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LUBRICANT FOAMING AND AERATION STUDY

Sydney Ross
Yaakov Suzin

Rensselaer Polytechnic Institute
Troy, N.Y. 12181

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Hoover A. Smith
HOOVER A. SMITH
Project Engineer

Howard F. Jones
HOWARD F. JONES
Chief, Lubrication Branch

FOR THE COMMANDER

Robert D. Sherrill
ROBERT D. SHERRILL
Chief, Fuels and Lubrication Division

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This research is directed towards the investigation of the mechanisms associated with lubricant foaming and aeration. Initial studies have included basestock ester and ester-additive systems. Foaming of these systems have been investigated with respect to various parameters including solubility, surface viscosity, surface tension and electrical properties. Studies have shown that total additive concentration and synergistic effects of non-foaming additives are important variables relative to foaming. Summary of literature search relative to foaming is also presented.

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PREFACE

This interim report contains the results of the first half of an effort to investigate foaminess and gas retention of turbine-engine lubricants for obtaining a fundamental understanding of the causes of such effects. The work was performed in the Colloid and Surface Chemistry Laboratories, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N.Y. 12181, by Professor Sydney Ross, Dr Yaakov Suzin, Mr D. F. Townsend, and Mrs Tammar Suzin during the period September 1980 to March 1982. The effort was sponsored by the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson AFB, Ohio, under contract F33615-80-C-2017. The work was accomplished under Project 3048, Task 304806, Work Unit 30480626, Foaming and Aeration Characteristics of Turbine Lubricants, with Mr H. A. Smith as Project Engineer.

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INTRODUCTION

In the functioning of a lubricating oil in engines and in various types of mechanism, it is not unusual to come across the formation of oil foam. Severe foaming of a turbine-engine lubricant can lead to breakdown of the normal operation of aircraft lubricating systems. Difficulties that can arise include fluctuations of oil pressure, oil-pump cavitation, decrease in lubrication and cooling efficiencies and, in extreme cases, loss of oil overboard through the breathers. Therefore, measures to combat foam are necessary. The problem has proved to be stubborn, as different types of oil respond differently to antifoam additives; and it is further complicated by the presence of proprietary compounds (additives) used to enhance lubricity, thermal stability, and extreme-pressure characteristics of the oils. These additives include oxidation inhibitors, viscosity -index improvers, pour-point depressants, dispersing agents and oil-soluble detergents. In addition, in order to neutralize corrosive acids, which are produced by the burning of petroleum fuels, colloidal dispersions of alkali-earth carbonates, in which the particles are stabilized by adsorbed layers of surface-active agents, are sometimes provided. Furthermore, oils can change during use or even during storage and produce undesirable results: in some cases used or stored oils have lost their antifoam additives; again, the oils may leach out organic products from sealants and elastomers, or they may generate oxidized or decomposition products that cause foaming. As the outcome of so many different causes, the problem of foam presents itself frequently. The basic mechanisms of foam formation, foam collapse, and foam inhibition are not sufficiently well understood to anticipate problems, to diagnose difficulties and to develop lubricants with improved foam properties. Unless such an understanding is reached of the fundamental principles that govern foam formation in a solution, each problem as it arises has to be tackled *de novo*. The purpose of this research project is to study the basic mechanisms that affect and control the foaming of turbine-engine lubricants.

The experimental approach is to select a typical synthetic lubricant and then to discover circumstances that cause it to foam. The nature of the foam thus produced is then to be studied as a function of pertinent variables, such as temperature, or the presence and amount of contaminants or additives present. The altered physical properties of the lubricant introduced by these controlled conditions are next to be studied, guided by the best available theories of the stability of liquid films, to find possible correlations with, and hence causes for, the formation and stabilization of foam.

SECTION II

SUMMARY OF LITERATURE SURVEY

1. RAYLEIGH-GIBBS THEORY OF FOAM

Pure liquids do not form stable foams, but allow entrained air to escape with no delay other than what is inseparable from the Stokesian rate of rise, which is controlled by the diameter of the bubble of dispersed air and the viscosity of the bulk liquid. Certain solutes are able to stabilize thin sheets (or lamellae) of liquid: if these solutes are present the escape of entrained bubbles is more or less retarded, and a head of foam is produced. Theories of foam postulate plausible mechanisms to account for this behavior, with the ultimate objective of understanding the phenomenon so thoroughly that predictions can be made about expected behavior of a given solute prior to actual observation. One may say at the outset that this final goal is not yet completely attained.

The earliest of these theories, the one usually designated the Rayleigh-Gibbs theory[1] [2] has best withstood criticism through the years. This theory refers the stability of foam to an elasticity or restoration of liquid lamellae, which depends on the existence of an adsorbed layer of solute at the liquid surface and the effect of this adsorbed layer in lowering the surface tension of the solution below that of the solvent. The two effects, surface segregation, or adsorption, and the lowering of the surface tension, are concomitant: a reduction of surface tension due to the addition of a solute is evidence, admittedly indirect but no less certain than were it given by direct observation, that the solute is segregated at the surface. The degree of the segregation is measured as excess moles of solute per square centimeter of surface, designated Γ_2, and is proportional to the variation of the surface-tension lowering with concentration of solute; i.e.,

$$\Gamma_2 = d\Pi/RT\ d\ \ln a_2 \qquad [1]$$

where Π is the lowering of the surface tension caused by a thermodynamic activity a_2 of solute in the solution. Equation [1] is based on thermodynamics, derived for a two-component system. In this report, the term "surface-active solute" denotes a solute that reduces the surface tension of a liquid to any appreciable extent, even by as little as 1 dyne/ cm.

When local areas of a foam lamella are expanded, as would happen for example when a bubble of air pushes through a liquid surface, new areas of surface are created where the instantaneous surface tension is large, because the adsorbed layer has not had sufficient time to form. The greater surface tension in these new areas of surface exerts a pull on the adjoining areas of lower tension, causing the surface to flow toward the region of greater tension. The viscous drag of the moving surface carries an appreciable volume of underlying liquid along with it, thus offsetting the effects of both hydrodynamic and capillary drainage and restoring the thickness of the lamella.[3] Gibbs elasticity is defined as the ratio of the increase in the tension resulting from an infinitesimal increase in the area and the relative increase of the area. For a lamella with adsorbed solute on both sides, the elasticity E is given by:[4]

$$E = 2\, d\sigma / d \ln A \qquad [2]$$

where σ is the surface tension and A is the area of the liquid surface. The factor 2 is required because the stretching of the lamella increases the area on both of its sides.

Attempts to test equation [2] have been made by measuring the dynamic (i.e., non-equilibrium) surface tension as the surface of a solution is abruptly extended. The measurement must be made coincidentally with the extension of the surface. Another measurement is the rate of decline of the dynamic surface tension with time.[5] [6] This has a better chance of being related to foam stability, as the surface flow also requires time: if the tension difference fades too soon, the surface flow is aborted.[7]

The Rayleigh-Gibbs theory depends therefore on a combination of two physical properties of the solution: the solute should be capable of lowering the surface tension of the medium; but this alone is not enough: a rate process is also required, by which a freshly created liquid surface retains its initial, high, non-equilibrium surface tension long enough for surface flow to occur. Many instances are known in which the mere reduction of surface tension by the solute does not lead to the stabilization of foam, presumably because it is not accompanied by the relatively slow attainment of equilibrium, after a fresh surface is made, which is the second requirement for the ability to stabilize bubbles.

2. ENHANCED VISCOSITY OR RIGIDITY AT THE LIQUID-GAS INTERFACE

A single surface-active species in solution does not usually confer any increase of the viscosity, much less rigidity, in the surface layer of the solution. Although foam is capable of being produced by such a solute, the foam is of brief duration. That kind of foam is called "evanescent foam," but it can nevertheless be a cause of concern; because if produced rapidly it can reach a large expansion ratio and so flood any container. Much more stable foam is created if, in addition to the Rayleigh-Gibbs effect described above, the surface layer of the solution has an enhanced viscosity or rigidity.[8] This phenomenon is known to occur in water with certain mixtures of solutes or with certain polymers, both natural and synthetic. The best known examples in aqueous systems are solutions of water-soluble proteins, such as casein or albumen. Common examples are the stable foams produced with whipping cream, egg white, beer, or rubber latex. In many other examples the highly viscous surface layer is made by having present one or more additional components in the solution. An example is the increase in surface viscosity of a mixture of tannin and heptanoic acid in aqueous solution, compared to the effect of the two constituents separately. In non-aqueous liquids, particularly in bunker oils and crude oils, surface layers of high viscosity have been observed; porphyrins of high molecular weight have been indicated as a possible source of this effect. In a hydrocarbon lubricant, the additive calcium sulfonate, for example, has been identified as creating a plastic skin (or two-dimensional Bingham body) at the air interface; it also acts as a foam stabilizer.[9] These viscous or rigid layers in non-aqueous liquids enhance the stability of foam, just as they do in aqueous solutions. [10] [11] [12]

3. MUTUAL REPULSION OF OVERLAPPING DOUBLE LAYERS

The adsorption of ionic surfactants into the surface layer is evident in aqueous solutions and readily leads to the formation of charged surfaces of the lamellae in foams.[13] The counter-ions in the liquid interlayer of the lamella are the compensating charges. When the thickness of the lamella is of the order of magnitude of twenty times the Debye thickness of the electrical double layer, the counter-ions adjacent to the two opposite surfaces repel each other more or less according to an exponential decline of electric potential with distance. This repulsion prevents further thinning of the lamella, and so preserves it from imminent rupture.

The mechanism of charge separation that operates in water cannot occur in non-ionizing solvents. Until relatively recently the conclusion was maintained, therefore, that electrostatic repulsion of overlapping electrical double layers could not be a factor in the stabilizing of liquid lamallae in oil foams. But we now recognize that other mechanisms of charge separation are possible, and indeed must operate; for zeta potentials of 25 to 125 millivolts have been observed for various kinds of particle dispersed in non-aqueous media of low conductivity.

Nevertheless no evidence has yet been reported to suggest that foam may be stabilized by charged surfaces in non-aqueous solutions.

4.EFFECT OF DISPERSED PARTICLES ON FOAM STABILITY

It was found experimentally by Ottewill et al.[14] that the presence of colloidally stable, suspended, solid particles increases the tendency to form stable foams over and above that of the matrix in the absence of such particles. The increase in foam stability is linked to the increased bulk viscosity of the dispersion with solids content, which is described by a relation of the following form:

$$\eta_D = \eta_0 (1 + k_1 \phi + k_2 \phi^2 \ldots.) \qquad [3]$$

where η_0 = viscosity of the liquid matrix, η_D = viscosity of the dispersion, and ϕ = volume fraction of dispersed solid. The coefficient k_2 was larger than predicted by purely hydrodynamic factors, being enhanced by the electrostatic repulsions between the solid particles, which effectively enlarges each particle and so creates a larger volume fraction of solids than is calculated from the density of the solid. In addition, the presence of a minimum in the pair-interaction energy curve introduces some association between the particles with increase in volume fraction, which leads to a viscosity enhancement at the low rates of shear experienced in a slowly draining lamella. The effect of bulk- dispersion viscosity on the ripples formed in the lamella surface by thermal fluctuations is not known with certainty, but it seems likely that this would have a damping effect on the magnitude of the ripples and thus lead to further enhancement of foam stability.

