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I. Physical Considerations

It is a common observation that oil, when spilled on water, tends to spread outward on the water surface in the form of a thin continuous layer. In those instances where this layer is as thin as a wave length of visible light, an iridescent color of the film, caused by light interference, is observed. This tendency to spread is the result of two physical forces: the force of gravity which causes the lighter oil to seek a constant level by spreading horizontally, just as it would on a plane horizontal solid surface, and the surface tension force of pure water, which is usually greater than that of the oil film floating on water. While the oil layer could spread while still remaining intact until it had formed a monomolecular layer, spreading usually stops when the layer is much thicker than this, most likely because of a change in the surface tension properties of the oil.

It might appear to be a paradox that the force of gravity, which acts downward, should cause a layer of oil to spread sideways. The horizontal motion is actually caused by outward pressure forces in the oil, but these pressure forces are themselves a result of the vertical gravitational force. It is perhaps easier to understand this spreading tendency if we note that a floating layer of oil (as indeed for any floating body of uniform density) has a more elevated center of gravity, and hence greater potential energy, than the fluid it displaces. Thus the gradual spread of an oil slick is accompanied by a loss of potential energy in the earth's gravitational field.

A similar loss of surface energy occurs as an oil slick spreads. For a given increase in slick area, the energy of the air-water

interface (or surface tension) is lost while those of an equal area of air-oil and oil-water interfaces are gained. For an oil which "wets" the water, and hence spreads, this results in a net loss of surface energy.

To conserve energy in the spreading process, the loss of gravitational energy and surface energy must be balanced by a gain in other forms of energy. There will be a gain in the kinetic energy of the moving oil and water and an increase in internal (heat) energy generated by viscous forces in both oil and water. In terms of forces, therefore, we expect gravity and surface tension to increase the spread while inertia and viscous forces retard it.

In the open sea, this spreading tendency is aided by water surface motions induced by waves, wind and tidal currents. These surface motions are characterized by randomness in strength and direction, so that different elements of a slick are moved about relative to each other and to the center of mass of the slick, even when there is a gradual drift of the slick as a whole due to wind, wave or current. Therefore there can be a dispersal of a slick caused by such random motions, which is quite analogous (in two dimensions) to the three dimensional dispersion of a puff of smoke emitted into the atmosphere on a windy day. This will certainly be the only cause of spread if the slick has been broken into small independent pieces, each of which has reached a stable size. The spread resulting from this random motion of the sea surface is very difficult to estimate, but appears to be smaller, under conditions for which observations have been made, than that caused by tension and gravity forces.

Most oils spilled are mixtures of components having varying vapor pressure and solubility in water. When initially spilled, the fractions of lighter molecular weight, being more volatile and soluble, are preferentially leached out, leaving a residue which is denser and more viscous. Because of the low molecular diffusivity of liquids, this is a slow process. Thus it can be expected that the bulk properties which are important to the spreading, such as density, viscosity and surface and interfacial tensions, will change slowly with time while the slick spreads.

11. The Rate of Spread of a Finite Quantity of Oil on Still Water

For the present purposes we shall be satisfied to estimate the order of magnitude of the rate of spread of an oil slick on the surface of still water, i.e., water which is free of motions induced by wind, wave and tidal currents. We shall assume that, at zero time t , a volume V of oil is dumped on the water, and that it subsequently spreads outward in a slick whose diameter l and thickness h change with time t . In order of magnitude, to conserve the volume of oil,

$$V = l^2 h \tag{1}$$

As it spreads outwards, the moving layer of oil drags with it a thin layer of water, because the oil cannot slip across the water surface. (The water is thus not entirely "still" during the spreading process, for it moves upward to replace the spreading oil as well as outward near the oil-water interface due to the viscous drag of the

oil film.) The thickness δ of the uppermost layer of water so set into motion by viscous forces has the magnitude

$$\delta = \{vt\}^{1/2} \quad (2)$$

in which ν is the kinematic viscosity of the water. This is the thickness of the boundary layer at the edge of a fluid in which the viscous force can accelerate the fluid up to the speed of a moving boundary (in this case, the outwardly moving oil film).

