/AS. Cambridge: Massachusetts Institute of Technology, 1976. 70 pp. \$2.00.
- Stewart, Robert J. THE INTERACTION OF WAVES AND OIL SPILLS. MITSG 75-22. NTIS: PB-262 458/AS. Cambridge: Massachusetts Institute of Technology, 1976. 201 pp. \$4.00.
- Devanney, John W., III, Joseph B. Lassiter III, et al. PRIMARY PHYSICAL IMPACTS OF OFFSHORE PETROLEUM DEVELOPMENT: REPORT TO COUNCIL ON ENVIRONMENTAL QUALITY. MITSG 74-20. NTIS: COM-74-11125/AS. Cambridge: Massachusetts Institute of Technology, 1974. 432 pp. \$8.00.

TABLE OF CONTENTS

	Page
ABSTRACT	2
ACKNOWLEDGEMENTS	3
1. INTRODUCTION	5
2. COMPOSITION OF OIL	10
3. THE SPREADING PHENOMENA	14
4. INVESTIGATION OF THE SURFACE AND SPREADING PROPERTIES OF FOUR CRUDE OILS	32
5. SPREADING OF 2- AND 3- COMPONENT HYDROCARBON MIXTURES	36
6. THE SPREADING OF DIESEL	52
7. CONCLUDING REMARKS	57
REFERENCES	59
APPENDIX I : MEASUREMENT INSTRUMENTS	61
APPENDIX II: THICK LAYER REGIONS OF THE SPREAD: EMULSIFICATION CONSIDERED	65

1. INTRODUCTION:

In the last twenty to thirty years a growing world population has become largely dependent on petroleum-based technology. Production of oil has reached more than three billion metric tons every year, and increasing, with almost 70% transported across the ocean. This, with the ever increasing offshore drilling operations have almost inevitably resulted in the increase in oil pollution in the oceans.

Tankers and offshore oil rigs are not the only or even the major sources of petroleum hydrocarbons in the seas. Ballasting, flushing of bilges or tanks, dumping of untreated industrial and municipal wastes into the ocean, spillage in ports and incomplete combustion of marine fuels all contribute to oil pollution of the sea. While the latter sources of pollution should be of no less concern, oil spills from tankers (Torrey Canyon, 1967, Argo Merchant, 1976 and Amoco Cadiz, 1978 are the better known) and offshore oil wells (Santa Barbara, 1969) are concentrated in space and time and are usually the results of accidents. Chronic or continuous spills are usually a matter of policy, or lack of it, and economics.

The deleterious effects of oil pollution, though not

wholly understood, are well known. Cleaning up of an oil spill is therefore important. To devise strategies for clean up requires knowledge of what happens to oil when spilled at sea. As listed by Milgram (1978), a number of physical processes take place when oil is spilled on water:

- 1) Spreading,
- 2) Mass transport due to winds,
tides and currents,
- 3) Dispersion into the water,
- 4) Sedimentation,
- 5) Evaporation,
- 6) Dissolution.

A state-of-the-art review of most of these topics is given by Stolzenbach, Madsen, Adams, Pollack and Cooper (1977).

A lot of spreading models have been developed assuming calm water and that the centre of mass of the spill does not advect.

The model developed by Blokker (1964) considers the effect of gravity giving the velocity of the leading edge of the slick,

$$\frac{dr}{dt} = K(\rho_w - \rho_o) \frac{\rho_o}{\rho_w} h$$

where K - "Blokker" constant (varies with oil properties)

- r - radius of slick
 ρ_o, ρ_w - density of oil and water respectively
 h - slick thickness

Fay (1971) in his spreading model considered the four forces which act on a film of oil as illustrated in Fig. 1-1. Gravity and surface tension are the spreading forces balanced by inertia of the oil and viscous friction of the water boundary layer giving the three spreading regimes:

- 1) The gravity-inertia regime,
- 2) The gravity-viscous regime,
- 3) The surface tension - viscous regime.

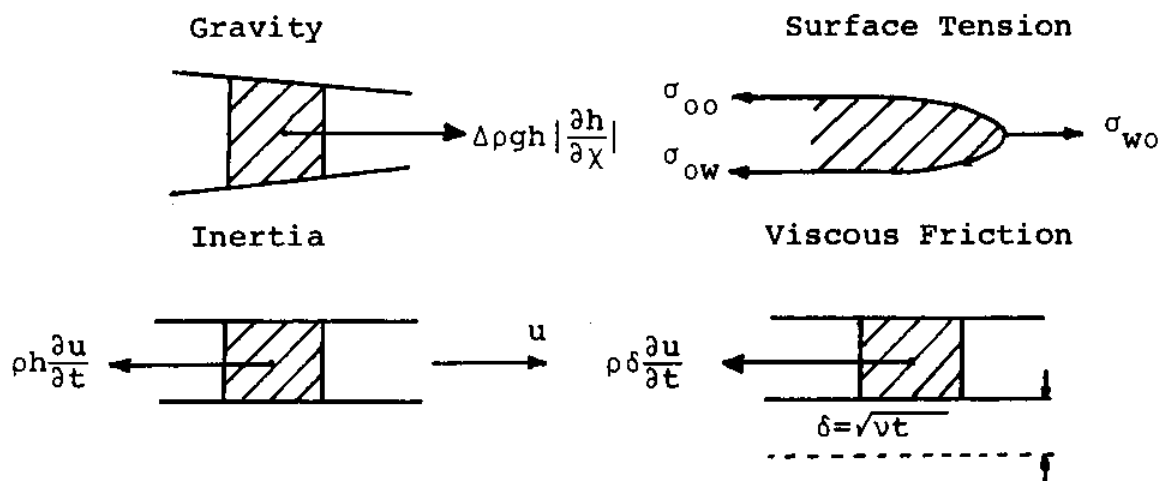


Fig. 1 - 1
(After Fay, 1971)

Fay's spreading laws have been verified by laboratory experiments of one dimensional spreading (Suchon, 1970, Lee, 1971) and by other analytical formulations (Buckmaster, 1973, Fannelop and Waldman, 1971) with differing values of coefficients (Table 1-2), but are not consistent with field measurements. The spreading laws are shown in Table 1-1.

Table 1-1: Spreading Laws for
Oil Slicks
(After Fay, 1971)

	One-dimensional	Axisymmetric
Inertial	$\ell = k_{1i} (\Delta g V t^2)^{1/3}$	$r = k_{2i} (\Delta g V t^2)^{1/4}$
Viscous	$\ell = k_{1v} (\Delta g V^2 t^{3/2} / \nu^{1/2})^{1/4}$	$r = k_{2v} (\Delta g V^2 t^{3/2} / \nu^{1/2})^{1/6}$
Surface tension	$\ell = k_{1t} (\sigma^2 t^3 / \rho^2 \nu)^{1/4}$	$r = k_{2t} (\sigma^2 t^3 / \rho^2 \nu)^{1/4}$

Subscripts

σ	Spreading coefficient or interfacial tension (with subscript)	1	One-dimensional spread
ν	Kinematic viscosity of water	2	Two-dimensional (axisymmetric) spread
Δ	Ratio of density difference between water and oil to density of water	i	Inertial spread
		t	Surface tension spread
		v	Viscous spread

Table 1-2: Spreading Law Coefficients
(After Fay, 1971)

	One-dimensional	Axisymmetric
Inertial	$k_{li} = 1.5$	1.14
Viscous	$k_{lv} = 1.5$	1.45
Surface tension	$k_{lt} = 1.33$	2.30

In the above models, it is assumed that the composition and concentration of oil in space and time is constant. Field observations of Berridge, Dean, Fallows and Fish (1968) and Jeffrey (1973) show that this is not a valid assumption. Part of the aim of this paper is to show that oil does fractionate. Some surface active components spread out faster than the other components.

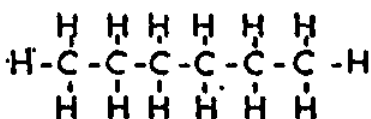
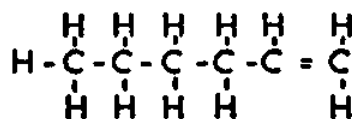
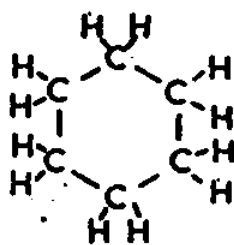
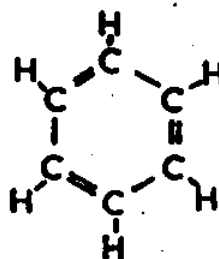
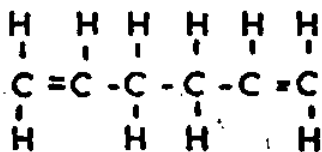
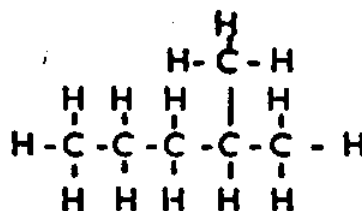
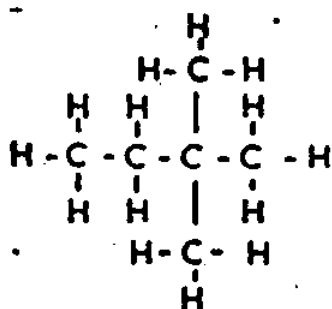
A phenomenon that is not taken into account by the spreading models is the spread of oil into thick clumps of oil and thin films which make up most of the surface of the slick. An initial attempt has been made in this paper to explain this behavior (Appendix II).

2. COMPOSITION OF OIL

Oil is a mixture of hundreds or thousands of hydrocarbons and traces of other organic compounds containing nitrogen, sulphur and oxygen. The chemical and physical properties of these compound vary widely and might individually or collectively affect the behavior of oil.

The major classes of hydrocarbons are:

- 1) Alkanes or paraffins. Also known as aliphatic compounds. These comprise a large portion of crude oil. Their molecules are straight or branch chained with each carbon molecule directly linked to four other atoms (Fig. 2-1 a and f). Examples of alkanes are methane (gas), hexane, octane (liquids), and eicosane (solid).
- 2) Cycloalkanes or naphthenes. These are known as alicyclic compounds because in spite of their cyclic configuration behave like straight chain aliphatic compounds. An example is cyclohexane (Fig. 2-1c).

(a) Normal Hexane C_6H_{14} (b) Normal Hexene, C_6H_{12} (c) Cyclohexane, C_6H_{12} (d) Benzene, C_6H_6 (e) Hexadiene -1,5, C_6H_{10} 2 Methylpentane C_6H_{14} 

(f) Isomeric Isoparaffin Compounds

2-2 Dimethylbutane C_6H_{14} FIGURE 2-1 Structural Formulas of Hydrocarbons
(After Nelson, 1958)

- 3) Aromatics. These are compounds that contain at least one benzene ring (Fig. 2-1 d). Benzene, toluene, cymene and naphthalene are examples of these.
- 4) Alkenes or olefins. Olefinic compounds are not usually found in crude oil, but are present in petroleum products like gasoline. These are unsaturated chain compounds where double or triple chemical bonds between carbon atoms are found. (Fig. 2-1 b and e).

Small quantities of other hydrocarbons and asphaltenes (compounds containing nitrogen, sulphur and oxygen) occur naturally in crude oil.

Oils are also classified according to their boiling points, which is related to the number of carbon atoms in the molecule. The classification is shown in Table 2-1.

TABLE 2-1

	Boiling Range	Approximate Carbon No.
Gas Fraction	Up to 40°C	C ₂ - C ₅
Gasoline	40 - 180°C	C ₆ - C ₁₀
Kerosene	180 - 230°C	C ₁₀ - C ₁₂
Light Gas oil	230 - 305°C	C ₁₃ - C ₁₇
Heavy Gas oil	305 - 405°C	C ₁₈ - C ₂₅
Lubricant Fraction	405 - 515°C	C ₂₅ - C ₃₈
Residuum	Above 515°C	Above C ₃₈

3. THE SPREADING PHENOMENA

The spreading or "wetting" behavior considered here arises from surface and interfacial properties of liquids. A liquid behaves as if it were surrounded by a tensioned skin with a tendency to contract. The molecules at the surface of a liquid are less completely attracted by neighboring molecules than the molecules in the bulk phase and hence have a greater free energy. Since the free energy of a system tends to a minimum, the surface will tend to contract attempting to decrease the surface area. The surface energy, known as the Hemholtz free energy, is measured in ergs/cm^2 . Early experimenters observed the tendency of the surface to contract and measured this force. The term surface "tension" was used and is the value of this force per unit length. The surface free energy, G , in ergs/cm , is numerically equal to the surface tension, σ , in dynes/cm .

When two different liquids are placed in contact, their interface also has a tendency to contract. This property is known as interfacial tension. (Actually, the surface tension of a liquid is the interfacial tension between the liquid and air or of the liquid and its own vapour.)

When a liquid B is placed on a liquid substrate A, as in Figure 3-1, one of two things can happen. Liquid B will either form a lens or spread into a thin film of one or a few molecules in thickness. (If unrestricted, spreading is allowed. A third possibility is one where both phenomena occur in restricted spreading as is explained later.)

If the equilibrium shape is a lens, the maximum lens thickness can be calculated. From Fig 3-2

$$a = \frac{(\rho_A - \rho_B)t}{\rho_A} = \Delta t$$

and, looking at horizontal forces,

$$\frac{1}{2} \rho_A (t - a)^2 g + \sigma_B + \sigma_{AB} = \frac{1}{2} \rho_B t^2 g + \sigma_A$$

giving,

$$(\sigma_B + \sigma_{BA}) - \sigma_A = \frac{1}{2} g t^2 \rho_B - \frac{1}{2} \rho_A \left(\frac{\rho_B}{\rho_A} \right)^2 t^2.$$

Finally,

$$t^2 = \frac{-2S\rho_A}{g\rho_B(\rho_A - \rho_B)} \quad (3.1)$$

where

$$S = \sigma_A - (\sigma_B + \sigma_{AB}) \quad (3.2)$$

At the edge of the lens where thickness is zero, equilibrium is determined by contact angles (Fig. 3-3). That is,

$$\sigma_A \cos \gamma = \sigma_B \cos \beta + \sigma_{AB} \cos \alpha \quad (3.3)$$

A lens will only be formed if S_{BA} (Equation 3.2) has a negative value. If $\sigma_A > \sigma_B + \sigma_{AB}$, the value of the spreading coefficient is positive and B will spread on A.