5. SOLUTION THEORY OF SURFACE ACTIVITY

While accepting the Rayleigh-Gibbs theory as an operative mechanism underlying the stability of liquid lamellae, it still gives no guidance to the character of a surface-active solute. To that end a theory of solubility is required.[15 16] Solution occurs when solute-solvent interaction (or adhesional force) is strong enough to overcome the cohesion of the solvent molecules to themselves and the cohesion of solute molecules to themselves. When adhesional forces are markedly larger than cohesional forces, negative deviations from Raoult's law are observed, and the two components are found to be miscible in all proportions. Such a condition is not conducive to surface activity, as solute has a lower potential energy (i.e., more interaction) in the bulk-phase solution than in the surface-phase solution. But when the adhesional forces are weaker than cohesional forces, the position is reversed; and the solute does not have its lowest potential energy in the bulk-phase solution. This condition offers a possibility for surface activity, as there is now an opportunity for more adhesional interaction with the solvent in the surface-phase solution than in the bulk-phase solution. We look, therefore, according to this theory, for positive deviations from Raoult's law as the first indicator of potential surface activity. If the positive deviations from Raoult's law are large, the system of solvent + solute may separate into two immiscible solutions. In such systems of partial miscibility were found correlations between surface activity, composition, and temperature. The partial miscibility by itself is not the cause of the surface activity, but is merely an indicator of the presence of positive deviations from Raoult's law, which in turn may also be considered as an indicator of weak adhesional forces between solvent and solute molecules.

This theory has promising and still unexplored corollaries. A binary system consisting of a Lewis acid and a Lewis base would have large adhesional interaction and so would lead to negative deviations from Raoult's law. This has been observed, for example, with the systems: chloroform (Lewis acid) + acetone (Lewis base); methyl ether (Lewis base) + hydrogen chloride (Lewis acid); pyridine (Lewis base) + acetic acid (Lewis acid); and water (Lewis base) + formic, nitric, hydrochloric, or hydrobromic acids (Lewis acids.) These solutions all show negative deviations from Raoult's law, and so would not be expected to have any significant surface activity. On the other hand, the combination of two Lewis acids or two Lewis bases leads to weak adhesional interaction and so is conducive to surface activity. The synthetic esters used as lubricants are weak Lewis bases and we should therefore be on the lookout for the possibility of surface activity (and foaminess) when they are combined with additives that are also Lewis bases. A future activity in this program is the identification of lubricant additives in terms of Lewis acids or bases.[17]

SECTION III

STUDIES INVOLVING TMP-HEPTANOATE

Most of the studies performed to date have been on the synthetic lubricant ester designated Base Stock 704, which is a practical grade of trimethylolpropane heptanoate (a more systematic name would be 2-2-diheptanoyloxymethyl-n-butyl heptanoate) and mixtures of this ester with various additives. This ester is designated tmp-heptanoate in this report.

1. PHYSICAL PROPERTIES OF TMP-HEPTANOATE.

Physical properties of interest to us are: (a) The variation of density with temperature, which is reported in Figure 1, along with a comparison of the same property of water. (b) The variation of the surface tension with temperature, which is reported in Figure 2. (c) The variation of the viscosity with temperature, which is reported in Figure 3.

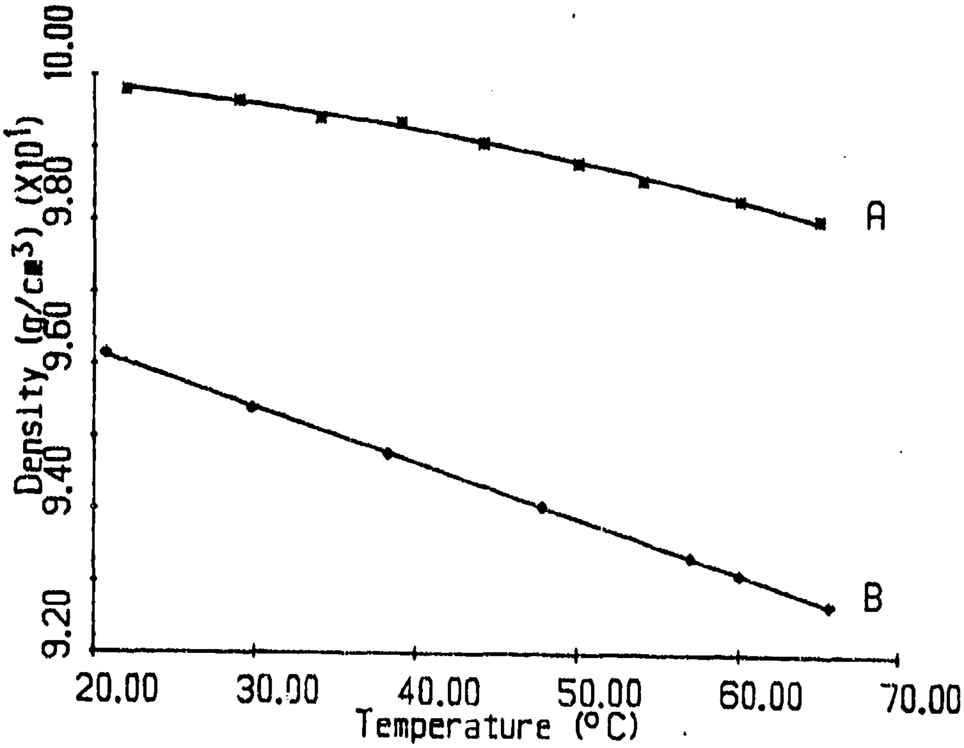


Figure 1 Variation of Density with Temperature for (A) Water and (B) Tmp-Heptanoate

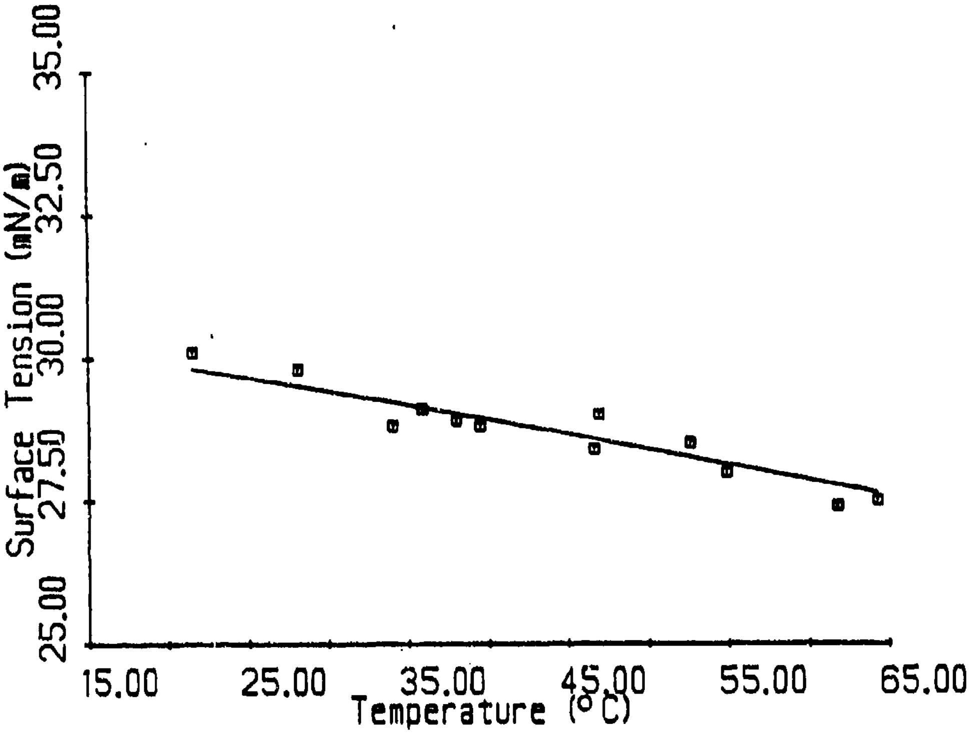


Figure 2 Variation of Surface Tension with Temperature for Tmp-Heptanoate

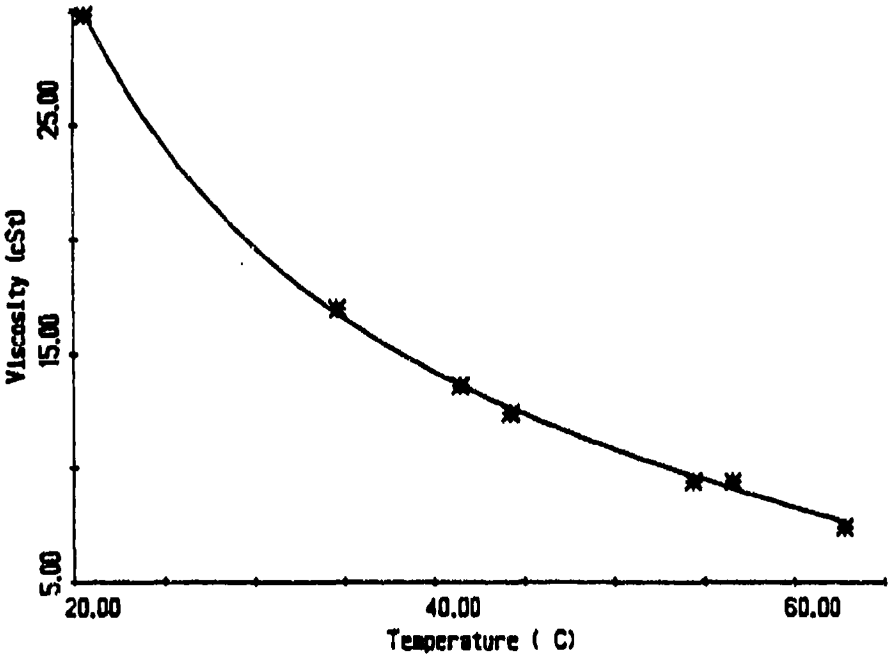


Figure 3 Variation of Kinematic Viscosity with Temperature for Tmp-Heptanoate, from 20 to 63°C

2. SOLUBILITIES OF POLYDIMETHYLSILOXANE IN TMP-HEPTANOATE

Measurements of solubilities of polydimethylsiloxane fractions, by whatever techniques they are determined, are subject to a peculiarity of the material, namely, that if the range of molecular weights in the sample is too wide, the higher members will register insolubility while the lower members will not yet have reached their saturation solubility. Consequently at concentrations well above the apparent solubility limit, some fraction of the material continues to be extracted into the solution. We have observed the effects of this phenomenon in the foaminess data, where the foaminess increases with concentration of added polydimethylsiloxane, although the latter is well above its apparent limit of solubility. If this had been a single molecular species the foaminess would have become constant when maximum solubility was reached, leaving out of account the possible foam-inhibiting effects of the insoluble residue.