Based on this model, we shall next estimate the order of magnitude of the forces (per unit volume of oil) which tend to accelerate or retard the spread. To this end, we first determine the surface tension force per unit volume of oil by dividing the net surface tension σ by the cross-sectional area of the slick, lh , and then use Eq. (1) to find

Surface tension: $\sigma/lh = \sigma l/V \quad (3)$

The other spreading force, gravity, produces a horizontal force per unit volume (pressure gradient) of $\Delta\rho gh/l$, or using Eq. (1),

Gravity: $\Delta\rho gV/l^3 \quad (4)$

in which $\Delta\rho$ is the difference in mass density between water and oil and g is the gravitational acceleration. The inertia force, which

retards the flow, is the product of mass density ρ and acceleration l/t^2 :

$$\text{Inertia:} \quad \rho l/t^2 \quad (5)$$

The viscous force per unit volume is the viscous stress $\rho\nu(l/t)/\delta$, or product of absolute viscosity $\rho\nu$ and velocity gradient $(l/t)/\delta$ in the water, divided by the film thickness h :

$$\text{Viscous:} \quad \rho\nu(l/t)/\delta h = \rho\nu^{1/2} l^3 / \nu t^{3/2} \quad (6)$$

in which Eqs. (1) and (2) were used to derive the expression on the right*.

Now consider the two forces which tend to spread out the slick, surface tension (Eq. (3)) and gravity (Eq. (4)). Since l increases monotonically as time passes, gravity will be the dominant spreading force at small times while surface tension will eventually dominate at long times. By setting the two forces equal to each other, and using Eq. (1), we may find the critical thickness h_c below which the spread of an oil slick is always dominated by surface tension:

$$h_c = (\sigma / \Delta\rho g)^{1/2} \quad (7)**$$

* Because this is only an order of magnitude estimate, we don't distinguish between the densities of water and oil (calling both ρ) except when their difference $\Delta\rho$ appears directly, as in Eq. (4).

** For typical values of σ and $\Delta\rho$ of 30 dynes/cm and 0.05 gm/cm³ respectively, h_c is 0.8 cm.

We may thus conclude that, early in the spreading process before the slick has thinned to h_c , gravity dominates while surface tension causes spreading for films much thinner than h_c .

Now consider the retarding forces of inertia (Eq. (5)) and viscosity (Eq. (6)). The ratio of viscous to inertia force varies as $l^2 t^{1/2}$ and must therefore become very small near the beginning of the spread. Thus early in the spreading process inertia forces dominate, while ultimately viscous forces will produce the major retarding effect. By reference to Eqs. (1) and (2), it can be seen that these two forces become equal when the film thickness h equals the thickness δ of the viscous layer in the water. This transition from inertially retarded to viscously retarded spread does not occur for a fixed thickness, nor at a given time, but varies with the size of the spill.

The transition from gravity to surface tension spread, and inertial to viscous retardation of spread, would occur simultaneously when $\delta = h_c$ or $t = h_c^2 / \nu^*$. This coincidence is unlikely to be achieved outside of the laboratory. In most large scale oil spills in the open, by the time the slick has thinned to the thickness h_c , δ is much greater than h_c , so that the viscous retarding force sets in before the surface tension spreading force become important. The history of the spread then passes through three phases:

(1) the beginning phase in which only gravity and inertia forces are important,

* For $\nu = 10^{-2} \text{ cm}^2/\text{sec}$ and $h_c = 0.8 \text{ cm}$, $t = 60 \text{ sec}$.

(ii) an intermediate phase in which gravity and viscous forces dominate and

(iii) a final phase in which surface tension is balanced by viscous forces.

The spreading laws for each of these phases may be found by equating, respectively, the pairs of forces as given in Eqs. (3) through (6):

$$\text{Gravity-inertia:} \quad l = (\Delta g V t^2)^{1/4} \quad (8)$$

$$\text{Gravity-viscous:} \quad l = (\Delta g V t^{3/2} / \nu^{1/2})^{1/6} \quad (9)$$

$$\text{Surface tension-viscous:} \quad l = (\sigma t^3 / \rho^2 \nu)^{1/4} \quad (10)$$

To illustrate the respective regimes of the different phases of spreading, we have plotted Eqs. (8) - (10) in Fig. 1 for the special case of a 10,000 ton spill of oil (about the size of the Torrey Canyon initial spill). The very slow spread of the slick, and the domination of viscous retardation after the first hour of spill life, are clearly illustrated. Of course, since these are only order of magnitude estimates, the transition point from one phase to another, as well as the exact size of the spill at a given time, are only approximately given by Eqs. (8) - (10).