For example, with benzene on water (Adamson, 1976)

$$S_{BA} = 72.8 - (28.9 + 35.0) = 8.9 \text{ dynes/cm}$$

where,

Surface tension of water	= 72.8 dynes/cm
Surface tension of benzene	= 28.9 dynes/cm
Interfacial tension between benzene and water	= 35.0 dynes/cm

However, when the benzene and water become mutually saturated, the values of σ_A , σ_B , and σ_{AB} change giving a negative final spreading pressure.

$$S_{B(A)/A(B)} = 62.2 - (28.8 + 35.0) = -1.6 \text{ dynes/cm}$$



Figure 3-1

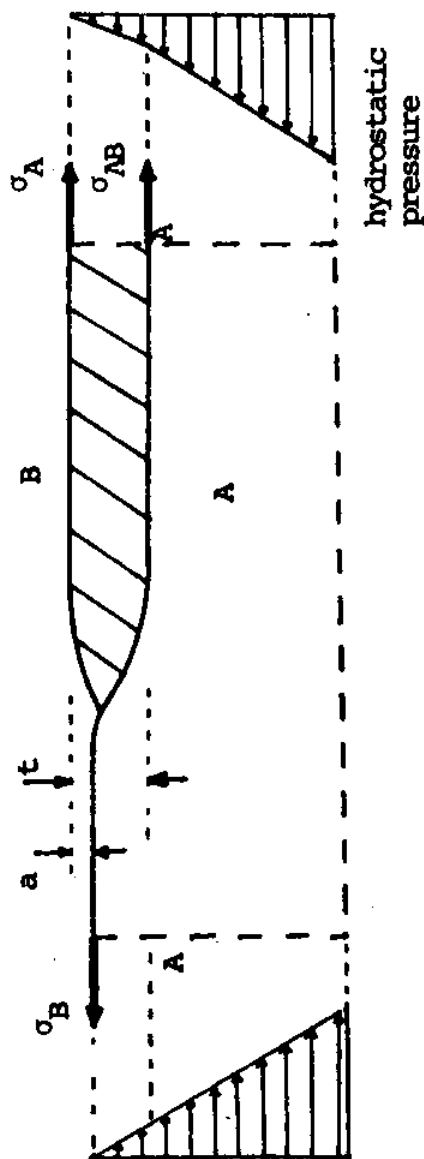


Figure 3-2
Free-body diagram for
horizontal forces



Figure 3-3

- σ_A - Surface tension of A
- σ_B - Surface tension of B
- σ_{AB} - Interfacial tension between A and B
- t - Maximum thickness of lens of B
- a - Height of B above the surface of A

Initially, with positive spreading coefficient, the benzene spreads into a monolayer (film of molecular thickness). However, this monolayer reduces the surface tension of water, the result being that the final spreading pressure is negative and the benzene retracts to a lens (Davies and Rideal, 1963). The reduction in the surface tension of a substrate by a monolayer is termed the film pressure of the monolayer. The film pressure of a monolayer of benzene on water is

$$\Pi = 72.8 - 62.2 = 10.6 \text{ dynes/cm}$$

When the film pressure is greater than the spreading coefficient of a material, this material forms a lens. The maximum thickness of the lens is given by

$$t_{\max}^2 = \frac{2(\Pi - S)}{g\rho_B(\rho_A - \rho_B)} \rho_A \quad (3.4)$$

There have been several investigations to measure the rate and understand the manner in which a monolayer spreads. Garrett and Barger (1970) have measured the rates of spreading of several surface active materials and have shown that the spreading velocities were a direct function of the spreading pressure. DiPietro, Huh and Cox (1978) have suggested that an advance film of mono-molecular or sub-micron thickness forms at the contact line between A and B,

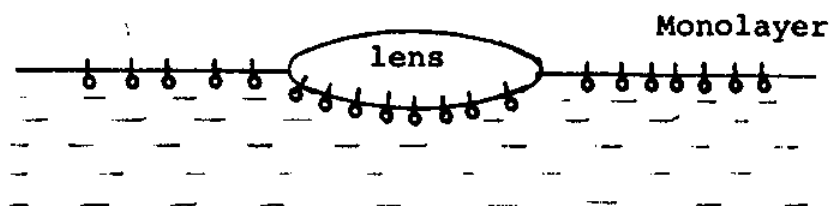


Figure 3-4 Lens Formation Due to Monolayer

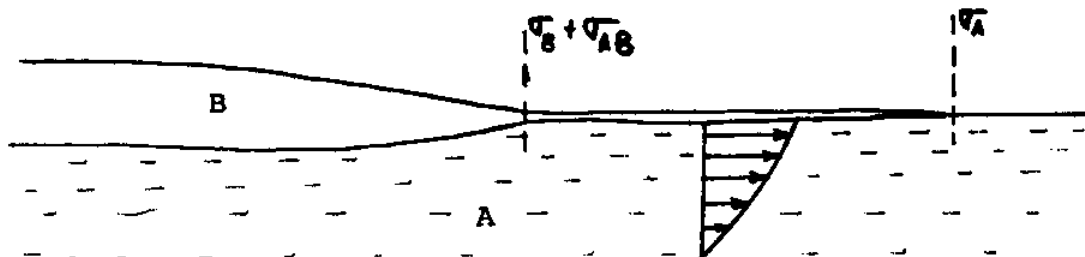


Figure 3-5 A dynamic spreading model with an advance film along which the surface tension varies from $\sigma_B + \sigma_{AB}$ to σ_A

distinct from the bulk phase. This film varies in thickness from bulk phase to the leading edge of the advance layer (Fig. 3-5). The composite interfacial tension would vary from $\sigma_{AB} + \sigma_B$ at the bulk phase to σ_A at the leading edge. Thus the spreading force S_{BA} is distributed over this advance film, rather than having a force acting along the three phase contact line producing infinite velocity there.

The governing equations for this model are the conservation of mass,

$$\frac{\partial h}{\partial t} + \nabla(h\underline{u}) = 0 \quad (3.5)$$

and the surface tension gradient balanced by the viscous shear stress

$$\nabla \underline{\sigma} + \underline{\tau} = 0 \quad (3.6)$$

The shear stress would be dependent on the kind of boundary layer under the spread. Most of the analysis carried out assume a laminar boundary layer, though a calculation of the Reynolds number for large oil slicks indicates that turbulent boundary layers may be present under such slicks.

The value of σ varies with thickness, h , and for multi-component spreading mixture (oils), with concentration of the components. Thus

$$\sigma = \sigma(h, c)$$

It is the purpose of part of this report (Chapter 5 & 6) to show that compositional differences do exist in this region of an oil slick.

4. INVESTIGATION OF THE SURFACE AND SPREADING PROPERTIES OF FOUR CRUDE OILS

In this chapter, the measurement of surface and spreading properties of four crude oils are reported followed by a comparative discussion of these properties.

Four crude oils - a Libyan crude oil called Zuetina (ZUE), an Algerian crude, Arzew (ARZ), an Arabian crude called Arabian Light (ABL) and THUMS (for Tidewater, Humble, Union, Mobile and Shell), a Californian crude oil, were investigated.

When each of these oils was allowed to spread on water in a petridish, the equilibrium state of the oil, after it stopped spreading, was of regions of spatially varying film thickness (Fig. 4-1).

ABL, ZUE, and ARZ spread into three distinct thickness formations. The thickest regions are small, dark, usually circular lenses. The less thin part of the spread occupies most of the spread area. It is less dark than the thick lenses and does not seem to assume a lens-like, circular formation. The thinnest region is almost colorless and maybe made up of a monolayer or very thin film. It is usually the outermost region and stops the other parts of the oil from spreading into it. These distinctions

are most apparent in ABL and are almost fuzzy in the case of ARZ. (Fig. 4-1)

In the case of THUMS, the equilibrium state is a thick dark region of oil surrounded by a colorless thin film. The film of intermediate thickness found in ABL, ZUE and ARZ is absent here.

It should be noted that in the above cases, the spreading of oil was restricted by the walls of the petridish. In an open water oil spill, there would not be such restraints.

Figure 4-1 illustrates the spreading of a relatively large amount of oil, all placed on the water at the same time. Figure 4-2 shows the spreading configuration when the oils are spread slowly, drop by drop, on the water. The oil was introduced to water, a drop at a time, each drop being permitted to spread, before the next one. The new drops were placed in the thick region of the original spread. In the case of ABL and ZUE, the surface-active components in the thin film created by the spreading of new drops pushing against the original thick film can be clearly seen. The same is true of ARZ but to a lesser extent. In the case of THUMS, however, after first drop, no more spreading takes place. The additional drops form thick distinct lenses and do not spread at all as seen in Figure 4-2d.

A gas chromatographic analysis, (See Appendix I), of the oils was done. The heavy asphaltene were first removed by dissolving the oils in pentane, centrifuging for 45 minutes and decanting the supernatant liquid.

The largest amount of precipitate was obtained from ABL, followed by THUMS and ZUE with ARZ having hardly any. The chromatograms are shown in Figure 4-3. The chromatograms of ARZ, ZUE and ABL show a striking similarity.

Several measurements of oil properties were done. They are listed in Table 4-1.

Surface and Interfacial tension: The surface tension and interfacial tension were measured by the du Noüy's Ring method. This involves the determination of the force required to detach a ring from a surface or interface (See Appendix I). The average values of σ_o and $\sigma_{o/w}$ measured at about 25°C are shown in the table.

Spreading Coefficient: The spreading coefficient is calculated from Equation 3.2. In this case the substrate A is water and the spreading liquid B is oil. For example, for ZUE, the spreading coefficient is

$$S = 72 - (24.3 + 23.1) = 24.6 \text{ dynes/cm}$$

Specific gravity: Specific gravity was measured using glass float hydrometers.

Viscosity (μ): Cannon-Fenske Routine Viscometers were used to measure the Kinematic viscosity (ν) of the oils. The dynamic viscosity (μ) is obtained from

$$\mu = \rho \nu$$

Average thickness of unrestricted spread: This was determined by allowing unrestrained spreading of a 1 μ l drop of oil. The extent of the spread was determined by first sprinkling the water surface with talc and then measuring the area of the region from which talc was pushed away by the oil. The average thickness of the oils measured (Table 4-1) show widely different values indicating different spreading modes.

Film pressure of monolayer: As described before and shown in Figure 4-1, spreading oil is preceded by an extremely thin, colorless film. It is, in all probability, made up of the more surface-active fraction of the oil which spreads out first and if it encounters a boundary or wall it then restricts the rest of the oil from further spreading. This film may be a monolayer and is certainly less than 300 Angstroms thick. Canevari (1969) has shown that oil becomes barely visible only when it is more than 300 Angstroms thick.

An experiment to determine the film pressure was performed. A Wilhelmy slide (See Appendix I) was partially immersed at one end of a narrow trough (12" x 3 1/2") of water (Fig. 4-4). A drop of oil, a little more than required to cover the surface of water in the trough, is let to spread at the other end.

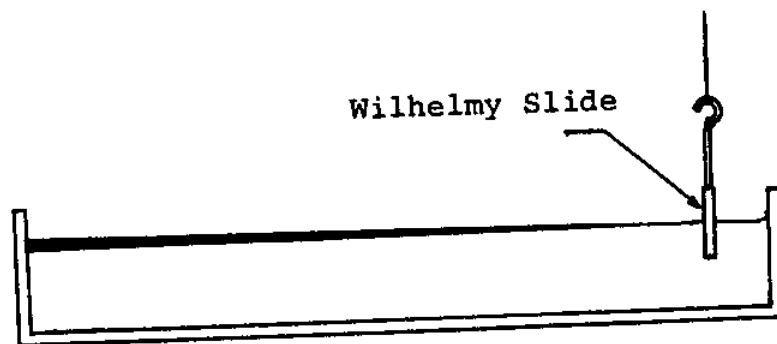


Fig. 4-4 (thickness of oil exaggerated)

This way, only the thin film surrounds the Wilhelmy slide when the oil has spread completely or to equilibrium. The reduction in the surface tension of water (film pressure of monolayer) is determined by measuring the change in pull on the slide due to the surface layer.

Spreading rate: The velocity of the leading edge of each of the oils was determined by spreading the oil in a long (6' x 1/2') channel of water. Talc was sprinkled at a known location along the channel and the time taken for the leading edge to reach it was measured. This was done for several distances along the channel for each oil. The average rate was then calculated.

TABLE 4-1

	<u>ZUE</u>	<u>ARZ</u>	<u>ABL</u>	<u>THUMS</u>
Surface tension (dynes/cm)	24.3	24.6	26.3	29.9
Interfacial tension with water (dynes/cm)	23.1	29.3	28.6	24.0
Spreading Coefficient (dynes/cm)	24.6	18.1	17.1	18.1
Specific gravity	.822	.804	.860	.923
Viscosity (Centi Poise)	4.04	2.91	8.43	136
Average thickness of unrestricted spread (Angstroms)	833	2500	1110	160
Film pressure of monolayer (dynes/cm)	1.4	0.3	1.7	3.9
Average rate of spreading (cm/s)	6.4	13.5	7.6	6.4

In a qualitative comparison, similarities can be seen in the spreading behavior (Figs. 4-1 and 4-2) and compositional make-up (Fig. 4-3) of ZUE, ARZ and ABL as opposed to THUMS. This also appears in the values for viscosity, average thickness (while ZUE, ARZ and ABL have average thicknesses of scores of molecules, THUMS has a very small - almost molecular average thickness); and in film pressure of the thin layer. The similarities may be due to the fact that ZUE, ARZ and ABL come from the same general region of the earth (Libya, Algeria and Saudia Arabia respectively) while the Californian THUMS occurs in an almost diametrically opposite part of the planet. From the large envelope in its chromatogram, it seems that THUMS has a large amount of heavy aromatic and asphatene components which could account for its high viscosity and specific gravity.