The determination of solubility is important because it is normally related to surface activity and hence to foaminess. As a solute, that interacts only slightly with the solvent, approaches its solubility limit it tends to concentrate in the surface phase in preference to the bulk phase; because in the surface region more interaction with the solvent is possible. The concentrating of solute in the surface phase is a manifestation of surface activity; and to a close first approximation it is accompanied by an increase of foaminess. As soon as nucleation and separation of solute occurs, the dispersed phase, if it is of lower surface tension than the medium, may act to inhibit foam. We have yet to find the proper conditions for this behavior with polydimethylsiloxane in tmp-heptanoate solutions; in fact we observe an increase in foaminess as concentrations are increased even beyond the solubility-point limit. This behavior may be explained by two effects: the increase in concentration in the solution of soluble polydimethylsiloxane of low molecular weight and the failure of the insoluble polydimethylsiloxane to behave as an antifoam because of its unsuitable degree of dispersion. Polydimethylsiloxane, or silicone oil, is a linear polymer that can be obtained commercially in a number of different viscosities. Each such sample is not of uniform molecular weight, but represents a distribution of molecular weights. The number average molecular weight of the mixture is related to the kinematic viscosity by the equation:

$$\text{log viscosity (centiStokes at } 25^\circ\text{C)} = 1.00 + 0.0123\, M^{1/2} \qquad [4]$$

This equation is reported to be reasonably valid for values of M above 2500.[18] Values of M calculated by this equation for some of the samples of polydimethylsiloxane used in this work are reported below:

Viscosity in cSt at 25°C	Number average mol. wt.
500	19,000
1000	26,000
10,000	60,000

The solubility in tmp-heptanoate of various polydimethylsiloxane fractions, distinguished from each other by the value of their kinematic viscosity, was determined by means of the Faraday-Tyndall effect (scattered light) and is reported in Figure 4. The solubility decreases with increasing molecular weight. Tmp-heptanoate to which various amounts (volume percent) of toluene have been added makes a better solvent, as is also shown in Figure 4.

The variation with temperature of the solubilities in tmp-heptanoate of polydimethylsiloxane fractions of 500, 1000, and 5000 centiStokes viscosity is reported in Figure 5.

3. FOAMINESS OF POLYDIMETHYLSILOXANE IN TMP-HEPTANOATE

When dissolved in tmp-heptanoate, polydimethylsiloxane of low molecular weight is a surface-active solute. This fact is demonstrated in Figure 6, which shows the variation with temperature of the surface tension of a solution of polydimethylsiloxane (100 centiStokes viscosity) in tmp-heptanoate at a concentration of 30 ppm The curve for the solution lies below that of the solvent, showing a lowering of the surface tension by about 6 mN/m at temperatures between 35°C and 85°C.

Although polydimethylsiloxane is a foam inhibitor in hydrocarbon lubricants, it only acts as such when it is present at concentrations above its solubility limit, and even then only when it is suitably dispersed. In our experiments to date we have made no attempt to disperse the insoluble fraction of the polydimethylsiloxane, nor have we yet included silicone polymers of viscosities greater than 1000 centiStokes. We plan in later experiments to take these factors into account. In the absence of the foam inhibiting action of the insoluble fraction, which has not shown up yet in our experience, we find the following:

Solutions of various concentrations of polydimethylsiloxane (1000 centiStokes) in tmp-heptanoate, in the range of 53 to 646 ppm were tested for foam with an apparatus consisting of a 60x3 cm jacketed glass cylinder having a flat chromatographic glass frit of 3.00 cm diameter at the bottom. Foam was generated with nitrogen gas, with flow rates up to 600 ml/minute and at temperatures of 25 to 95°C. The test results are reported in Figures 7, 8, and 9. A summary of results follows:

(a) No significant foam is observed at concentrations less than 51 ppm at the temperatures and flow rates studied.
(b) In the range of concentrations of 50 to 324 ppm the foaminess increases with concentration of polydimethylsiloxane.
(c) In the range of concentrations of 324 to 646 ppm the foaminess no longer shows an increase with concentration of polydimethylsiloxane.
(d) In the range of temperatures from 25 to 95°C the foaminess increases with temperature at all concentrations of solute.

At the higher concentrations reported, the polydimethylsiloxane is beyond its solubility limit and turbidity is evident in the solutions. Nevertheless, the advent of insolubility and the presence of undissolved spherical droplets of silicone oil in the medium is not accompanied by the onset of foam inhibition, as has been our experience with many other binary systems. At the present

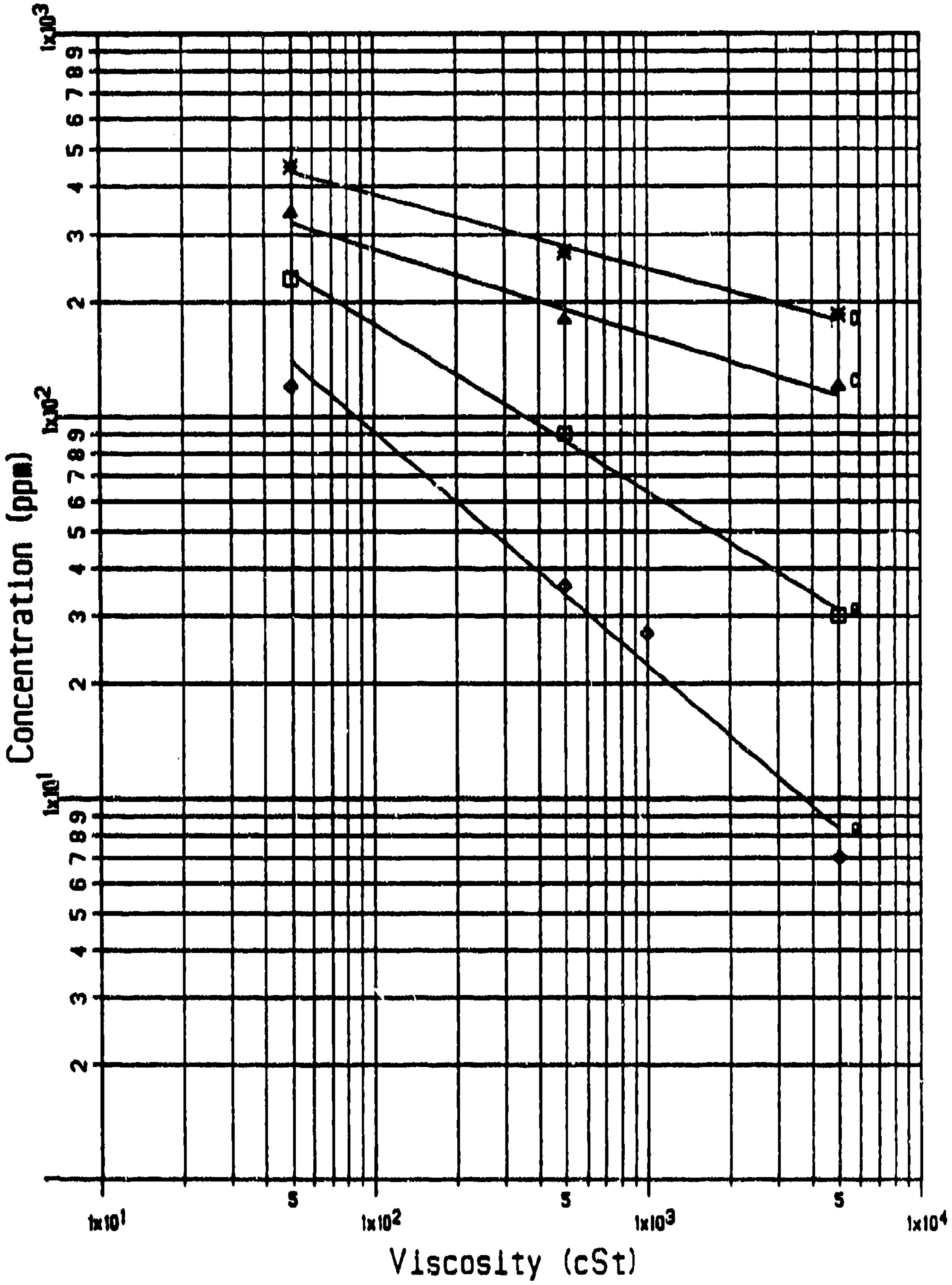


Figure 4 Variation of Solubility of Polydimethylsiloxane in Various Solvents at 20°C as a Function of its Kinematic Viscosity. Solvents are:A = Tmp-Heptanoate; B = Tmp-Heptanoate containing 10% Toluene (v/v); C = Tmp-Heptanoate containing 20% Toluene (v/v); D = Tmp-Heptanoate containing 30% Toluene (v/v)