For smaller spills, the third phase of spread (surface tension-viscous) becomes dominant earlier in the history of the spread. For practical purposes, it may be sufficient to use Eq. (10) describing the final phase for any time later than the first hour or two after initiating the spill.

The final phase of spreading (Eq. (10)) shows a growth which is independent of the volume V of the oil spill. This is a result of the fact that the thickness of the slick is no longer important in determining the major forces.

III. Spread of a Slick from a Steady Source in a Moving Stream

With only slight modifications, it is possible to estimate the width l of a slick spreading from a stationary source of volume flow rate \dot{V} located in a stream of uniform speed u . This would be a suitable model for an oil well or grounded tanker leaking steadily into a sea with uniform tidal current. We may use the force estimates previously described provided we replace time t by the flow time x/u , where x is the downstream distance from the source, and the conservation of oil Eq. (1) by

$$\dot{V} = hlu \quad (11)$$

With these changes the surface tension, gravity, inertia and viscous forces become:

$$\text{Surface tension:} \quad \sigma u / \dot{V} \quad (12)$$

$$\text{Gravity:} \quad \Delta \rho g \dot{V} / l^2 u \quad (13)$$

$$\text{Inertia:} \quad \rho l u^2 / x^2 \quad (14)$$

$$\text{Viscous:} \quad \rho \nu^{1/2} l^2 u^{5/2} / \dot{V} x^{3/2} \quad (15)$$

The three spreading regimes are readily found to be:

$$\text{Gravity-inertia:} \quad \ell = (\Delta g \dot{V} x^2)^{1/3} / u \quad (16)$$

$$\text{Gravity-viscous:} \quad \ell = (\Delta g \dot{V}^2 x^{3/2} / \nu^{1/2} u^{7/2})^{1/4} \quad (17)$$

$$\text{Surface tension-viscous:} \quad \ell = (\sigma x^3 / \rho^2 \nu u^3)^{1/4} \quad (18)$$

As for the case of instantaneous spill, the final phase of spreading is independent of the strength of the source. Other remarks previously made, as to the significance of h_c and δ , apply equally well to this case.

IV. Comparison with Field Observations

There are a very limited number of reports of observations of the spread of oil slicks on the open sea. Smith¹ gives data on the spread of the slick from the Torrey Canyon, while Stroop² describes small scale spill tests conducted by the U.S. Navy in 1927. We have plotted these observations of slick size ℓ as a function of time t since initiating the spill in Fig. 2. Also shown in Fig. 2 is Eq. (10) for the final phase of spread.

The observations almost always show a rapid spread to a size which increases with volume of the spill, followed by a long period of no further growth. In no case were observations made of the earlier, growing phase.

We ascribe this behavior to a sudden reduction of the net surface tension σ at a time when evaporation and dissolving of the lighter components of the oil has occurred. For thinner slicks (smaller volumes)

this evaporation occurs sooner and leads to the cessation of spreading at an earlier time (and hence smaller size l). If this is so, the observed sizes should all lie below a line of the form given by Eq. (10). This is approximately true of the data shown in Fig. 2 if we choose

$$l = 10(\sigma^2 t^3 / \rho^2 v)^{1/4} \quad (19)$$

as an upper bound for these points.

We have tested this hypothesis by determining the thickness h for which molecular diffusion to the upper or lower surface of the oil film could have depleted components of the oil in the time t required to reach this thickness. Setting

$$h = \sqrt{Dt} \quad (20)$$

in which D is the molecular diffusivity of oil (about 10^{-5} cm²/sec), and using Eqs. (10) and (1), we can solve for the scale l_{∞} at which Eq. (20) is satisfied:

$$l_{\infty} = (\sigma^2 v^6 / \rho^2 v D^3)^{1/16} \quad (21)$$

This theoretical relation is shown in Fig. 3, together with the measured size of slick taken from Fig. 2. Although the agreement is not good, the

slow rate of increase of l_{∞} (and consequently h) with slick volume V is about as predicted by the theory.