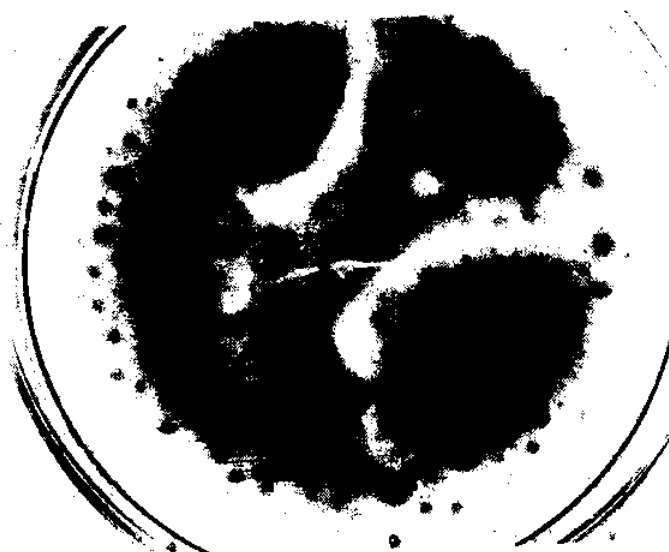
From Table 4-1, it can be seen that while ZUE has a relatively high spreading coefficient, it does not seem to effect the other properties investigated. ARZ, for example, which has a lower spreading coefficient and the lowest film pressure of all four, yet for some unknown reason has the fastest spreading rate. THUMS has largest film pressure which could explain its very low average thickness.

There is little correlation in properties investigated and it could be conjectured that the chemical and physical properties of the individual components of the oils are more important than the bulk values of these properties.



ARZ

(a) SPREADING OF ARZ



ZUE

(b) SPREADING OF ZUE

Figure 4-1



ABL

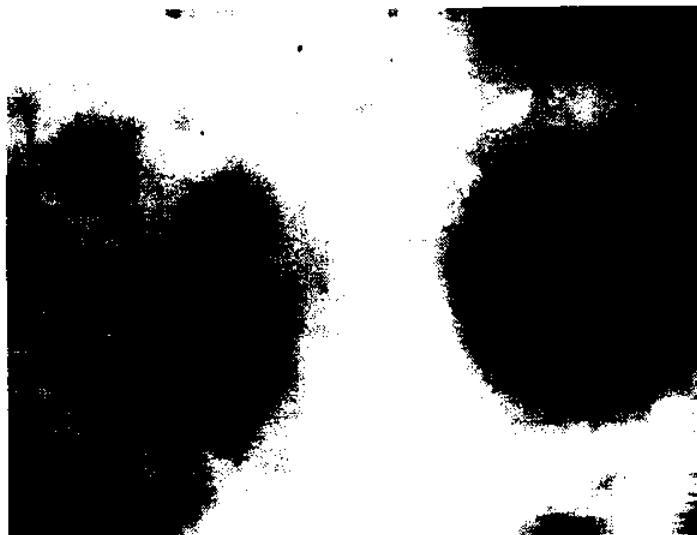
(c) SPREADING OF ABL



THUMS

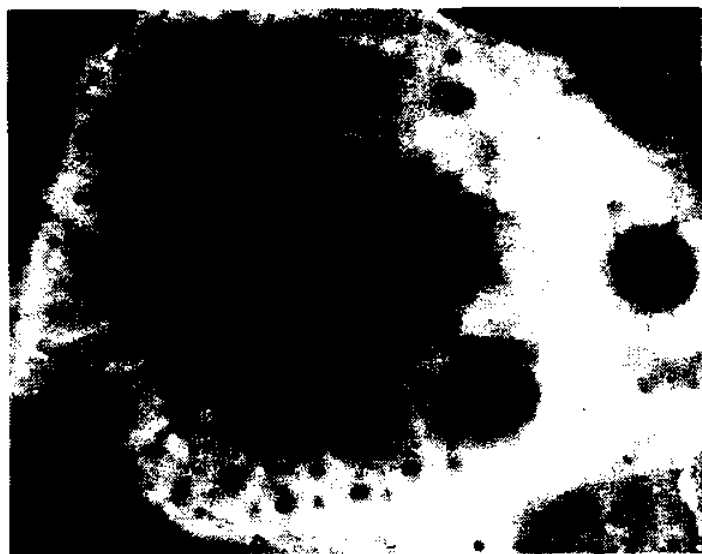
(d) SPREADING OF THUMS

Figure 4-1



ARZ

(a) ARZ



ZUE

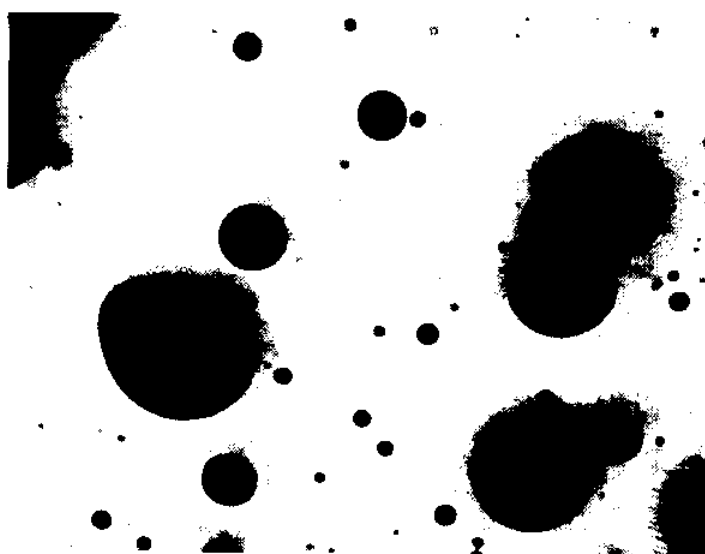
(b) ZUE

Figure 4-2



ABL

(c) ABL



THUMS

d) THUMS

Figure 4-2

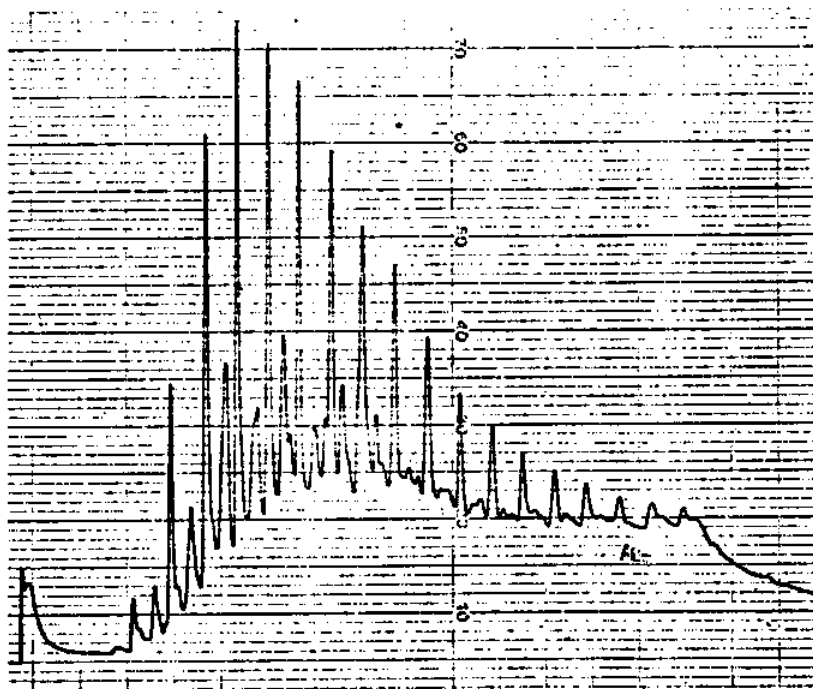


Figure 4-3(a) Gas Chromatogram of ARZ

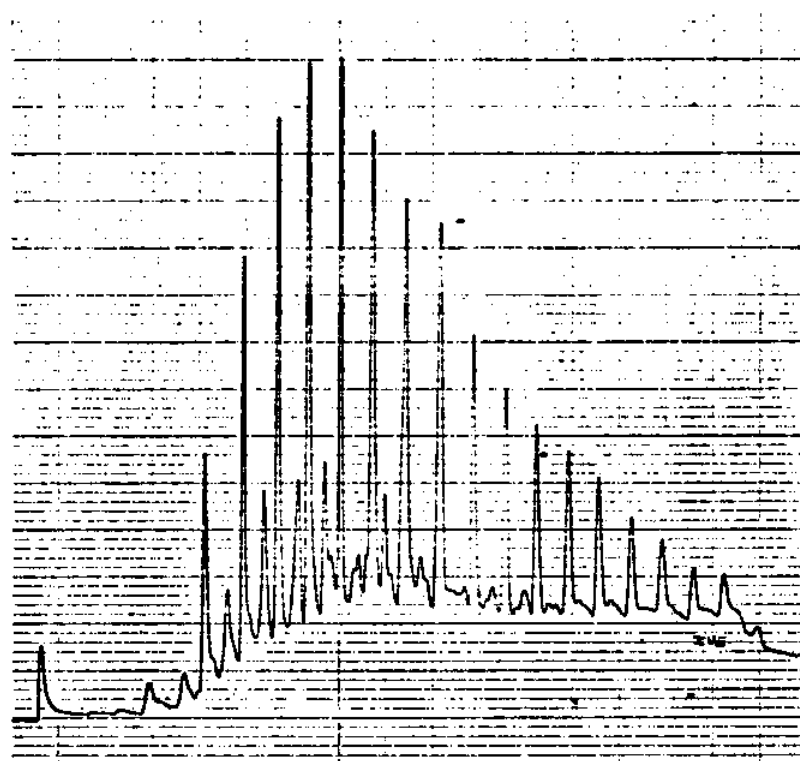


Figure 4-3(b) Gas Chromatogram of ZUE

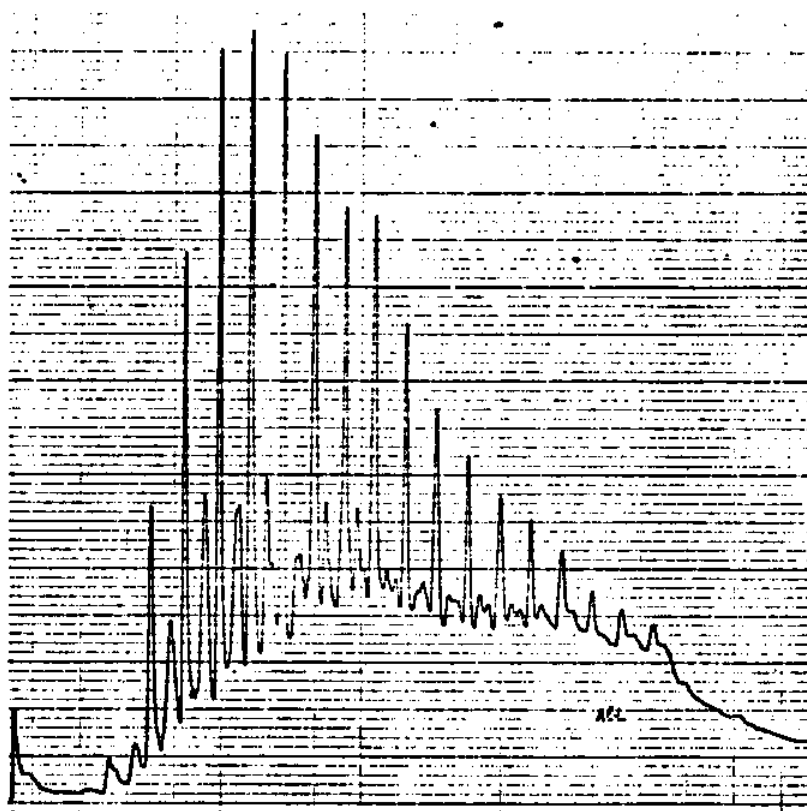


Figure 4-3(c) Gas Chromatogram of ABL

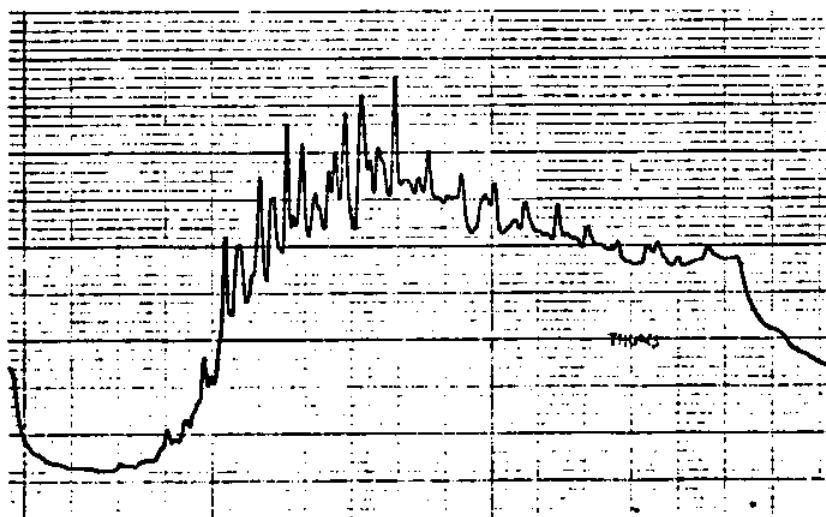


Figure 4-3(d) Gas Chromatogram of THUMS

5. SPREADING OF 2- AND 3- COMPONENT HYDROCARBON MIXTURES

To show that components of a hydrocarbon mixture (crudes are mixtures of hundreds of hydrocarbons and other organic compounds) spread out and fractionate in relation to the spreading coefficients of the components, synthetic mixtures of hydrocarbons with known spreading coefficients were made and spread. Similar experiments have been performed by Philips and Groseva (1975) with a mixture of toluene, octane and decane. However, the time interval after commencement of spreading and the size of the surface area of water they used (bowl of diameter 35cm with samples taken 5 and 15s after beginning) indicate there may have been interaction with the wall. Experiments done by the author show that it takes 16s for 0.1ml of toluene - octane - decane mixture to spread to a radius of 45 cm. It is known that the initial rate of spreading, just after inception is much higher.

In the experiments with the toluene - octane - decane mixture, it was noted that when the film got very thin, the toluene evaporated (vapor pressure of toluene at 20°C is high compared to that of octane and decane), reducing the accuracy of sampling.

In order to overcome these difficulties, it was decided that p-cymene was a more suitable surface active hydrocarbon for the experiment.