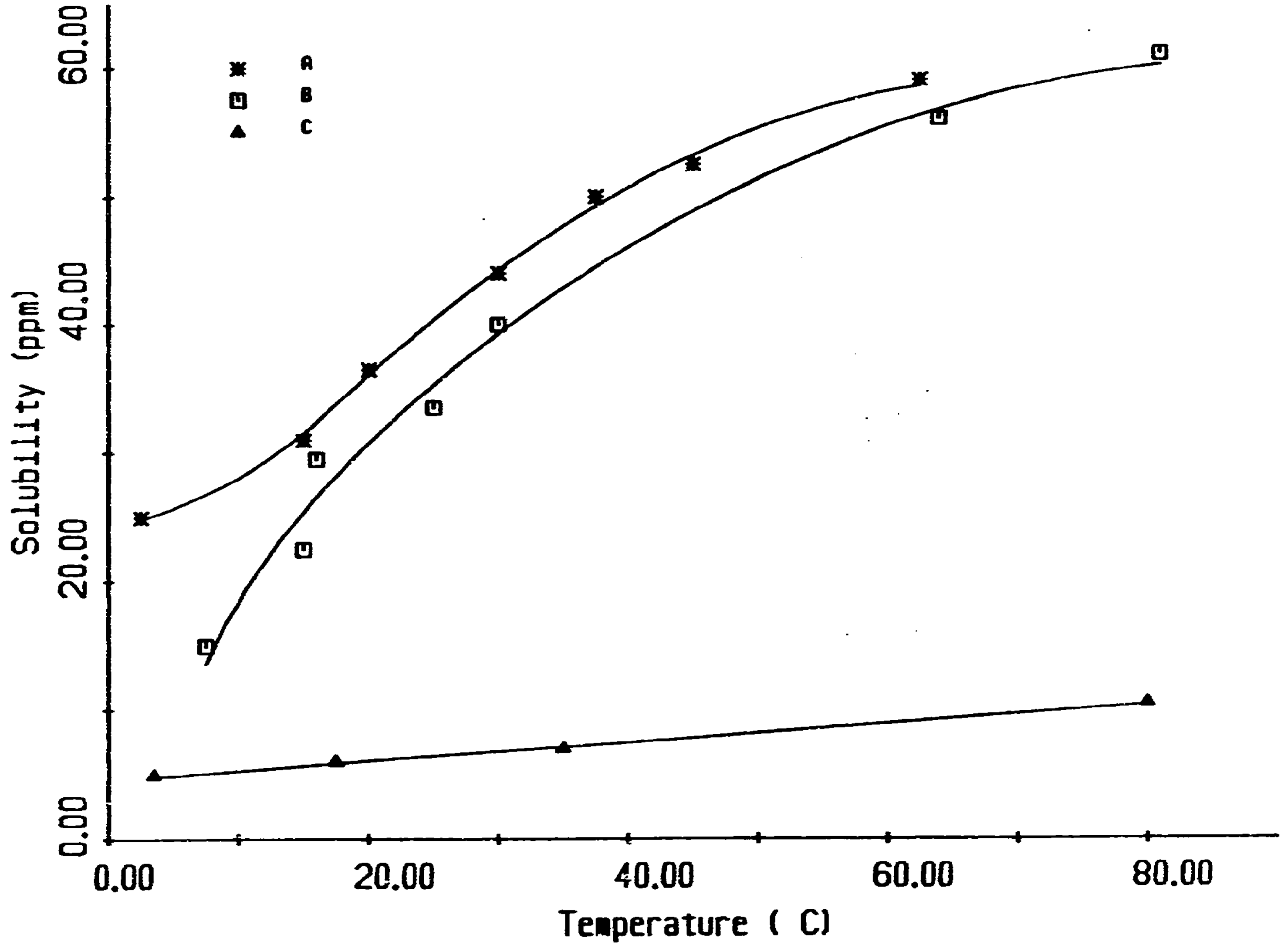


Figure 5 Variation of Solubility with Temperature for Polydimethylsiloxane of different Viscosities in Tmp-Heptanoate.
A = Polydimethylsiloxane of 500 cSt
B = Polydimethylsiloxane of 1000 cSt
C = Polydimethylsiloxane of 5000 cSt

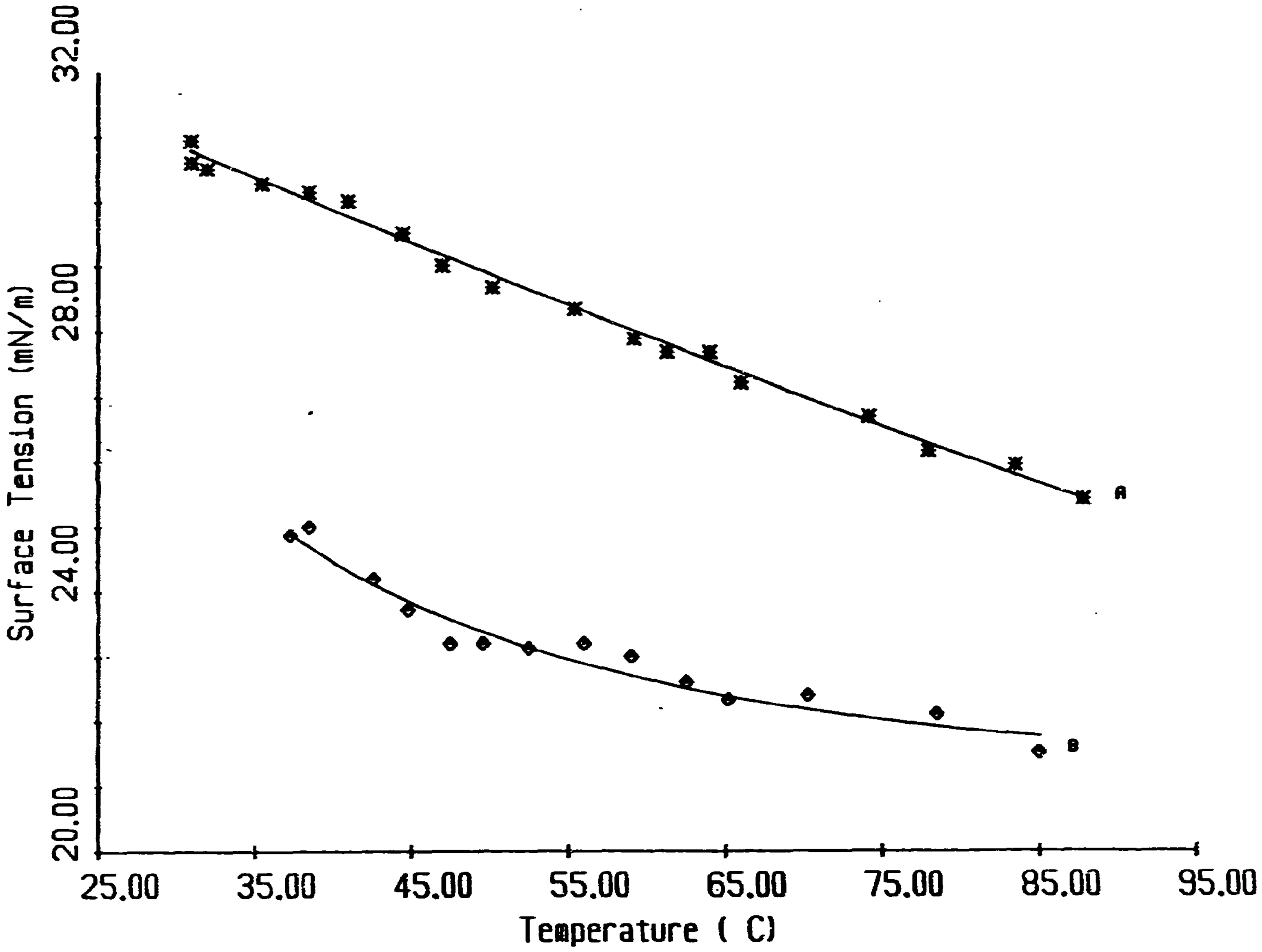


Figure 6 Variation of Surface Tension with Temperature of Tmp-Heptanoate (A) and of a Solution of Polydimethylsiloxane (100 cSt), 30 ppm in Tmp-Heptanoate(B)

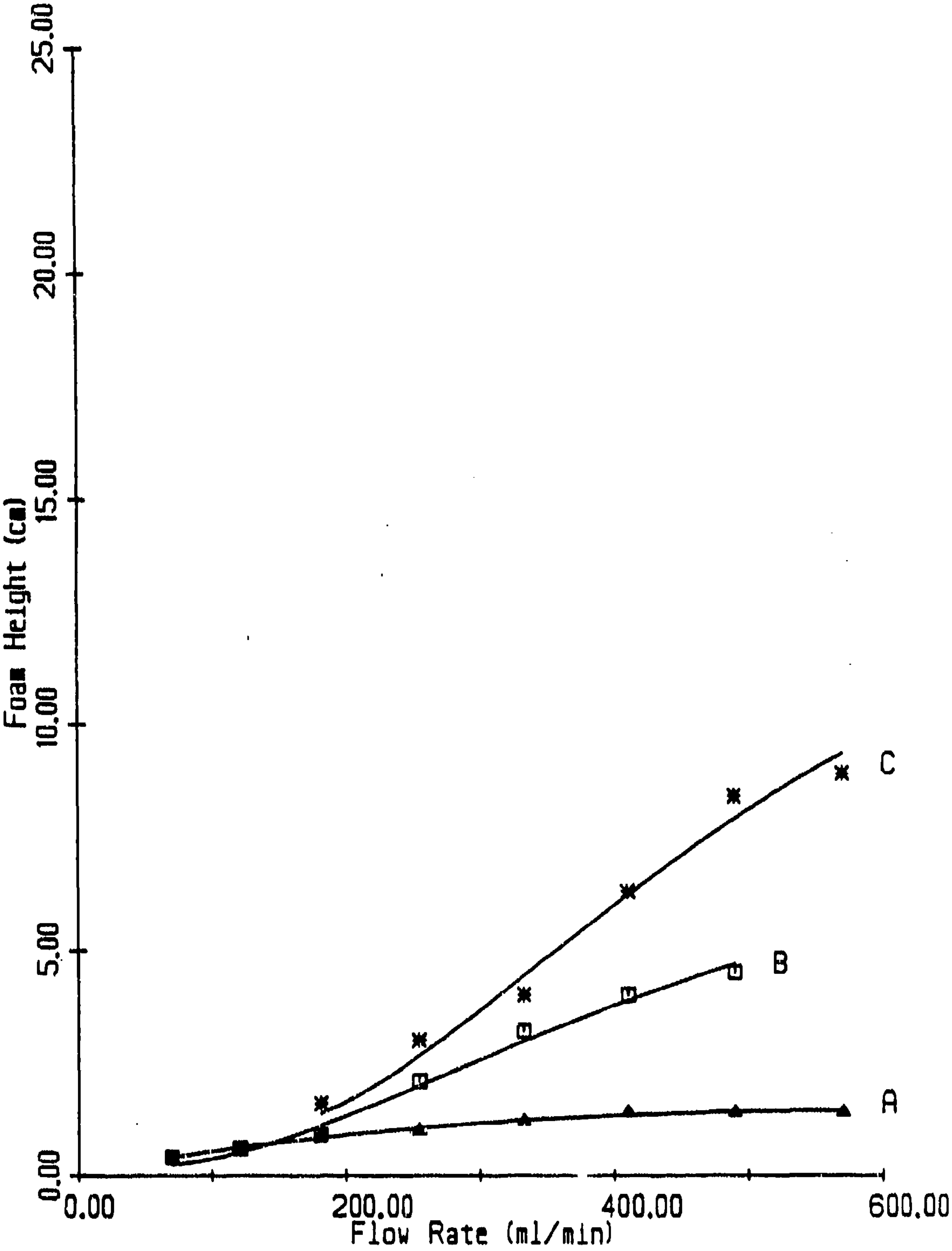


Figure 7 Variation of Foam Height with Flow Rate of Nitrogen Gas (ml/minute) through a Solution of Polydimethylsiloxane (1000 cSt) at a Concentration of 89.2 ppm in Tmp-Heptanoate at different Temperatures.
A is 85°C; B is 90°C; C is 94.5°C.