References

1. Smith, J. E., (ed.), 'Torrey Canyon' Pollution and Marine Life, Cambridge University Press (Cambridge, 1968)
2. Stroop, D. V., "Report on Oil Pollution Experiments - Behavior of Fuel Oil in the Surface of the Sea," pp. 41-49, Pollution of Navigable Waters, Bureau of Standards, Washington (1927)

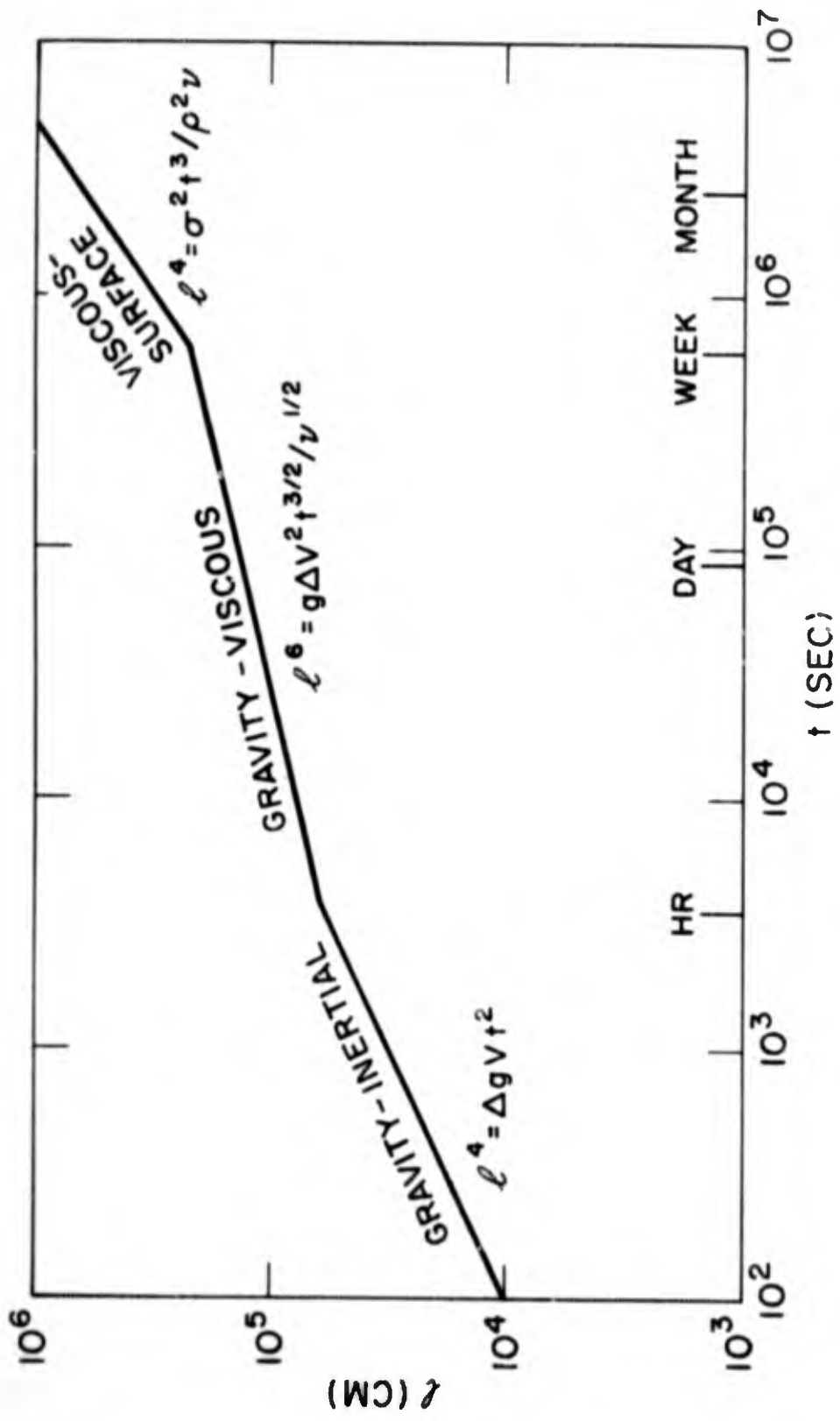


Fig. 1 The size l of an oil slick as a function of time t for a 10,000 ton spill.