Experiments

Equivolume mixtures of cymene-decane, cymene-octane, and cymene-octane-decane were used in these experiments. The spreading was done in a tank of 90cm by 90cm by 15cm deep containing water. Properties of the components are given in Table 5-1. 0.5 ml volumes of these mixtures were placed on the surface of the water in the center of tank and let to spread.

TABLE 5-1

	<u>Surface Tension (dynes/cm)</u>	<u>Interfacial Tension (dynes/cm)</u>	<u>Spreading Pressure (dynes/cm)</u>
Cymene		34.6	10.1
Octane	21.8	50.8	.2
Decane	23.9	51.2	-2.3

Samples of the spread at various radial distances from the center were collected using open-ended glass cylinders of 25mm inner diameter. Four or five such cylinders were held in a frame. Five seconds after beginning of spreading the frame was placed on the tank such that the cylinders were

lowered sharply through the surface of the water. The cylinders were then closed at both ends with stoppers, enclosing a cylinder of water with a thin layer of mixture on its surface. This film was extracted by putting 1 ml of carbon disulfide in the cylinder and shaking. The carbon disulfide and water was poured into a cone-bottomed centrifuge tube. The carbon disulfide settled to the bottom as it is heavier than water and was drawn out with a syringe. The samples were analyzed in a temperature programmed gas chromatograph using OV-17 as the liquid phase in the column (See Appendix I). An example is shown in Figure 5-1. The area under the peak is proportional to the amount of component in the sample. However, equal volumes or equal masses of different components will not necessarily have the same area under their peaks.

Results

The raw data from the gas chromatograph were analyzed by using data obtained from a calibrating mixture containing one part of the equivolume mixture to a hundred parts of carbon disulfide. The relative volume of each component at various distances is computed using

$$\% \text{ volume of } X_n = \frac{\text{Area of } X_n \text{ peak} / F_n \times 100}{\sum_i (\text{Area of } X_i \text{ peak} / F_i)} \quad (5-1)$$

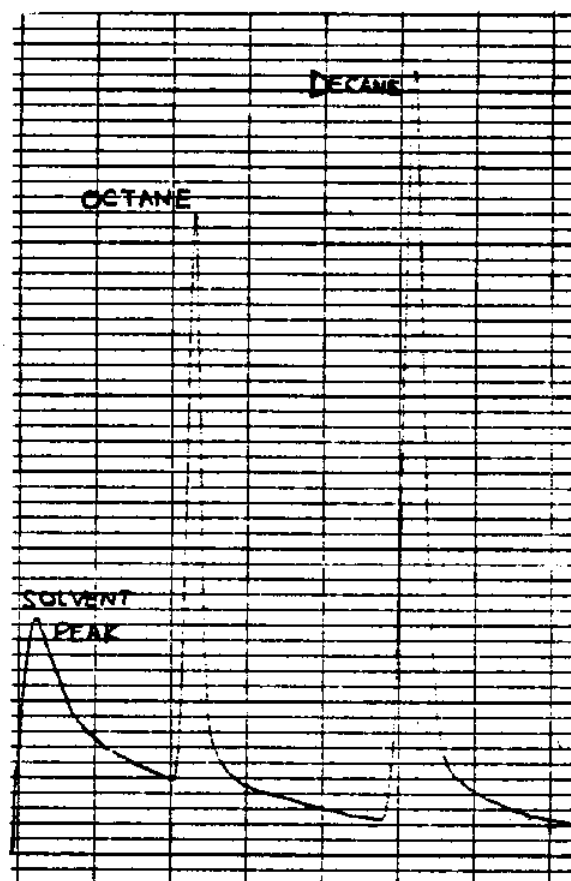


Figure 5-1 Gas Chromatogram of an octane-decane sample

where X_i are the individual components and F_i their correction factors. The correction factors are obtained from the chromatograms of the calibration samples and are the ratios of areas of different components produced by this sample. For example, if there are two components A and B whose equivolume calibration produced areas a and b respectively, then if the correction factor $F_A = 1$, implies $F_B = \frac{b}{a}$. Now, suppose for a particular location in the spread the areas are p and q for A and B respectively, then

$$\% \text{ volume fraction of A} = \frac{pb}{pb + qa} \times 100$$

The results of this analysis is shown in Figure 5-2 for the cymene-decane mixture, in Figure 5-3 for the cymene-octane mixture and in Figure 5-4 for the cymene-octane-decane mixture. It is clear that mixtures which are equivolume to begin with (50% of each component in the cymene-decane and cymene-octane mixtures, and 33 1/3% of each component in the cymene-octane-decane mixture) change in their relative compositions with distance along the spread.

In Figure 5-2 and 5-3, p-cymene is the dominant component with increasing distance from the center. This is in good agreement with the spreading coefficients in Table 5-1. The 3-component mixture is a little more complicated. n-Octane

is the dominant component at about 25cm but almost completely disappears at the edge of the spread. This may be due to evaporation or dissolution. Again cymene comes out as the component with the highest fraction at the edge, but is not as preponderant as in the case of the cymene-decane mixture.

Figures 5-5 to 5-9 show the exact volume per 5 square centimeters (area of sampling cylinder) as a function of distance. When this value is divided by 5cm^2 , the film thickness is obtained. Octane spreads in lenses and a thin layer, most of which is concentrated around the center. The spreading is not uniform, hence the scatter of the data points. When just decane is spread, it forms a lens about 15cm in diameter which is not stable and breaks up into smaller lenses.

Using Fay's inertia-gravity and viscous-gravity laws (Table 1-1), if they are valid for such a small volume, 5 seconds after the commencement of spreading, the leading edge would be at 7.5cm and 6cm respectively, indicating that all the spreading in the experiments is due to surface energies.

It is interesting to note that the film of a cymene spread is thinner than the films of the mixtures (Fig. 5-10). The film of the three-component mixture is thicker than the other films at the leading edge and may be moving faster since

it shows signs of boundary reflection. This seems to suggest the components with lower or negative spreading coefficients push the more surface-active components away from the center - more than they would when spreading by themselves.

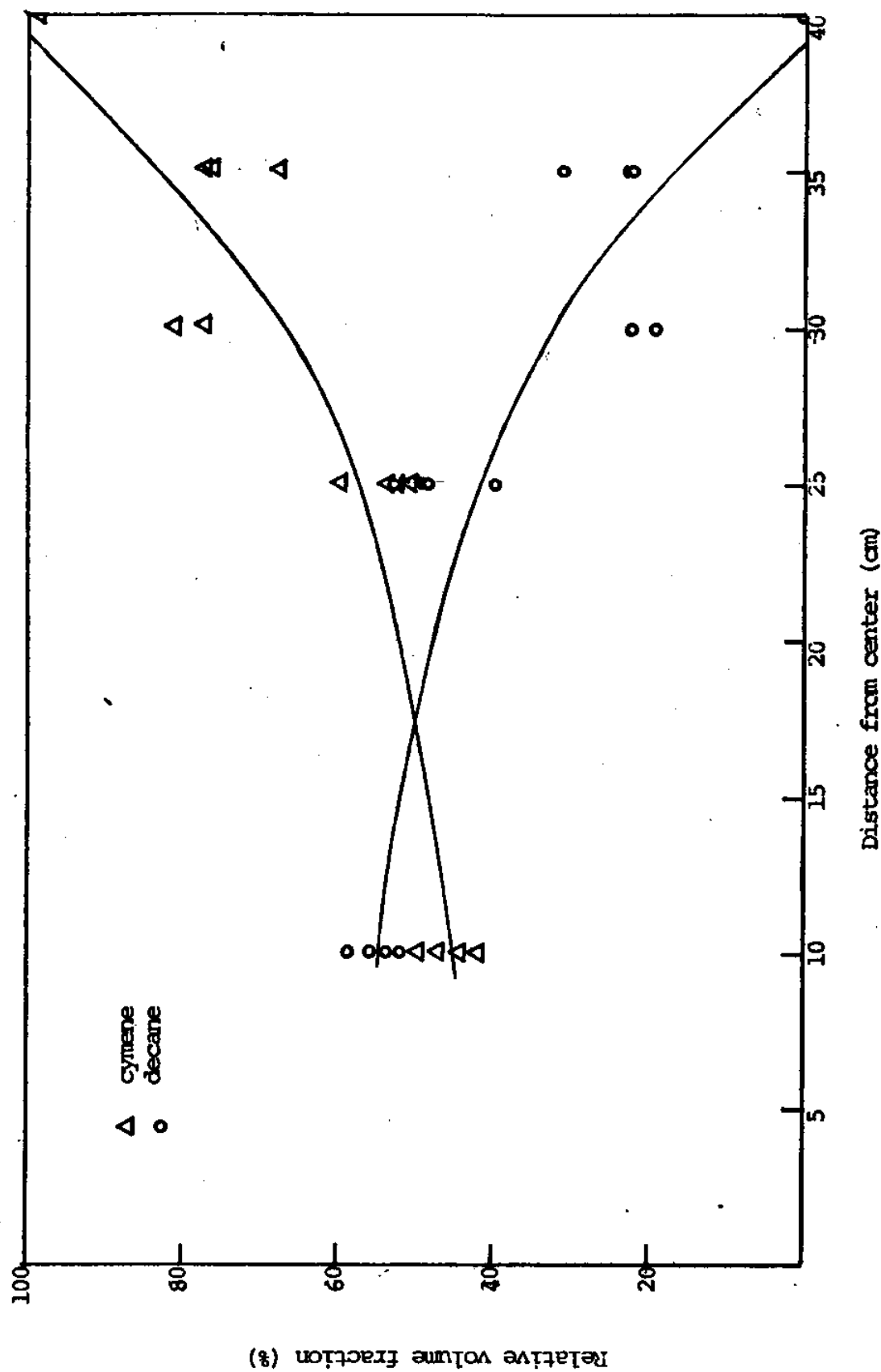


Figure 5-2: Relative volumetric fractions vs. distance for decane-cymene mixture at 5s.

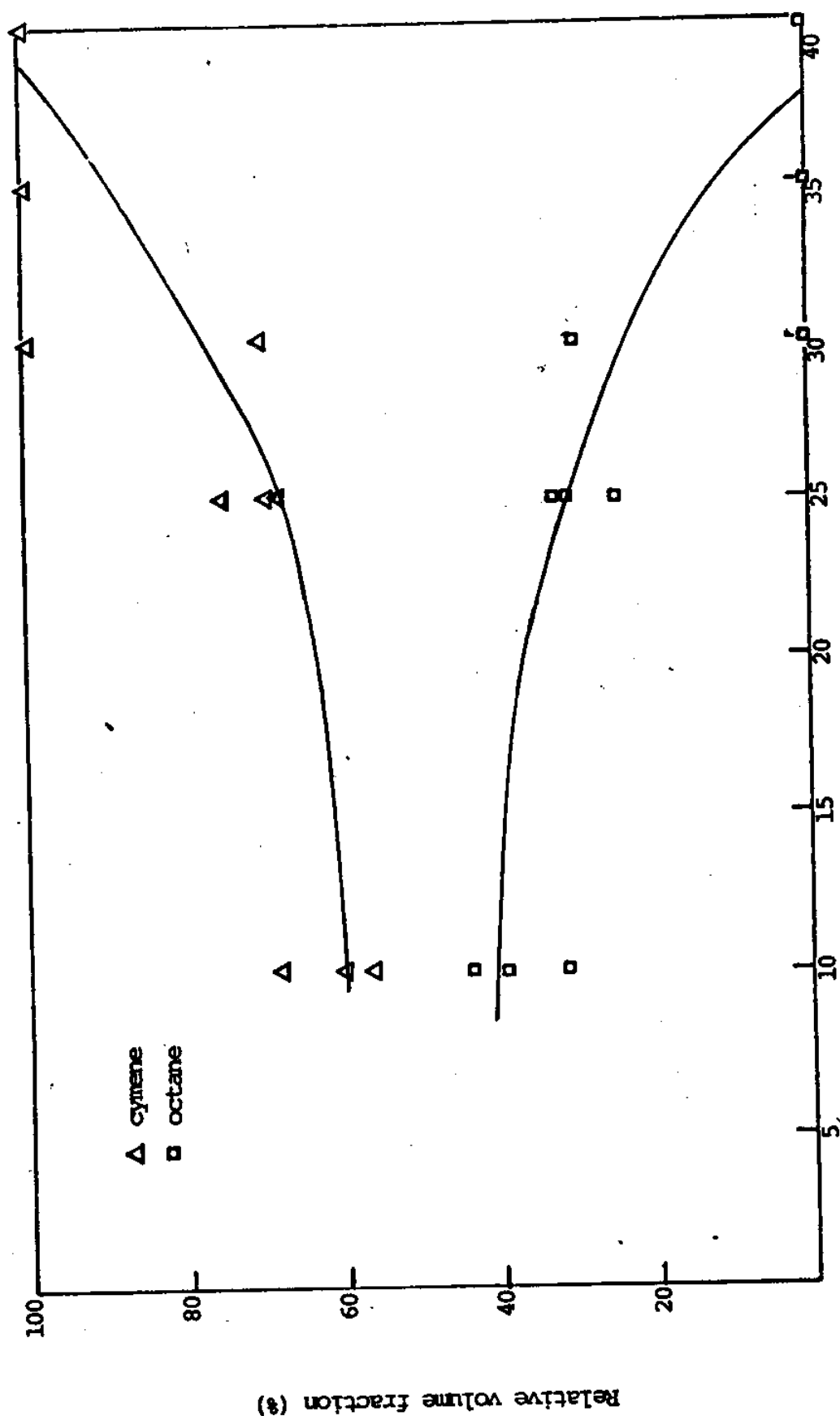


Figure 5-3: Relative volumetric fractions vs. distance for cymene-octane mixture at 5s.