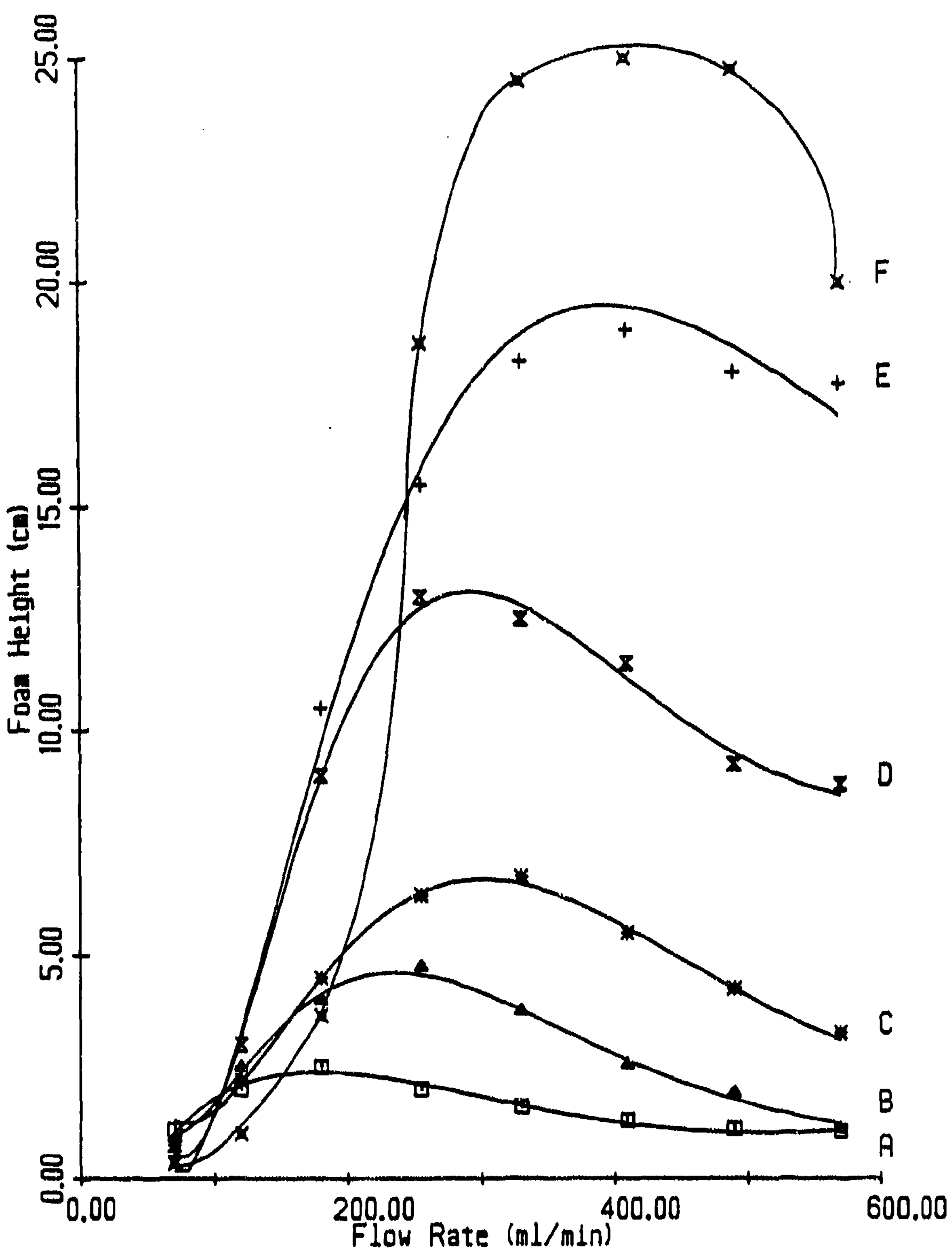


Figure 8 Variation of Foam Height with Flow Rate of Nitrogen Gas (ml/minute) through a Solution of Polydimethylsiloxane (1000 cSt) at a Concentration of 324.3 ppm in Tmp-Heptanoate at different Temperatures.
A is 32°C; B is 42°C; C is 52°C; D is 61°C; E is 71°C; F is 82°C.

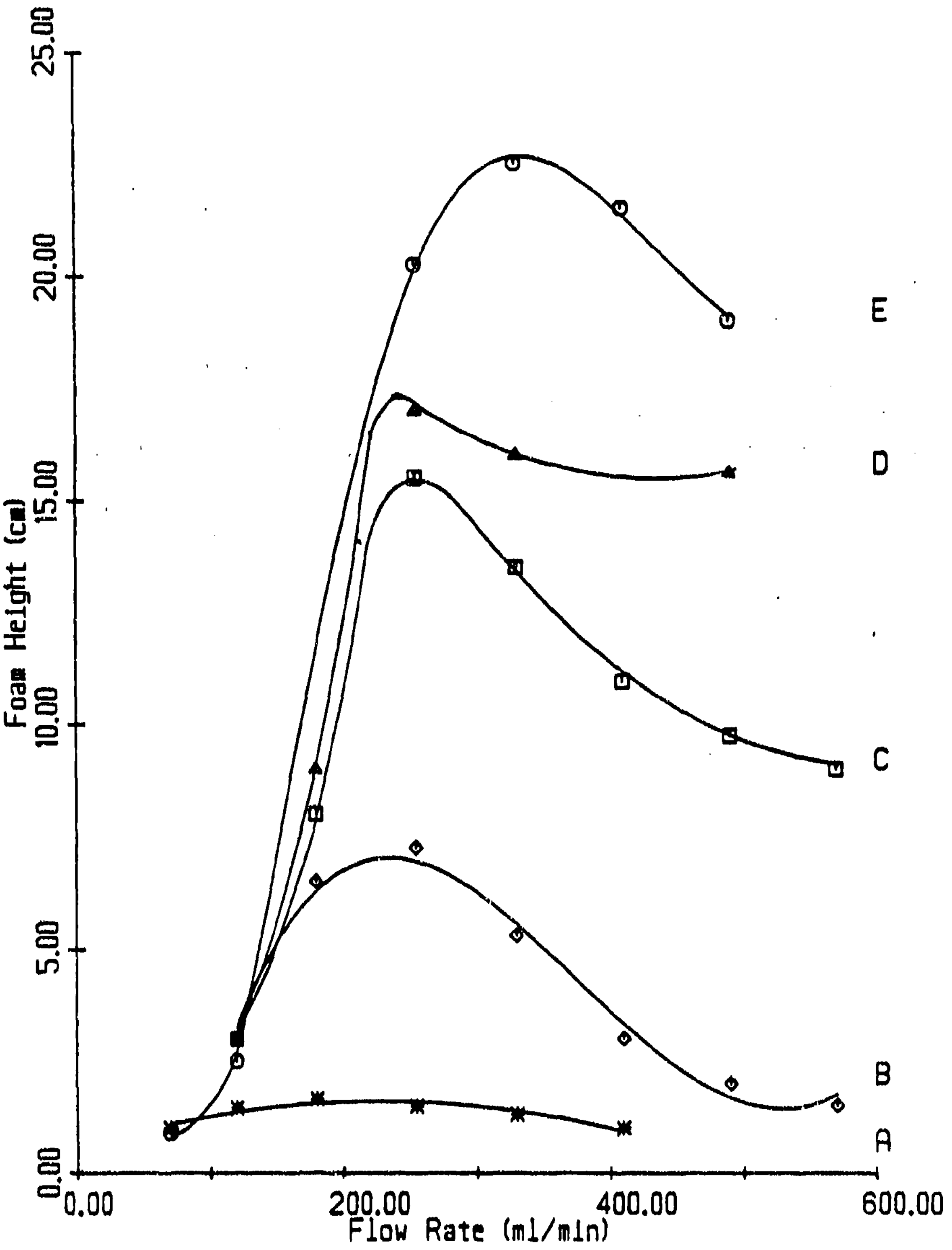


Figure 9 Variation of Foam Height with Flow Rate of Nitrogen Gas (ml/minute) through a Solution of Polydimethylsiloxane (1000 cSt) at a Concentration of 646 ppm in Tmp-Heptanoate at different Temperatures.
A is 33.5°C; B is 43.5°C; C is 53.5°C; D is 63°C; E is 73°C.

stage of the work on the contract, we anticipate that we shall observe the foam inhibiting action when we experiment with silicones of much higher molecular weight than those we have used hitherto. The inhibition of foam is well known to occur in hydrocarbon lubricants with silicones of viscosity from 1,000 to 60,000 centiStokes.

Although we have not yet observed polydimethylsiloxane act as an inhibitor for foamable solutions of this synthetic lubricant, we have found other materials that can inhibit their foaminess. Of these the most effective, without evidence of "fatigue" in its action even after continual bubbling for 24 hours, is G.E. FF-150, a fluoro-silicone fluid of viscosity = 10,000 cSt

4. PHYSICAL PROPERTIES OF SOLUTIONS OF VARIOUS OIL ADDITIVES

SOLUTIONS OF THE FOLLOWING OIL ADDITIVES WERE MADE IN TMP-HEPTANOATE:

A: N-PHENYL-1-NAPHTHYLAMINE WITH MAXIMUM CONCENTRATION OF 2% (W/W)
B: PHENOTHIAZINE WITH MAXIMUM CONCENTRATION OF 2% (W/W)
C: QUINIZARIN WITH MAXIMUM CONCENTRATION OF 0.05% (W/W)
D: TRICRESYL PHOSPHATE WITH MAXIMUM CONCENTRATION OF 2% (W/W)

The variation with temperature of the density of solutions of A, of B and of D are reported in Figures 10, 11, and 12.