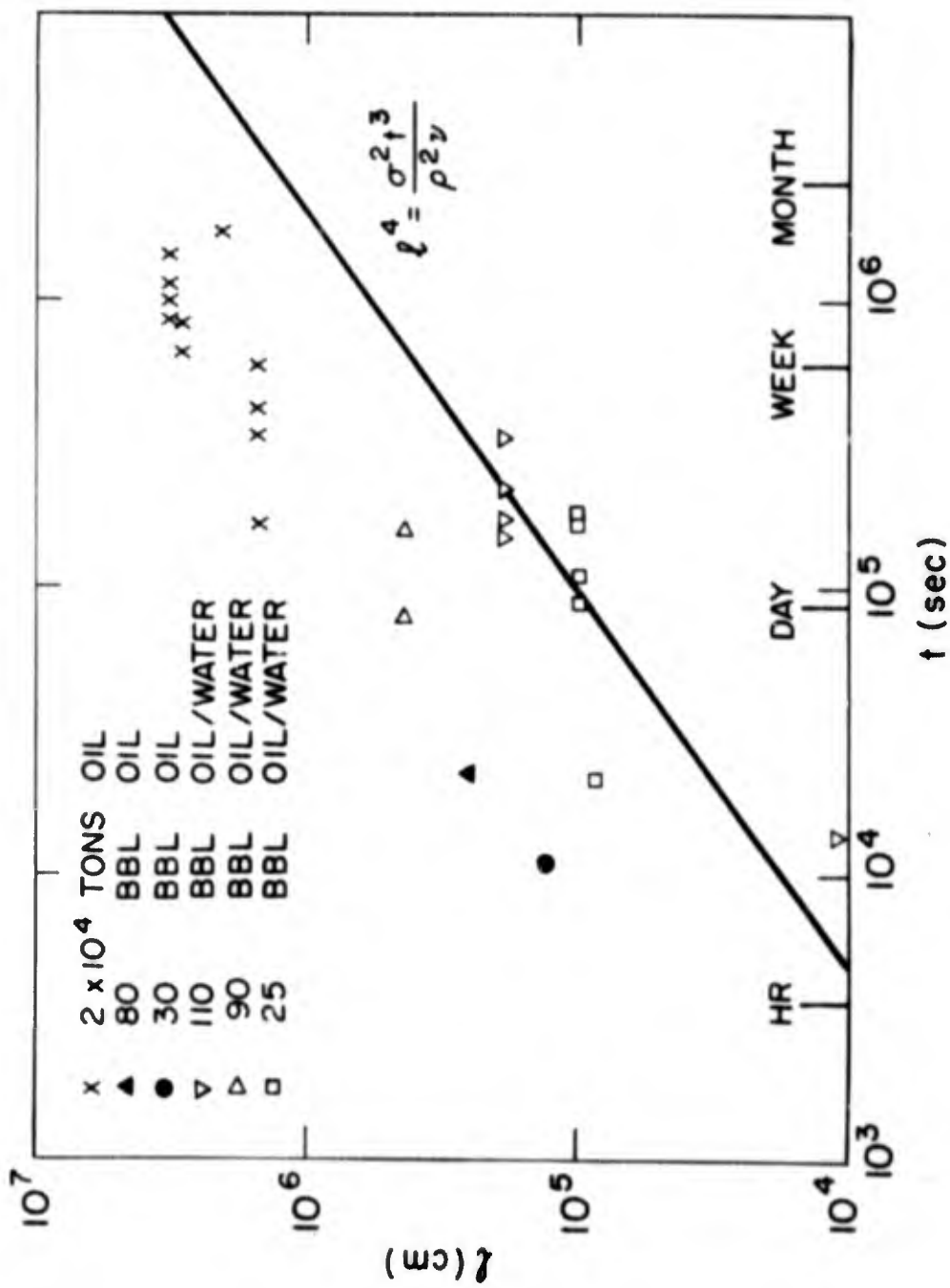


Fig. 2 A comparison of measured oil slick size and the theoretical estimate for surface tension-viscous spreading.