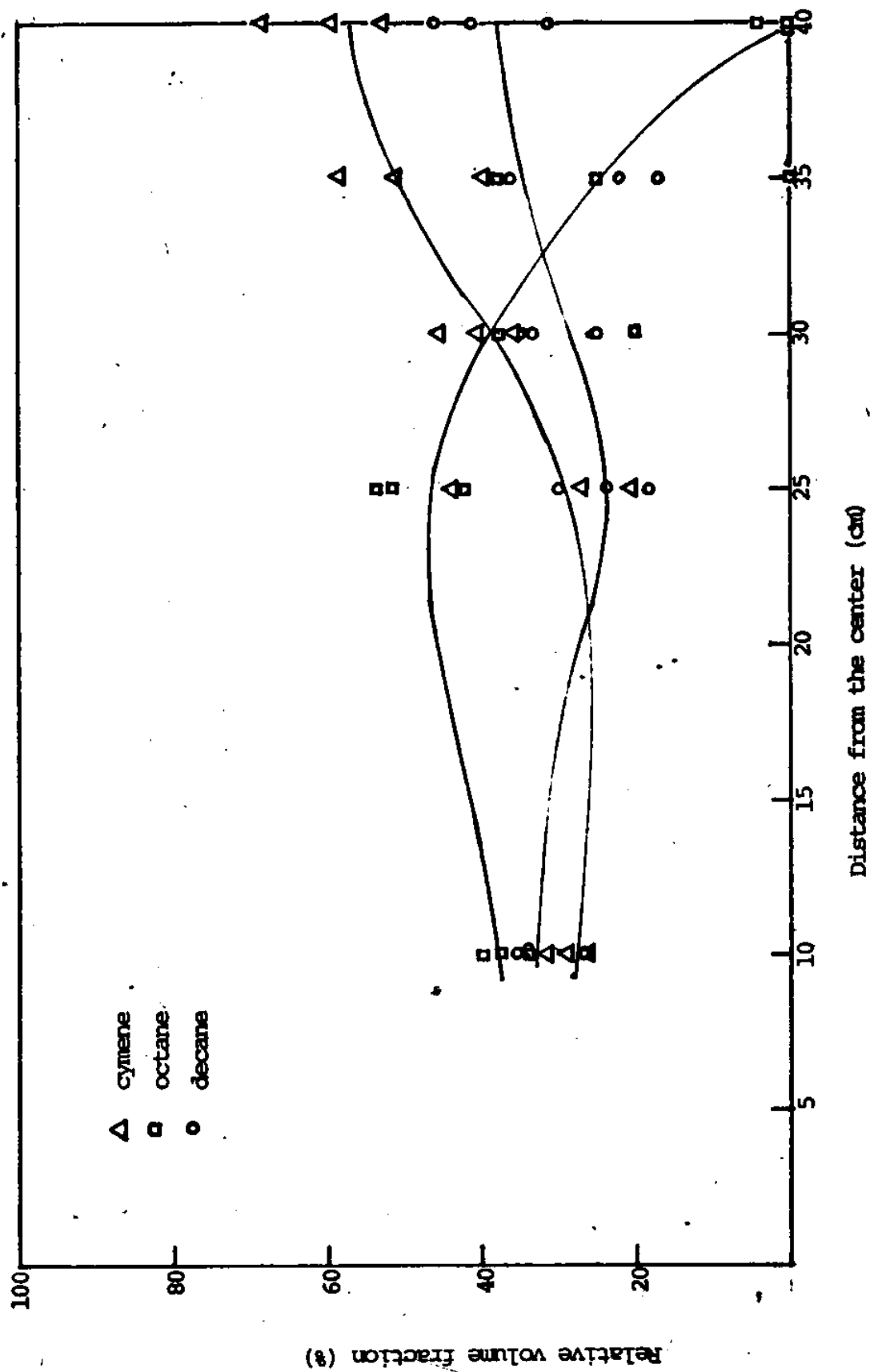


Figure 5-4: Relative volumetric fractions vs. distance for cymene-octane-decane mixture at 5s.

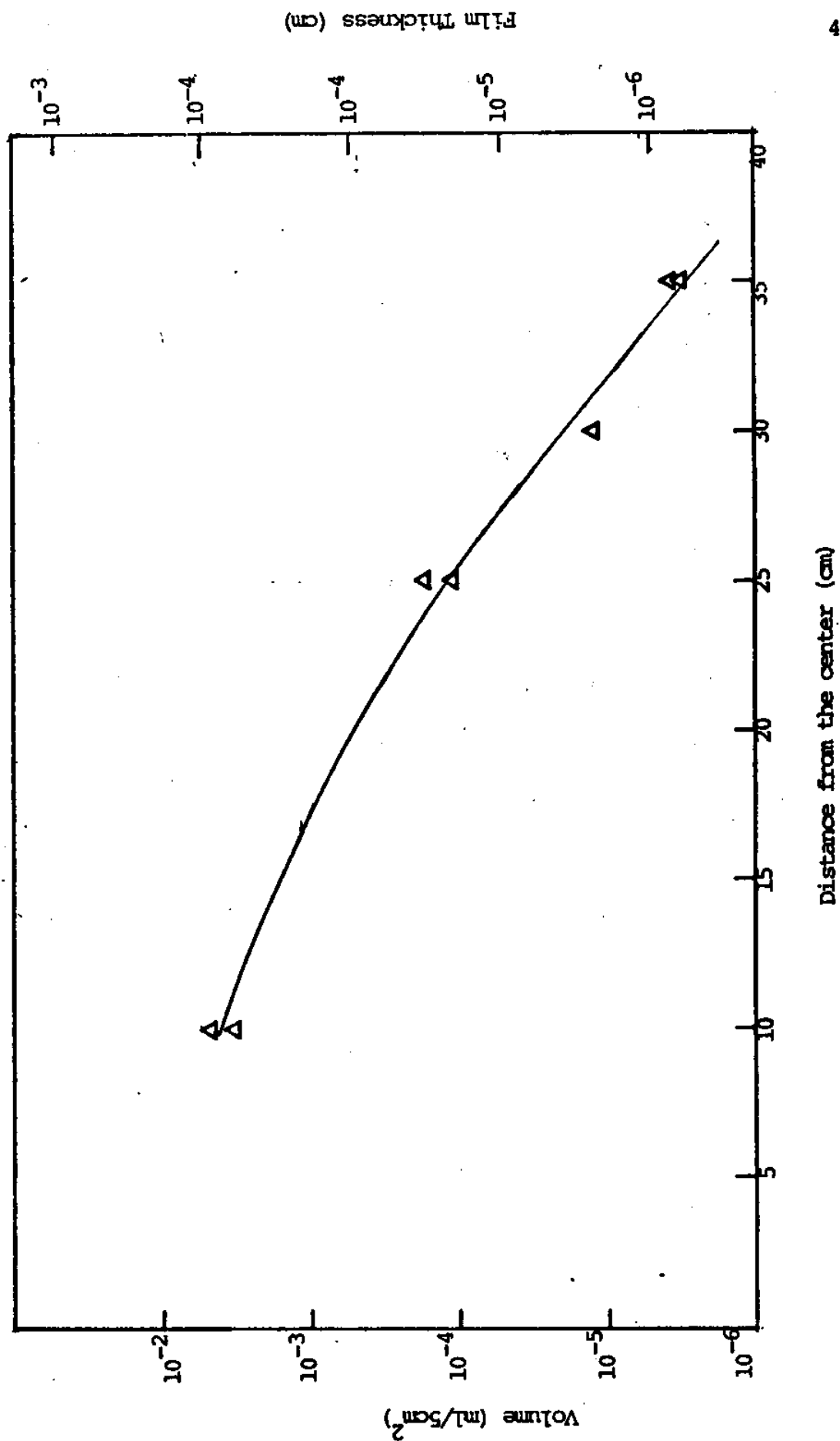


Figure 5-5: Volume/Film Thickness vs. distance for cymene after 5s.

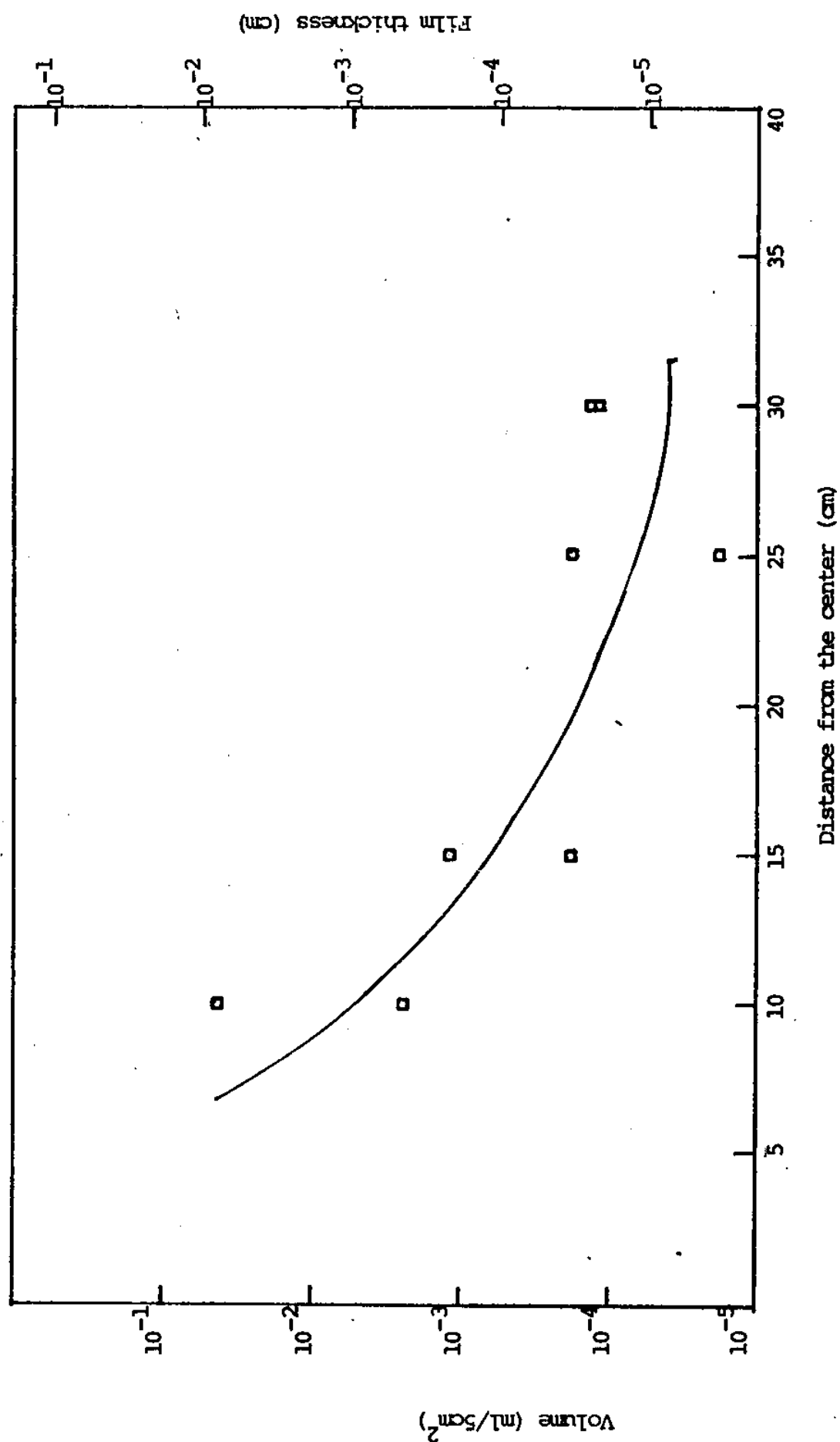


Figure 5-6: Volume/Film Thickness vs. distance for octane after 5s.

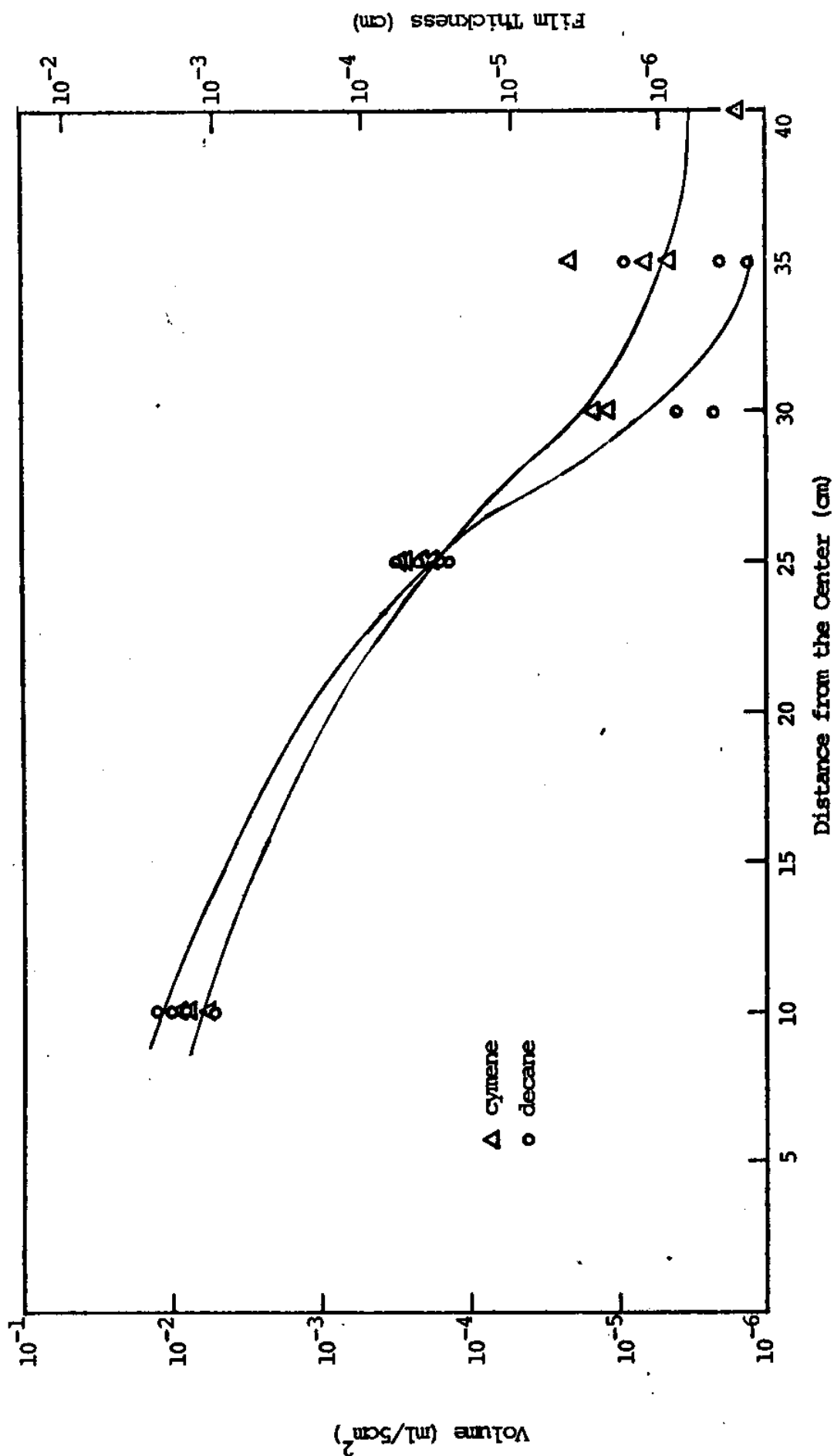


Figure 5-7: Volume/Film Thickness vs. distance for cymene-decane mixture after 5s.