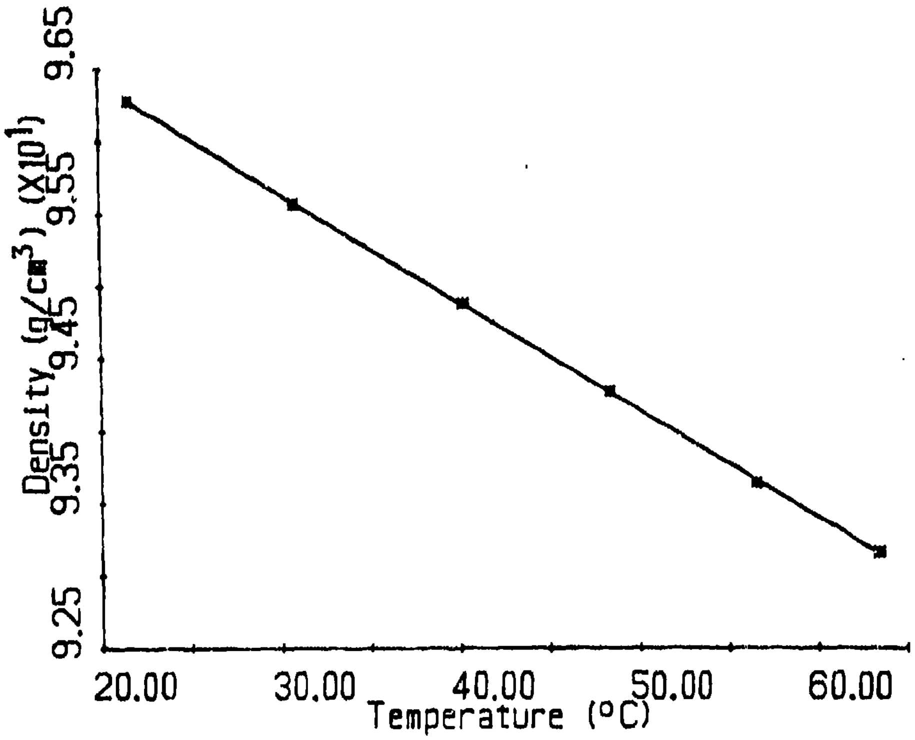


Figure 10 Variation of Density with Temperature for Tmp-Heptanoate Containing N-Phenyl-1-Naphthylamine (1.96% w/w)

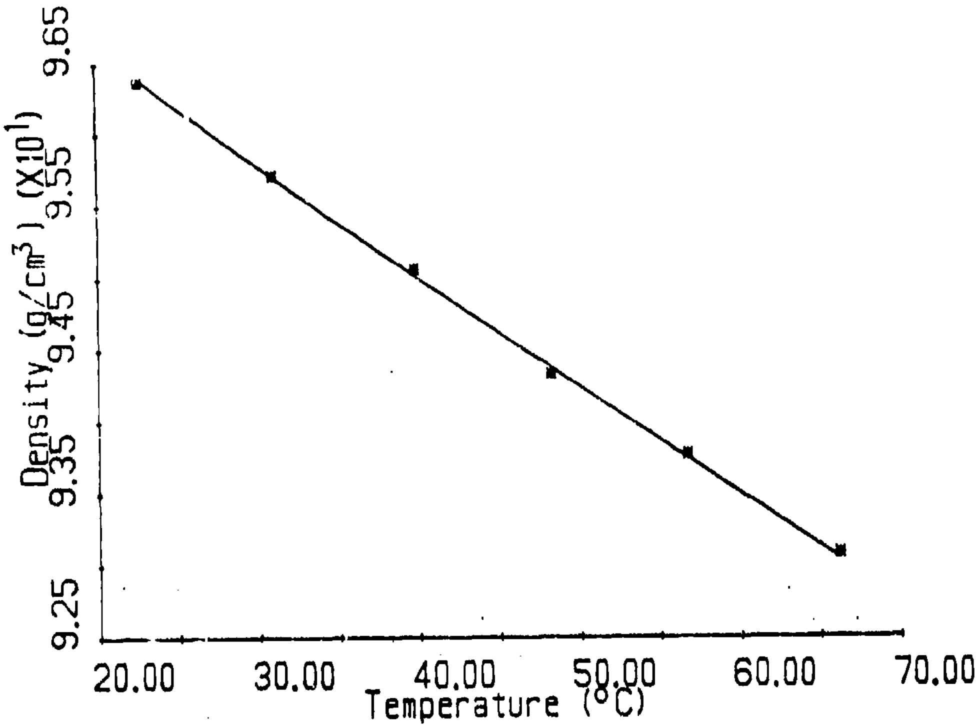


Figure 11 Variation of Density with Temperature for Tmp-Heptanoate Containing Phenothiazine (1.86% w/w)

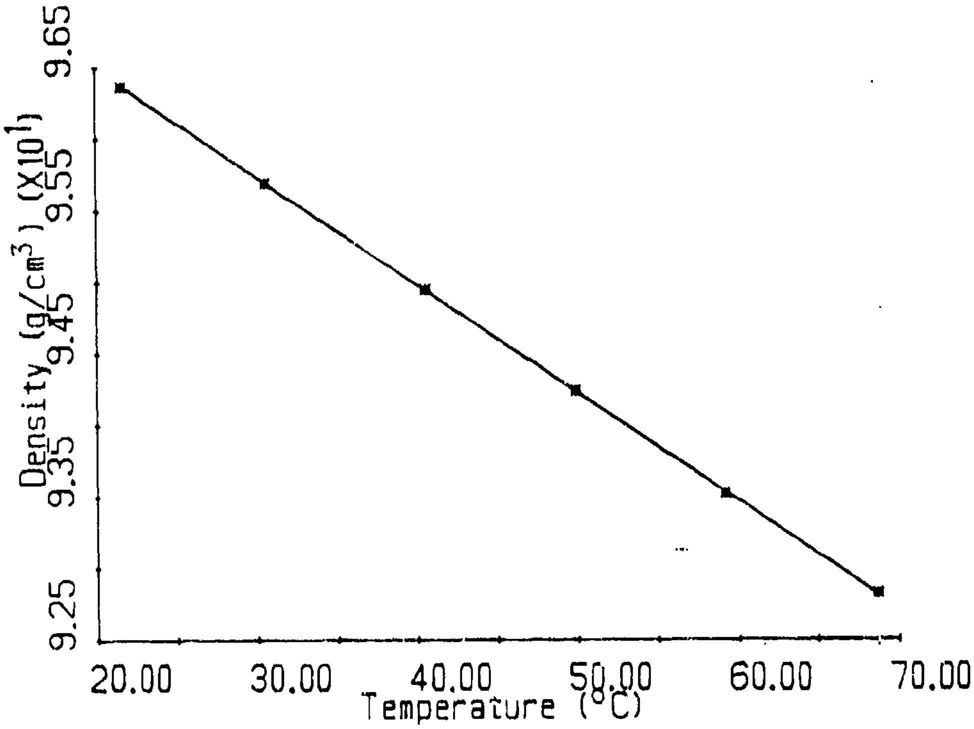


Figure 12 Variation of Density with Temperature for Tmp-Heptanoate Containing Tricresyl Phosphate (2.05% w/w)

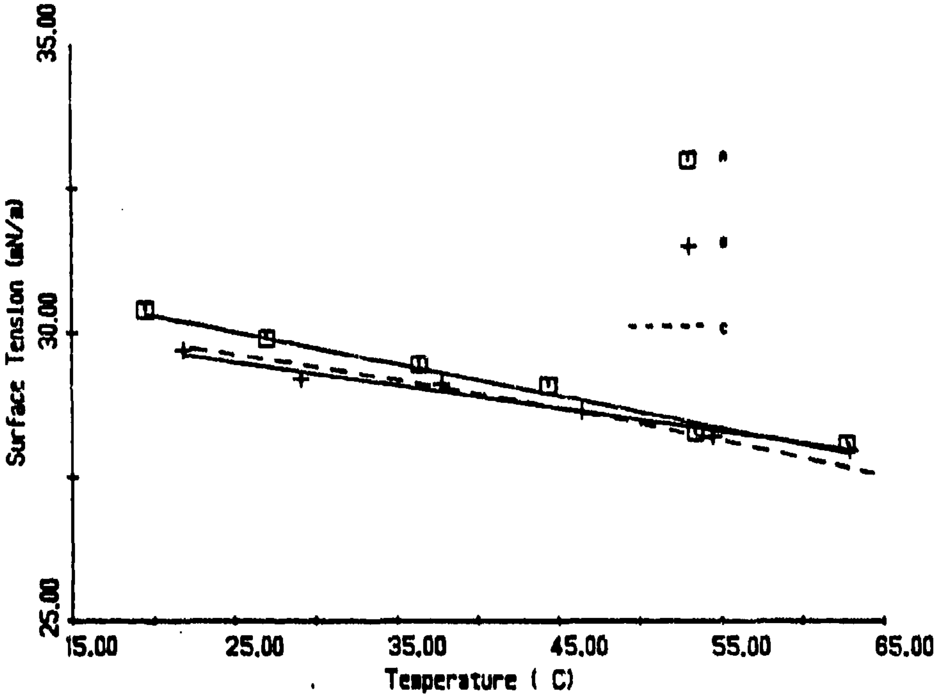


Figure 13 Variation of Surface Tension with Temperature for Tmp-Heptanoate Containing N-Phenyl-1-Naphthylamine
Broken Line is Solvent Alone; A is 1.86% (w/w) N-Phenyl-1-naphthylamine; B is 0.96% (w/w) N-Phenyl- 1-naphthylamine

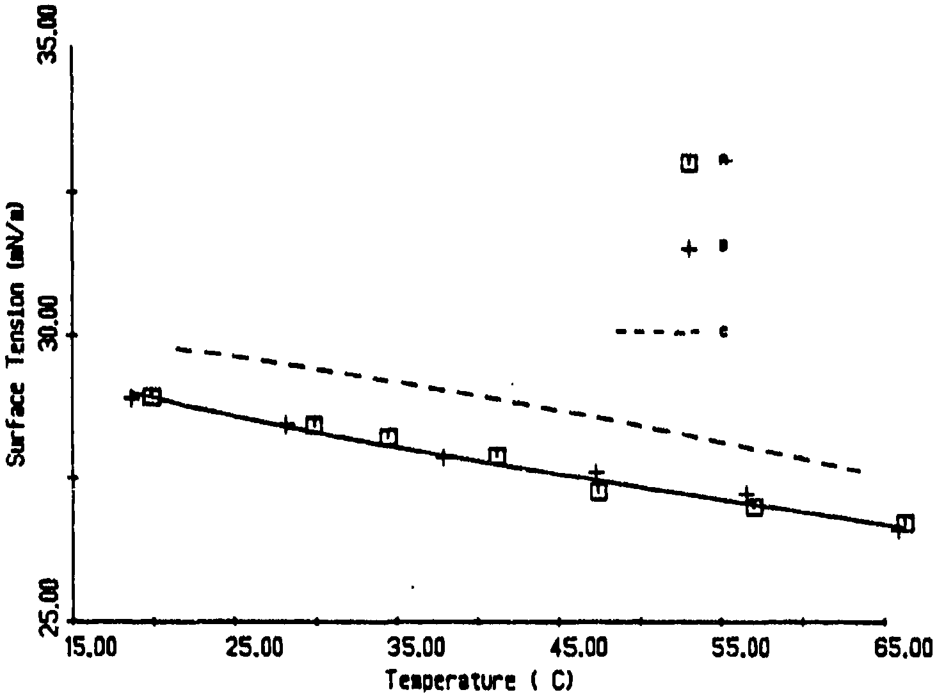


Figure 14 Variation of Surface Tension with Temperature for Tmp-Heptanoate Containing Phenothiazine
Broken Line is Solvent Alone; A is 1.86% (w/w) Phenothiazine; B is 0.935% Phenothiazine (w/w)