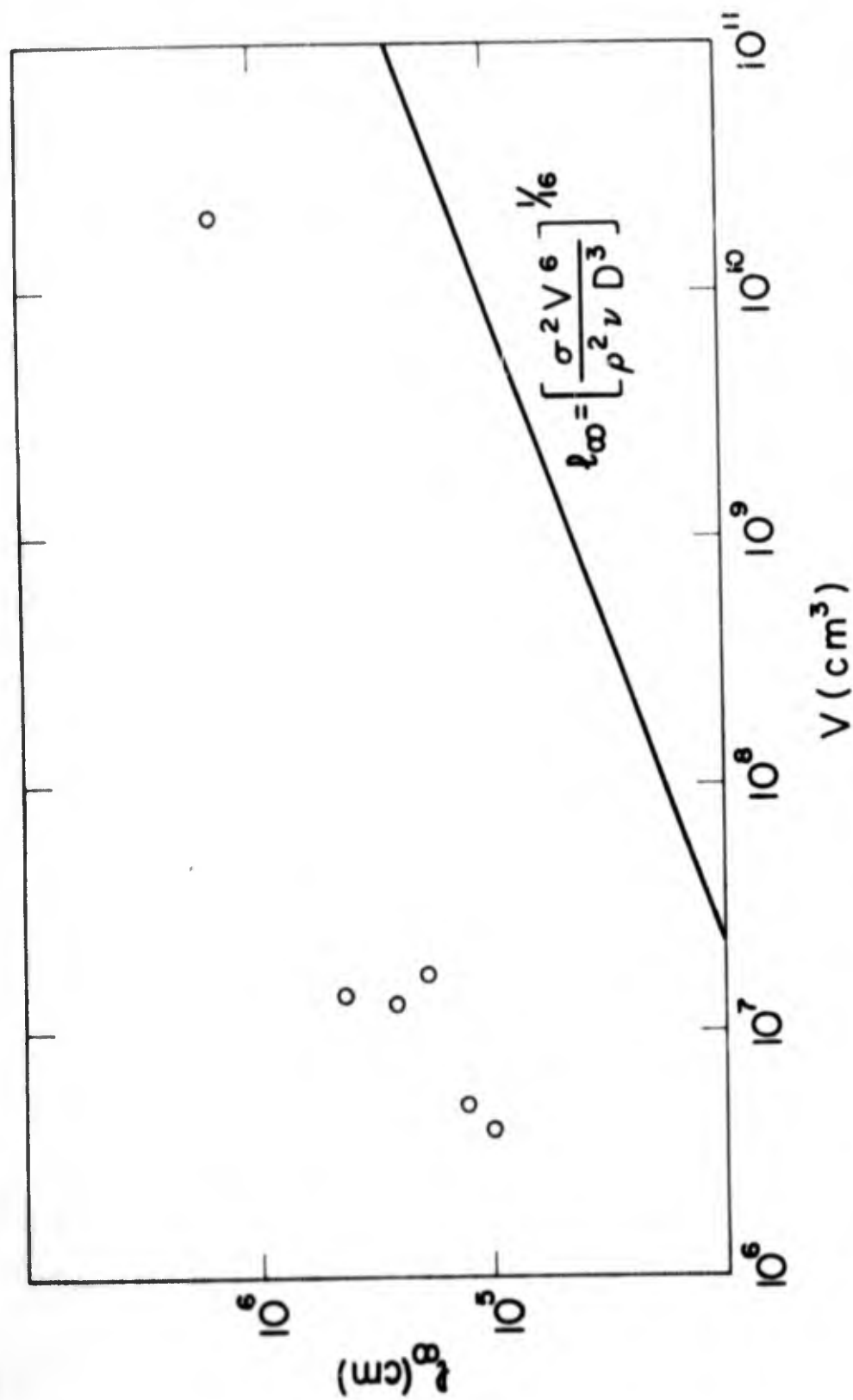


Fig. 3 A comparison of measured and theoretical values for the final size l_{∞} of a slick as a function of the spill volume V .