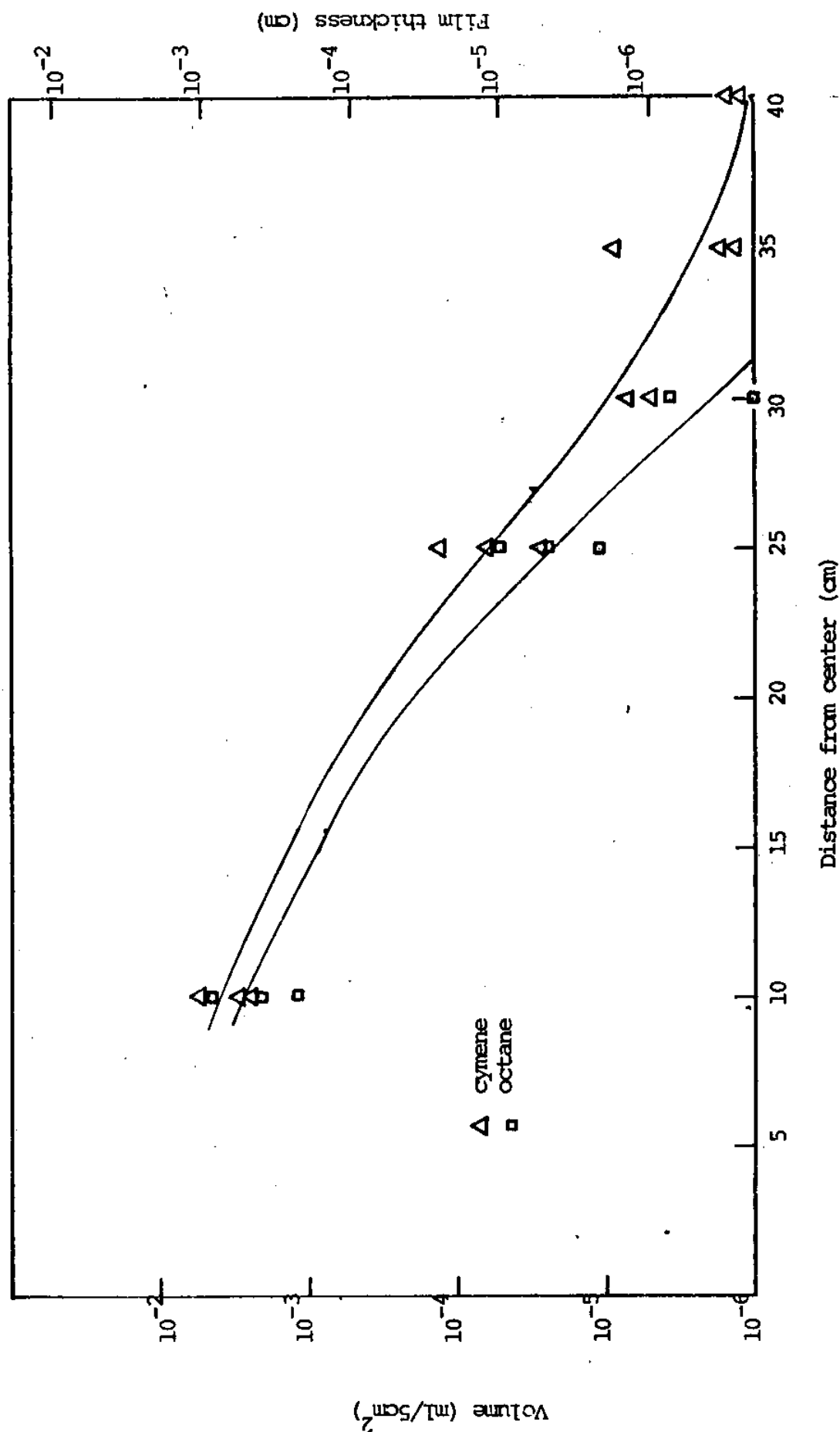


Figure 5-8: Volume/Film Thickness vs. distance for octane-cymene mixture at 5s.

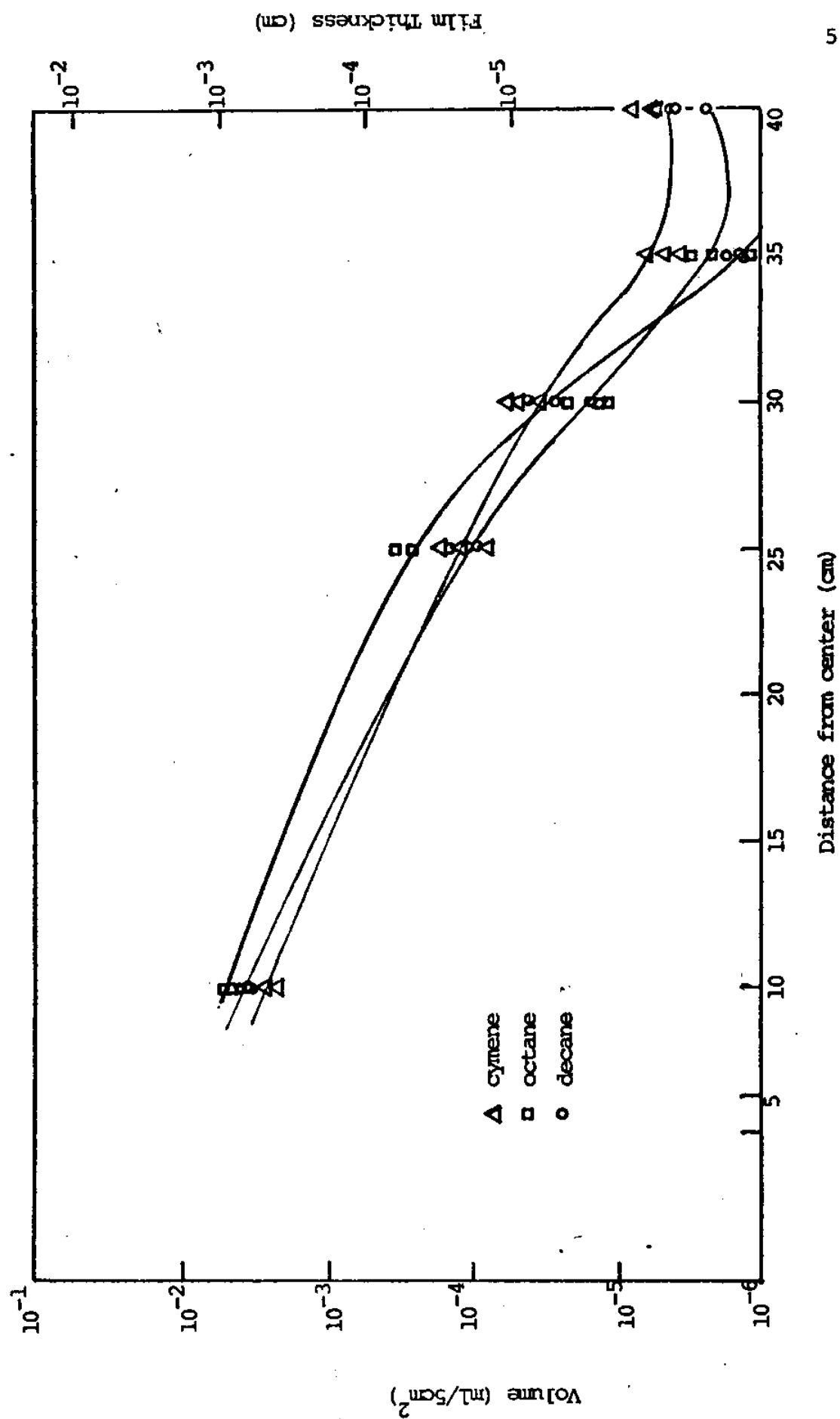


Figure 5-9: Volume/Film Thickness vs. distance for cymene-octane-decane mixture at 5s.

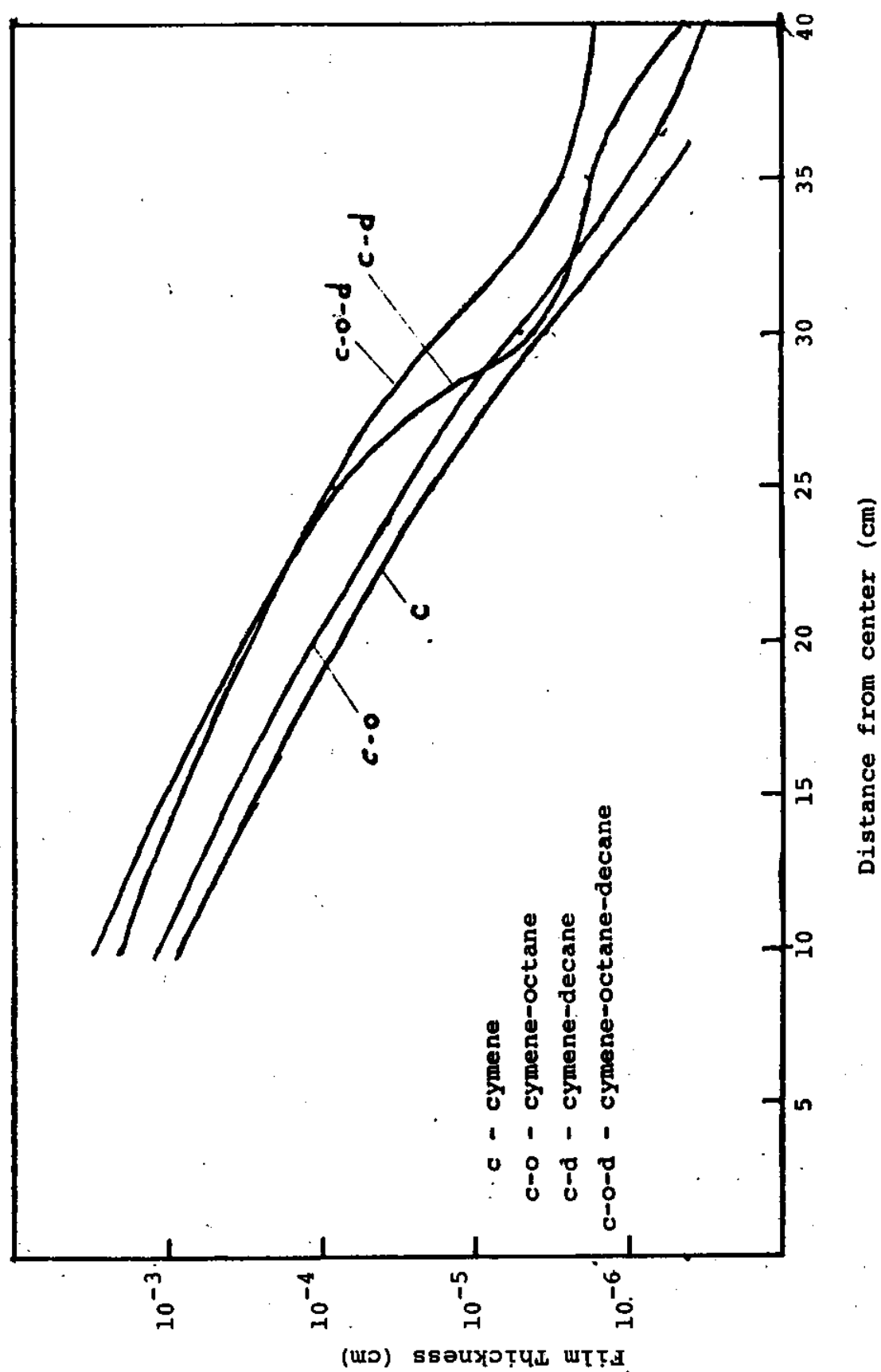


Figure 5-10. Average film thickness of the different mixtures 5s after commencement of spreading.

6. THE SPREADING OF DIESEL OIL

In the last chapter it was shown that for a synthetic mixture of hydrocarbons fractionation does occur whilst spreading. The more surface active components spread out further and faster than the less surface active components. However, the phenomenon is not that simple. The surface active components while spreading out carry with them some non-spreading components. In some cases, components are found farther from the centre than components with a higher spreading coefficient (octane and decane, in the cymene-octane-decane mixture).

Here it is shown that fractionation occurs in the more complicated multi-component petroleum products too. The oil used was No. 2 Diesel fuel. Diesel fuel was chosen instead of the heavier crudes since diesel does not contain the heavier hydrocarbon and asphaltenes and did not have to be centrifuged to remove these components before injection into the gas chromatograph. The experimental procedure used was similar to that used for the "synthetic oil" mixtures. Samples were taken at 15, 25 and 35cm from the center and 5 seconds after inception of spreading. The extraction procedure was the same as described in Chapter 5. Fig. 6-1 is a chromatogram of unspread diesel dissolved in carbon disulfide. Figures 6-2 and 6-3 show the results of spreading. There are distinct changes in composition with distance away from the center. The unresolved envelope

(the unresolved hump under the peaks, see Fig. 6-1) gets smaller with distance away from center. While other changes are not consistent and difficult to identify, there is a prominent relative increase of the nC_{14} component at the outer edges of the spread. This is also true of the smaller isoprenoid peaks on both sides of nC_{16} . Not enough information was obtained to make a quantitative analysis, but the fractionation effect is clearly demonstrated.