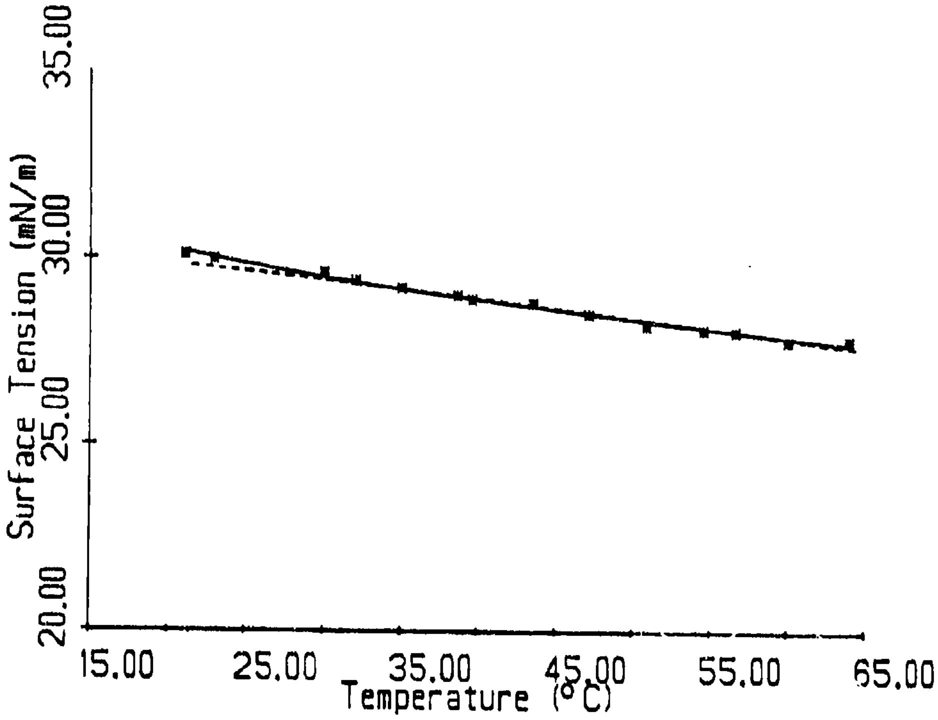


Figure 15 Variation of the Surface Tension with Temperature for Tmp-Heptanoate Containing Quinizarin
<u>Broken Line</u> is Solvent Alone; <u>Continuous Line</u> is 0.0238% (w/w) Quinizarin

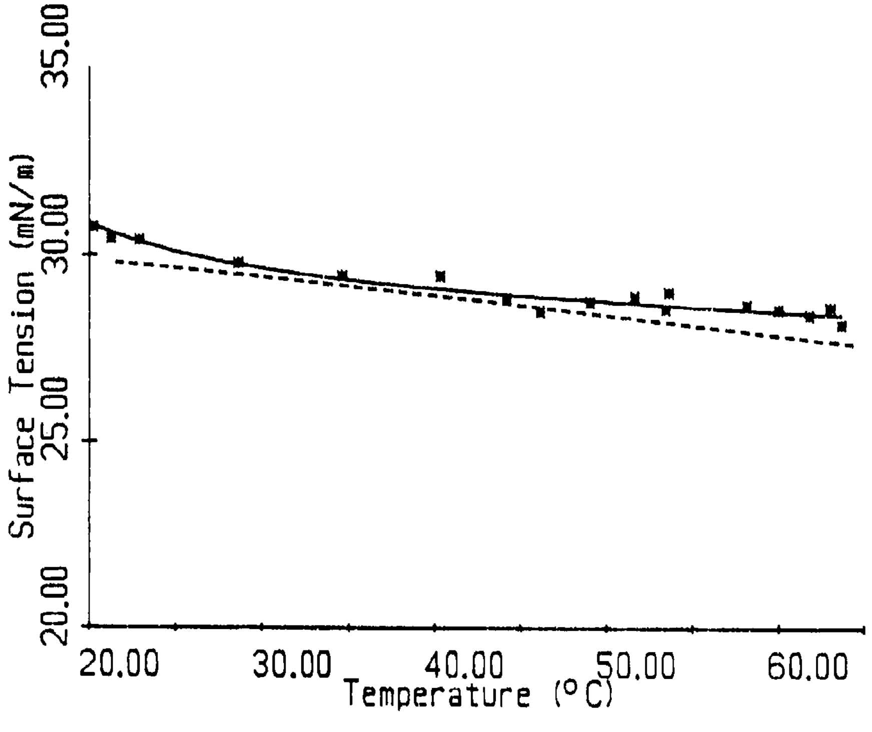


Figure 16 Variation of the Surface Tension with Temperature for Tmp-Heptanoate Containing Quinizarin
<u>Broken Line</u> is Solvent Alone; <u>Continuous Line</u> is 0.0477% (w/w) Quinizarin

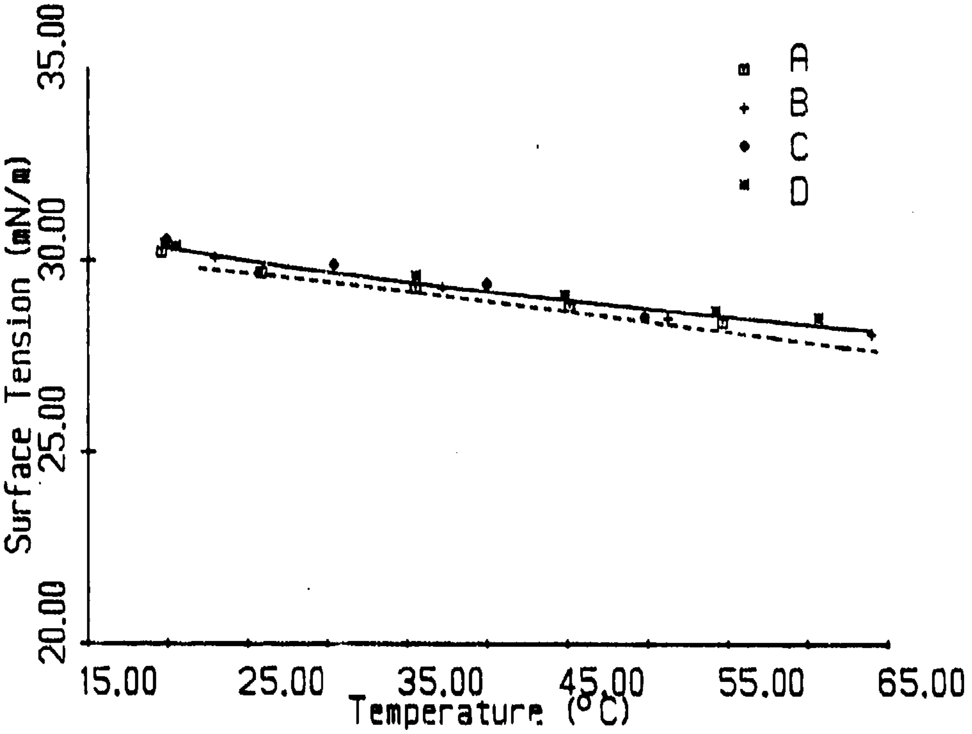


Figure 17 Variation of the Surface Tension with Temperature for Tmp-Heptanoate Containing Tricresyl Phosphate <u>Broken Line</u> is Solvent Alone; A is 2.05% (w/w) Tricresyl Phosphate; B is 1.99% (w/w) Tricresyl Phosphate, Temperature increasing; C is 1.99% (w/w) Tricresyl Phosphate,

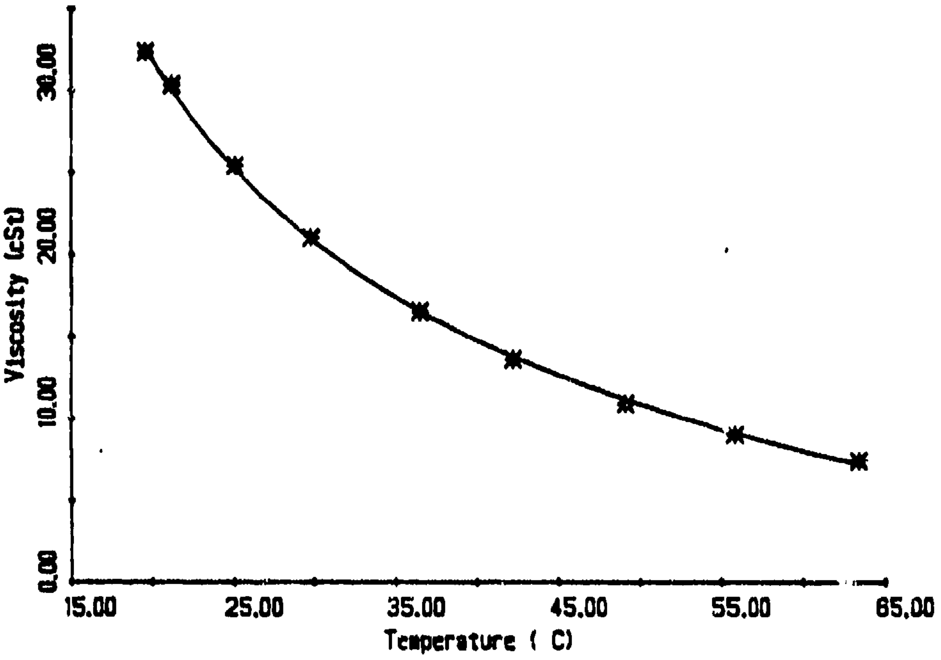


Figure 18 Variation of the Kinematic Viscosity (cSt) with Temperature for Tmp-Heptanoate Containing 1.86% (w/w) Phenothiazine

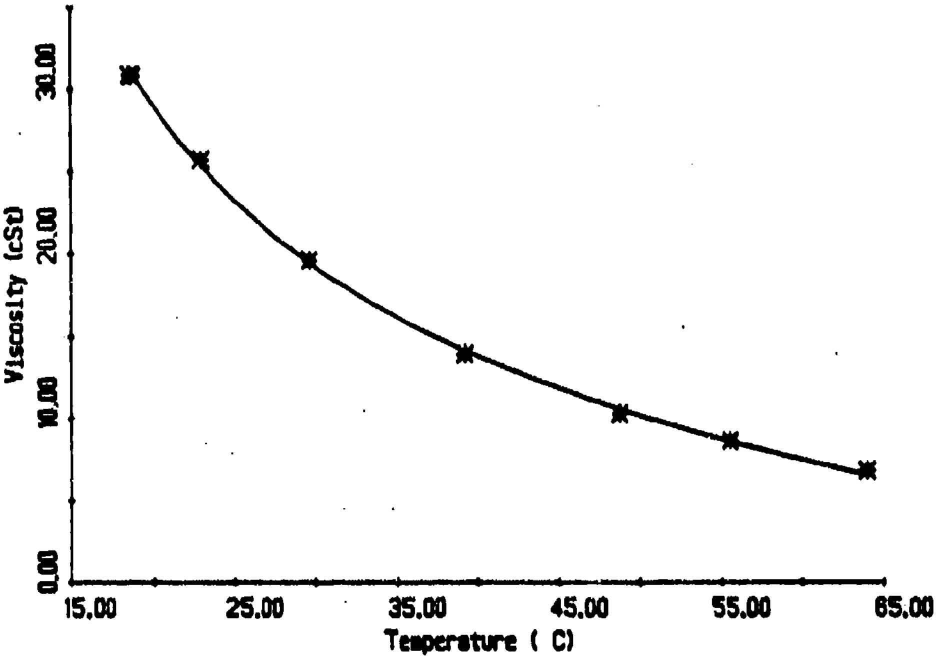


Figure 19 Variation of the Kinematic Viscosity (cSt) with Temperature for Tmp-Heptanoate Containing 0.0477% (w/w) Quinizarin