In the equilibrium state, when the leading edge has reached the boundaries and enough time has elapsed for the spread to become stable, the spread is made up of two regions. There is the "thick" region (about 0.5mm in thickness) that makes up most of the spread and the thin monolayer on its outer edge. Several attempts were made to concentrate and identify the surfactant in the monolayers. The quantities involved are very small and none of the attempts were successful.

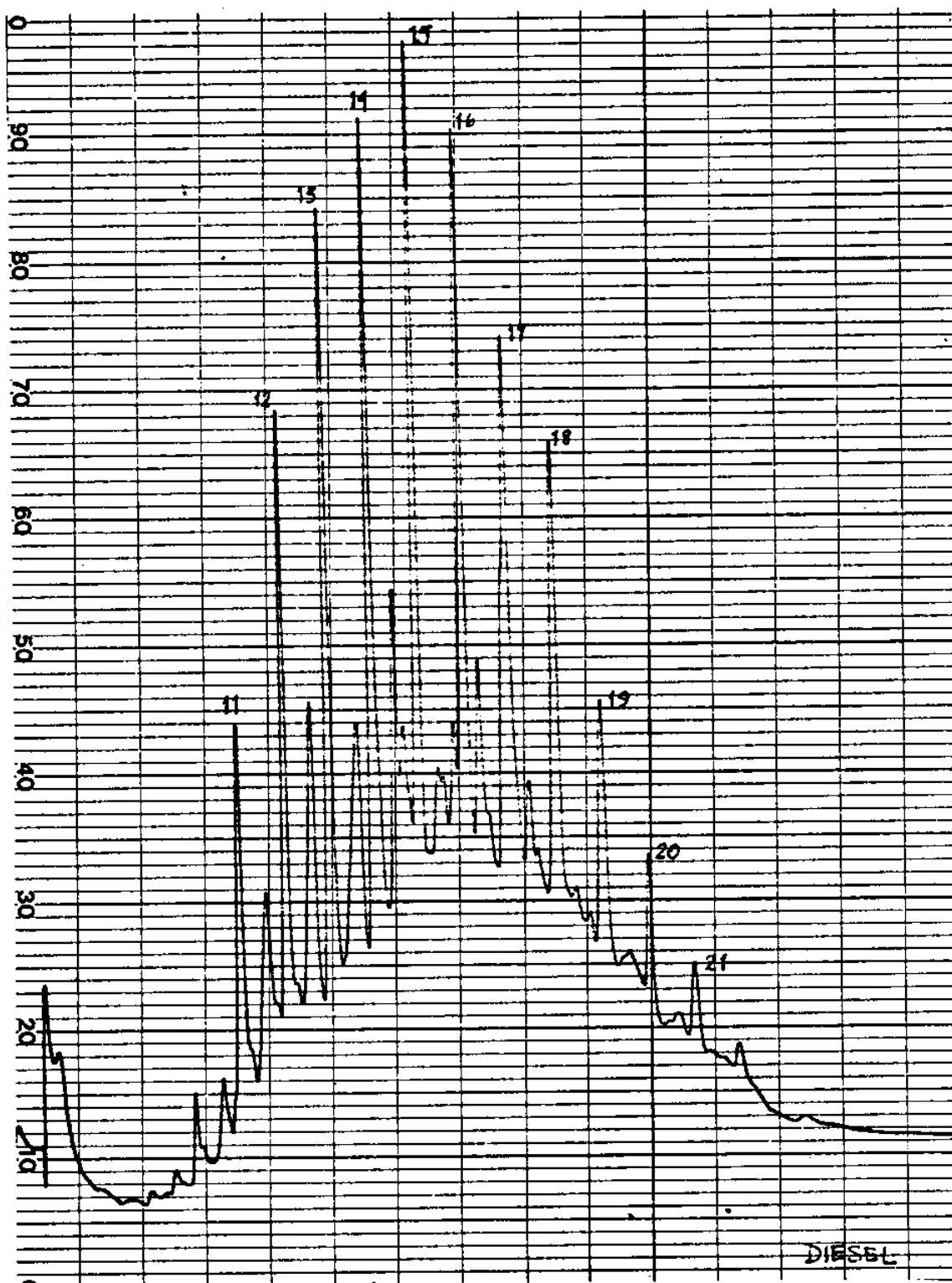
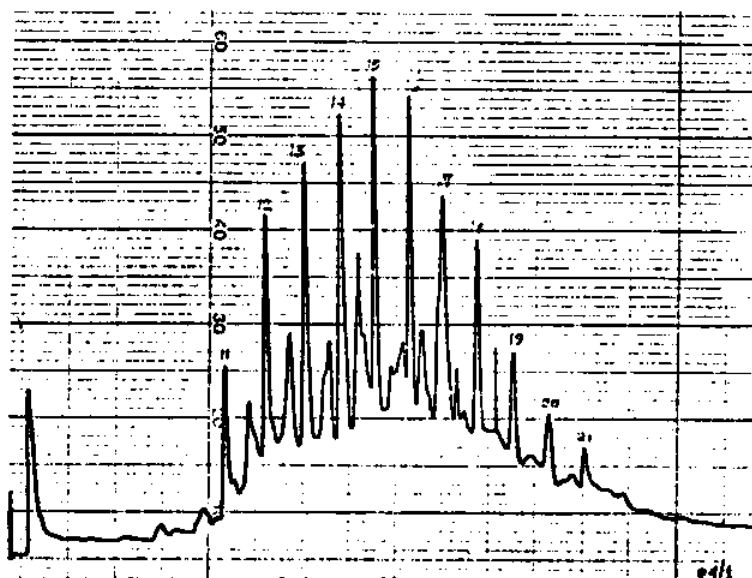
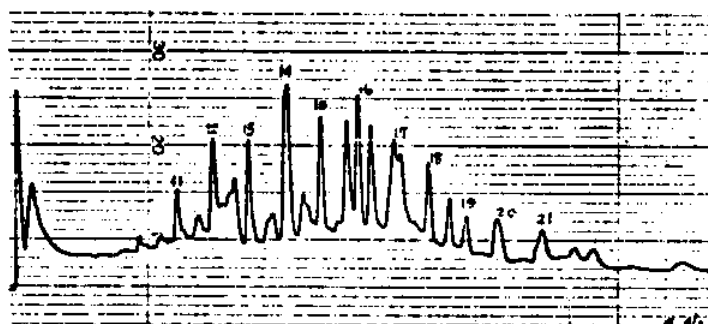


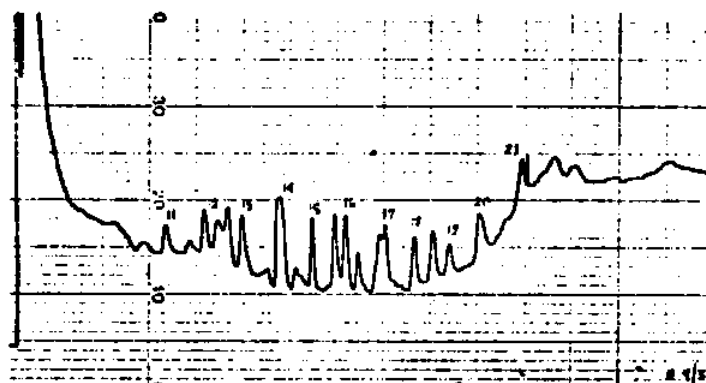
Figure 6-1 Gas Chromatogram of Unsprea Diesel



(a) 15 cm from center

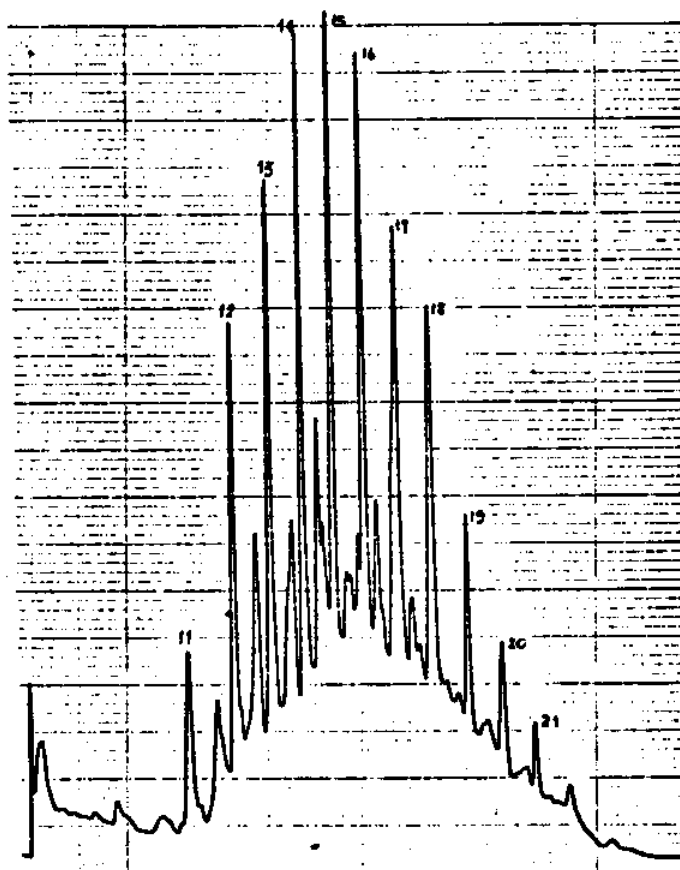


(b) 25 cm from center

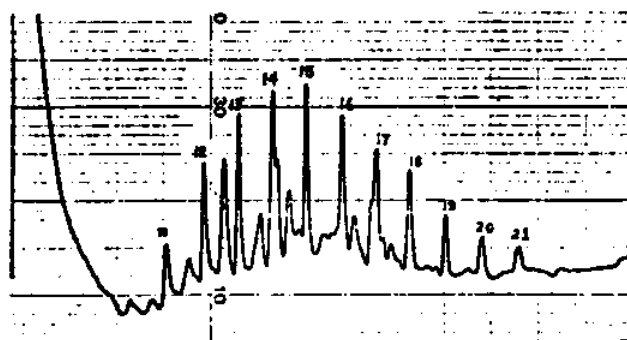


(c) 35 cm from center

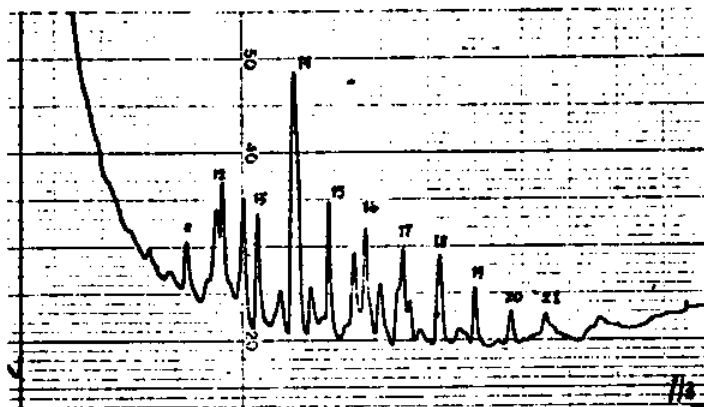
Figure 6-2 Gas Chromatogram of Spread Diesel



(a) 15 cm from center



(b) 25 cm from center



(c) 35 cm from center

Figure 6-3 Gas Chromatogram of Spread Diesel

7. CONCLUDING REMARKS

From the experiments described in Chapter 5, it can be concluded that in a multi-component mixture the spreading of the individual components is dependent upon the spreading pressures of the components. The non-spreading components are sometimes "carried" by the spreading components and spread further out than they would by themselves. As the number of components increase, the spreading mode becomes more complicated. Other physical processes like evaporation and dissolution also affect spreading.

From a number of experiments done with four crude oils, it was seen that the bulk values of the properties of oils were not representative of their spreading behavior. Properties of individual components or group of components dominate certain actions of the spread. It would seem, therefore, to predict spreading modes, knowledge of the physical and chemical properties of the individual components, or at least the dominant components would be required - which is hardly a simple problem.

Results from various experiments (See Appendix II) indicate that the thick layer regions observed in oil slicks at sea is made of water-in-oil emulsions. Micro-

photographs of samples taken from thick layer regions of oil slicks in at-sea experiments show water-in-oil emulsions. Similar emulsions have been prepared in the laboratory and it has been shown that the capacity to form stable emulsions is directly related to the asphaltene content of the petroleum stock.

REFERENCES

- Adamson, A.W., (1976), "Physical Chemistry of Surfaces," 3rd Edition, Wiley - Interscience.
- Buckmaster, J., (1973), "Viscous-Gravity Spreading of an Oil Slick", J. of Fluid Mechanics 49, (3), 117-135.
- Berridge, S.A., R.A. Dean, R.C. Fallons and A. Fish, (1968), "The Properties of Persistent Oils at Sea", Proceedings of Institute of Petroleum Symposium, October 1968.
- Berridge, S.A., M.T. Thew and A.G. Loristen-Clarke, (1968), "The Formation and Stability of Emulsions of Water in Crude Petroleum and Similar Stocks", Journal of the Institute of Petroleum 54 (530), 333-357.
- Blokker, P.C. (1964), "Spreading and Evaporation of Petroleum Products on Water", Proc. 4th International Harbor Conference, Antwerp.
- Canevari, G.P. (1969), "The Role of Chemical Dispersants in Oil Clean-up", in Oil on the Sea, ed. D.P. Hoult, Plenum Press.
- Davies, J.T. and E.K. Rideal (1963), "Interfacial Phenomena", 2nd Edition, Academic Press.
- DiPietro, N.D., C. Huh and R.G. Cox (1978), "The Hydrodynamics of the Spreading of One Liquid on the Surface of Another", J. of Fluid Mechanics 84 (3) 530-548.
- Drapeau, G., W. Harrison, W. Bien and P. Leinonen (1974), "Oil Slick Fate in a Region of Strong Tidal Currents", Proc. 14th Coastal Eng. Conf., Copenhagen, Vol. III, 2245-2259.
- Fannelop, T.K. and Waldman, G.D. (1971), "The Dynamics of Oil Slicks or Creeping Crude", Paper No. 71-4. Am. Institute of Aero and Astro, New York.
- Fay, J.A. (1971), "Physcial Processes in the Spread of Oil on a Water Surface", Proc. of the Joint Conf. on the Prevention and Control of Oil Spills, June 15-17, Publ. by API, 463-467.

- Garret, W.D. and B.R. Barger (1970), "Factor Affecting the Use of Monomolecular Surface Films to Control Oil Pollution on Water", Environmental Science and Technology 4 (2) 123-127.
- Jeffrey, P.G. (1973), "Large Scale Experiments on the Spreading of Oil at Sea and Its Disappearance by Natural Factors", Proc. Joint Conf. on Prevention and Control of Oil Spills, Publ. by API, 469-474.
- Lee, R.A.S. (1971), "A Study of the Surface Tension Controlled Regime of Oil Spread", M.S. Thesis, Mechanical Engineering, MIT.
- Milgram, J. (1978), "The Role of Physical Studies Before, During and After Oil Spills", Proc. of Conf. at Center for Ocean Management Studies, URI, "In Wake of the Argo Merchant".
- McNair, H.M. and E.J. Bonelli (1969), "Basic Gas Chromatography", 5th Edition, Varian Aerograph
- Nelson, W.L. (1958), "Petroleum Refinery Engineering", McGraw-Hill, New York.
- Phillips, C.R. and V.M. Groseva (1975), "Separation of Multicomponent Hydrocarbon Mixtures Spreading on a Water Surface", Separation Science 10 (2) 111-118.
- Stolzenback, K.D., O.S. Madsen, E.E. Adams, A.M. Pollack and C.K. Cooper (1977), "A Review and Evaluation of Basic Techniques for Predicting the Behavior of Surface Oil Slicks", MIT Sea Grant Report No. 77-8.
- Strassner, J.E. (1968), "Effect of pH on Interfacial Films and Stability of Crude Oil-Water Emulsions", Journal of Petroleum Technology (20) 303-312.
- Suchon, W. (1970), "An Experimental Investigation of Oil Spreading over Water", M.S. Thesis, Mechanical Engineering, M.I.T.

APPENDIX I: MEASUREMENT INSTRUMENTS

Surface and Interfacial Tensions

The du Noüy's ring method was used for the measurement of surface and interfacial tensions. A platinum-iridium ring of precisely known dimensions is suspended from a counterbalanced arm, immersed a little below the surface of the liquid being measured. The arm is clamped to a stainless steel wire to which torque can be applied to keep the arm horizontal. The force required to detach the ring from the surface, with the arm horizontal is measured. Interfacial tension is measured the same way at the interface of two liquids either pulling the ring up or pushing it down. The ring was cleaned before each measurement by rinsing it and heating it in a gas flame. The instrument balance used was a Fisher Surface Tensiomat, Model 21.

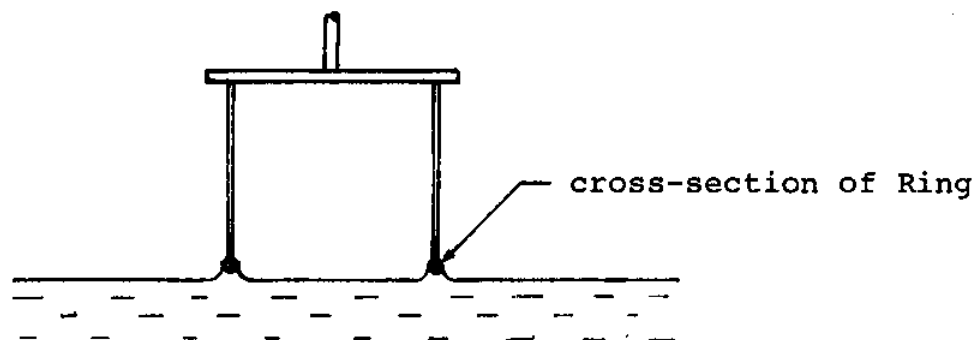


Figure I-1

Film Pressure

The film pressure of a monolayer on a substrate is the difference between the surface tension of the pure substrate and that of the substrate surface covered by the monolayer.

The film pressure can be measured using a film balance or using a Wilhelmy slide (Adamson, 1976). The Wilhelmy slide method was used in this case. The slide was partly immersed in water and suspended from a counter-balanced horizontal arm. The change in pull on the slide with the introduction of the monolayer was measured, with the arm kept horizontal. Film pressure was computed by dividing the total change in force by the wetted perimeter of the slide.

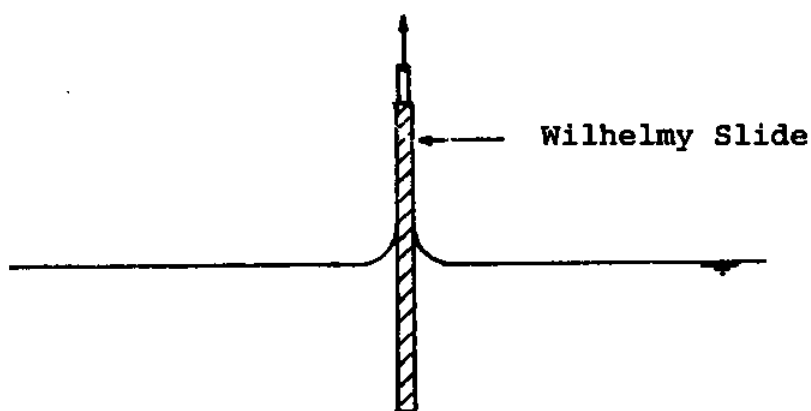


Fig. I-2

The Gas Chromatograph

Gas Chromatography or Gas-Liquid Chromatography (when the other phase is a liquid, as is the case in most gas chromatographs) involves the separation of the components of volatile mixtures. The separation takes place in the column (Fig. I-3). The column is a tube containing a non-volatile solvent supported on an inert size-graded granular solid. The sample is introduced into the system through the injection port (at a temperature high enough for vaporization of components) and carried through the column by an inert gas (Nitrogen or Helium). The stationary phase (the solvent) should be carefully chosen such that the various components have varying solubilities in it. As the carrier gas with the sample flows through the column, the components are retarded at different rates and hence elute at different times. The time taken from injection to the elution of the component is known as the retention time. The longer the column the better the resolution, however, retention times will be greater. The retention time is also affected by the column temperature. At high temperatures retention is reduced and resolution decreased. Most gas chromatograms have columns in ovens which are

temperature programmable allowing for good resolution and rapid analysis. At the elution end of the column is the detector connected to a strip-chart recorder.

The chromatograph used for the experiments was a Bendix Series 2600 laboratory chromatograph with flame ionization detectors. For all the GC separations the stationary phase was 4% OV-17 on Chromosorb W-H.P. (solid support) of 80/100 mesh in a six foot long, 1/4" OD stainless steel column. Nitrogen was used as carrier gas. For the "synthetic oil" (Chapter 5) separation, the column was temperature programmed for 25°C to 100°C at 10°/min. For the crude oil separation, the column was programmed from 50°C to 240°C and for diesel from 50° to 200°C, both at the rate of 10°/min.

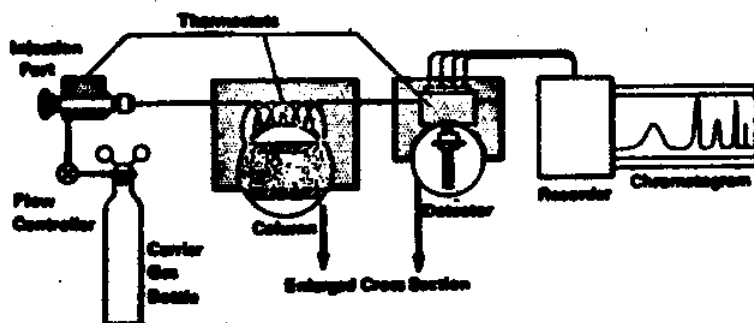


Fig. I-3
(From McNair and Bonelli, 1969)

APPENDIX II: THICK LAYER REGIONS OF THE SPREAD:
EMULSIFICATION CONSIDERED

In actual oil spills, the oil has been observed to spread to thick layers of up to 0.5 inches in thickness (thickness of up to 6", probably exaggerated, have been reported) and thin layers which range from invisible monomolecular films (monolayers) to films 0.05 inches thick.

An examination of the spreading coefficient (or the difference between the film pressure Π , and the spreading coefficient, S necessary to sustain thick layers, show very large values are required. Using Equation 3.4, the negative spreading pressure S required to sustain a thick layer of 15 millimeters (about 0.6 inches) with varying oil densities is shown in Table II-1. The unrealistically high values of the (negative) spreading coefficients suggest that there is probably a different explanation for the existence of the thick layer.

TABLE II-1

Spreading Coefficients Required Sustain
15mm Thick Layer

Δ	.98	.95	.93
$\Pi-S$	21.6	52.4	71.8

The Torrey Canyon oil spill was one of initial oil spills where it was recognized that water-in-oil emulsification had a significant effect on the slick. Miles of beach area were contaminated with this thick viscous emulsion which was difficult to handle, and from its appearance and texture was dubbed "chocolate mousse." Jeffrey (1973) in the North Atlantic and Drapeau, Harrison, Bien and Leinonen (1974) in the St. Lawrence estuary released small spills which showed that oil slicks developed thick layer and thin layer regions (See Fig. II-1). In both the experiments, the thick layer regions were identified as water-in-oil emulsions and that it was formed a few hours after spilling. In the St. Lawrence spill the emulsion which looked like a viscous spongy type of "crocodile skin" was analyzed and found that it contained 71 percent water just two hours after the spill. Microphotographs of the samples showed emulsions of water in oil.

An emulsion is defined (Adamson, 1976) as a mixture of particles or droplets of one liquid with a second liquid. In most cases, one of the liquids is aqueous in nature hence the two common emulsions are oil-in-water and water-in-oil, where oil is used as a general term defining a water-insoluble fluid.

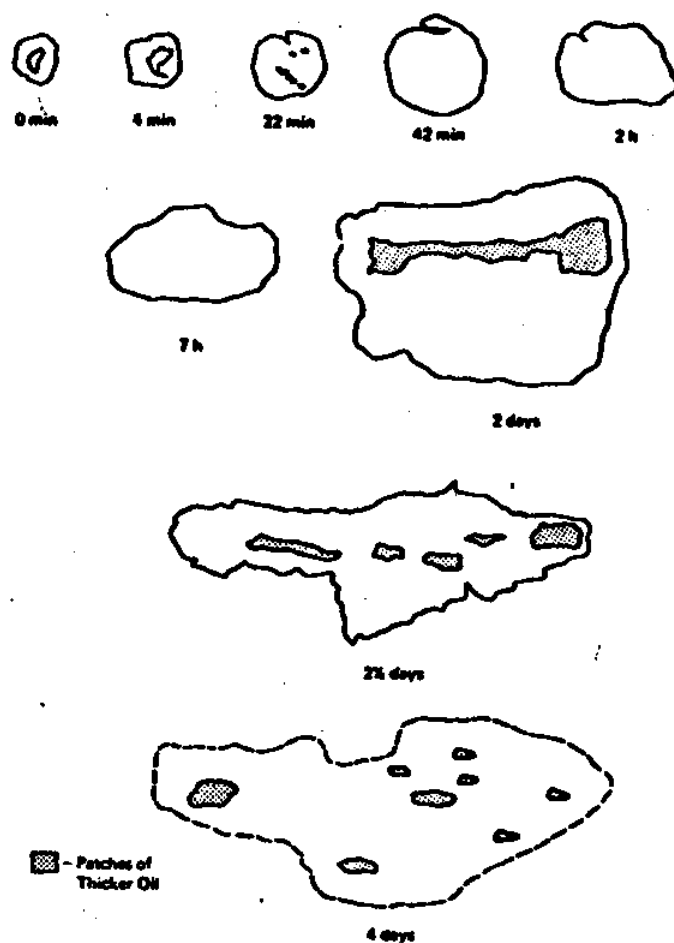


Figure II-1 Diagram showing patches of thicker oil in the development of an oil slick (After Jeffrey, 1973)

If two immiscible liquids are shaken together they will form a dispersion in each other. There is an increase in interfacial area and the energy required for the increase in interfacial energy is obtained from the shaking. The lower the interfacial tension between the two liquids the easier it is to form emulsions.

Spontaneous emulsions occur when there is localized diffusion at the interface or the interfacial tension is lowered due to unequal distribution of a surface active material. However, most emulsions are formed by mixing or stirring. A relatively large drop in the continuous phase (e.g., water is the continuous phase in oil-in-water emulsions) is subjected to mechanical or fluid forces that elongate it to a cylindrical type of shape. Such shapes are unstable and break-up into bubbles whose total interfacial area is less than that of the cylinder.

While it is relatively easy to disperse particles or droplets of one liquid in another phase separation will occur if the emulsion is not stable. The stability of the emulsion depends on the presence of surfactant components which form an interfacial film around the droplets preventing coalescence. Surfactants which are more water-than-oil-soluble will tend to stabilize

oil-in-water emulsions and conversely surfactants which are more oil-than-water-soluble will tend to stabilize water-in-oil emulsions.

Strassner (1968) showed the such films existed in oil-water interfaces of petroleum stocks and measured the film forming capacity of several oils. It was shown the film forming capacity was directly related to the asphaltene content of the oil and the viscosity. The viscosity relationship however could be attributed to the fact asphaltenes which make up the heavy, non-volatile residues increase the viscosity. Therefore, high asphaltene content will probably result in high viscosity. Berridge, Thew and Loristone-Clarke (1968) found also that asphaltene content was important for stability but concluded the kinematic viscosity was not. They prepared water-in-oil emulsions of varying water content and found that the rigidity of the "mousse" increased with water content. For most of the crudes tested the maximum amount of water the oil could take was about 80 percent. The emulsions were prepared by stirring and were similar to the "chocolate mousse" observed in the Torrey Canyon oil spill. Microphotographs of the emulsions showed clearly the water droplets in oil. Simulated rough sea conditions resulted in emulsions after

about one hour. Addition of oil dispersing agents reduced the emulsion forming capacity of the oils.

From the above, there is good reason to believe that at least part of thick layer regions observed in many oil spills at sea is due to water-in-oil emulsions. There is sufficient kinetic energy on the sea surface for the formation of these emulsion and there are components in petroleum stocks, most likely being asphaltenes, which form surfactant films to stabilize to emulsions for long periods.