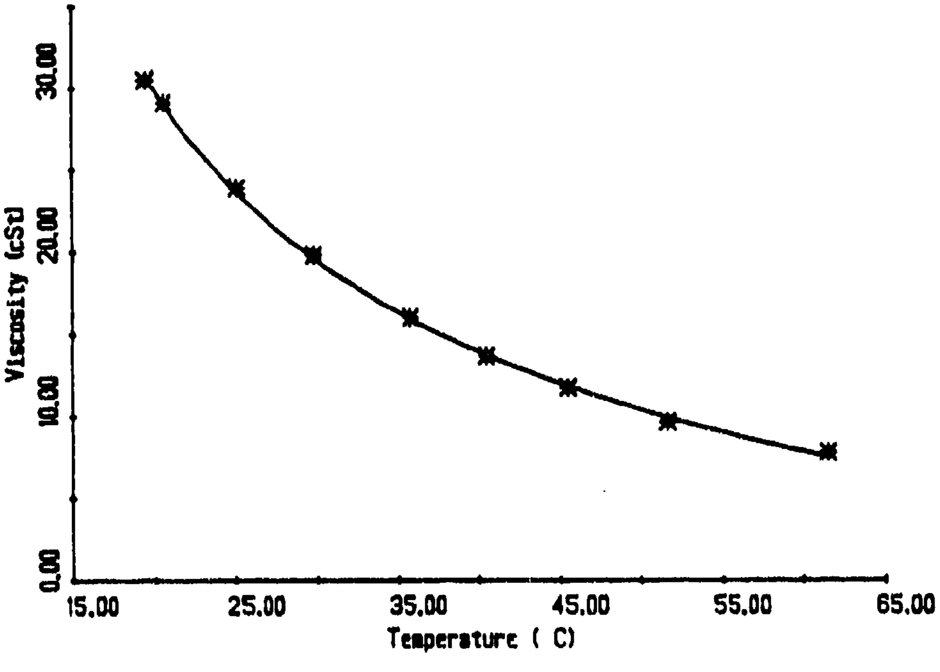


Figure 20 Variation of the Kinematic Viscosity (cSt) with Temperature for Tmp-Heptanoate Containing 1.99% (w/w) Tricresyl Phosphate

The variation with temperature of the surface tension of solutions of A, of B, of C, and of D are shown in Figures 13, 14, 15, 16, and 17. For comparison, the surface tension of the solvent is also shown on each of these diagrams.

The variation with temperature of the kinematic viscosity (centiStokes) of solutions of B, of C, and of D are shown respectively in Figures 18, 19, and 20.

5. FOAMINESS OF TMP-HEPTANOATE WITH VARIOUS OIL ADDITIVES

Tmp-heptanoate mixtures with various additives were tested for foaminess using method 3213 of federal test method standard 791.[19]
The four additives tested were:
A: N-Phenyl-1-naphthylamine with maximum concentration of 2%(w/w)
B: Phenothiazine with maximum concentration of 2%(w/w)
C: Quinizarin with maximum concentration of 0.05%(w/w)
D: Tricresyl phosphate with maximum concentration of 2%(w/w)
Compositions made of different combinations of additives A to D were tested, using the foam test apparatus of method 3213, nitrogen gas flow rate of 1000 ± 20 ml/minute; Temperature = 80 ± 1°C. The results of the foaminess tests are reported in Table 1. The apparatus does not give readings of foam volumes larger than 500 cc.

Table 1 shows:

(a) The mixtures containing a single additive at maximum concentration(2% w/w) do not foam.
(b) Three out of the six combinations of two additives show foaminess: namely, AD, AB, BD.
(c) The foam height starts at room temperature and increases with temperature.
(d) The foam height is concentration dependent. On increasing the total concentration of additive composition made up of any two or all three components selected from A, B, and D, the onset of foaminess is abrupt, moving without much prior indication from non-foaming to off-scale on the foam test. This occurs at a <u>total</u> concentration of about 2.5% (w/w).
(e) The foam collapse time decreases with increasing temperature.
(f) All four different combinations of the four additives, taken three at a time, cause the tmp-heptanoate to foam.

TABLE 1. FOAMINESS OF TMP-HEPTANOATE SOLUTIONS WITH VARIOUS OIL ADDITIVES, BY FEDERAL TEST METHOD STANDARD 791, METHOD 3213

NO.	COMBINATION	CONCENTRATIONS (%W/W) A	B	C	D	TEMP. (°C)	FOAM VOLUME cm^3	FOAM COLLAPSE TIME (sec)
1	A	1.99				80.2	None	
2	B		1.93			80.4	None	
3	C			0.050		79.8	None	
4	D				2.03	79.6	None	
5	AD	1.96			2.14	79.9	> 500	18-24
6		2.07			1.99	26.1	310	52
7		2.07			1.99	39.3	430	49-60
8		2.07			1.99	50.0	465	41
9		2.07			1.99	61.1	500	31
10		2.07			1.99	78.6	> 500	30
11		1.03			1.13	80.0	None	
12		1.12			1.07	21.3	None	
13		1.12			1.07	29.9	None	
14		1.12			1.07	44.1	None	
15		1.12			1.07	64.2	None	

NO.	COMBINATION	CONCENTRATIONS (%W/W) A	B	C	D	TEMP. (°C)	FOAM VOLUME cm^3	FOAM COLLAPSE TIME (sec)
16	AD	1.12			1.07	71.9	None	
17	AD	1.12			1.07	80.0	None	
18	AC	2.06		0.049		47.0	None	
19		2.06		0.049		63.8	None	
20		2.06		0.049		79.9	None	
21		1.94		0.050		81.0	None	
22	AB	2.03	1.89			25.2	495	63
23		2.03	1.89			61.0	> 500	32
24		2.03	1.89			80.0	> 500	22
25	BC		2.01	0.052		79.8	None	
26	BD		2.03		2.01	79.8	> 500	17
27			2.03		2.01	27.0	420	51
28			2.03		2.01	45.4	475	33
29			2.03		2.01	58.1	425	27
30			1.02		1.01	79.0	None	
31	CD			0.049	1.90	80.0	None	
32	BCD	1.97	0.051	2.03		79.8	500	16

NO.	COMBINATION	CONCENTRATIONS (%W/W)				TEMP. (°C)	FOAM VOLUME cm^3	FOAM COLLAPSE TIME (sec)
		A	B	C	D			
33	ABC	1.90	2.03	0.049		80.0	>500	17
34	ABD	1.98	1.85		2.05	30.0	500	78
35	ABD	1.98	1.85		2.05	56.0	> 500	46
36	ACD	1.97		0.048	1.87	80.0	> 500	13
37	ABCD	1.76	2.03	0.032	2.51	80.2	>500	39
38	A	4.01				79.6	>500	17
39	AD	2.03			1.12	80.0	175	10
40	AD	1.11			2.07	80.0	65	7
41	AB	1.02	2.01			80.0	455	21
42	AB	2.00	1.00			79.8	> 500	14
43	B		3.94			79.8	>500	18
44	BD		2.00		1.13	79.8	>500	15
45	BD		0.93		2.05	79.9	30	
46	D				4.04	79.9	50	5
47	A	3.01				79.8	> 500	14
48	B		3.01			80.0	> 500	14
49	D				3.01	80.1	None	
50	AD	2.98			1.03	80.2	>500	15

NO.	COMBINATION	CONCENTRATIONS (%W/W)				TEMP. (°C)	FOAM VOLUME cm^3	FOAM COLLAPSE TIME (sec)
		A	B	C	D			
51	AD	1.00			3.04	79.8	>500	14
52	BD		1.03		2.98	80.0	395	11
53	BD		2.97		1.20	79.8	>500	18
54	AD	2.46			0.52	79.9	>500	12
55	AD	0.50			3.59	79.8	460	12
56	BD		0.50		3.58	80.2	130	8
57	BD		1.50		1.59	79.8	100	7
58	BD		0.98		1.01	79.8	None	
59	AB	1.11	0.97			80.2	None	
60	AD	1.01			1.01	80.2	None	

6. SYNERGISM OF TRICRESYL PHOSPHATE ADDITIVE IN PROMOTING FOAMINESS OF OTHER ADDITIVES IN SOLUTIONS OF TMP-HEPTANOATE

The foaminess at 80°C of solutions of A in tmp-heptanoate is reported as a function of weight percent in Figure 21a. No foam is observed at concentrations below 2.5%, but a great increase of foaminess occurs at concentrations only slightly above 2.5%. Almost identical behavior for solutions of B in tmp-heptanoate is reported in Figure 21b. Both these solutes A and B display essentially the same behavior when combined with D (tricresyl phosphate) in solutions of tmp-heptanoate as solvent; that is, they will begin to show foaminess at lower concentrations by weight as tricresyl phosphate replaces either A or B in solution. For example:

1% concentration of A normally does not foam; neither does 3% concentration of tricresyl phosphate; but combined they produce enough foam to go off-scale on the test.

1% concentration of B normally does not foam; neither does 3% concentration of tricresyl phosphate; but combined they produce enough foam to go off-scale on the test.

These combinations, (A + tricresyl phosphate; B + tricresyl phosphate), at various compositions, at a combined concentration of 4% are reported on the foam test at 80°C in Figures 22a and 22b. The foaminess of the same compositions at a total concentration of 3%, at a temperature of 80°C., are reported in Figures 23a and 23b.

The same compositions at a combined concentration of 2% or less do not foam at all on the foam test at 80°C.

The results of the foregoing experiments allow us to make the following statement about the nature of the synergism of tricresyl phosphate in tmp-heptanoate solutions.

By itself in solution tricresyl phosphate is not a profoamer, even at concentrations as high as 4%, but when combined with either A or B in a solution in non-foaming concentrations of A or B as low as 1%, it behaves, as far as foam is concerned, as if it were some additional A or B; and when the combined concentration of A + tricresyl phosphate, or B + tricresyl phosphate, is raised to levels above 2.5%, copious foam is produced.

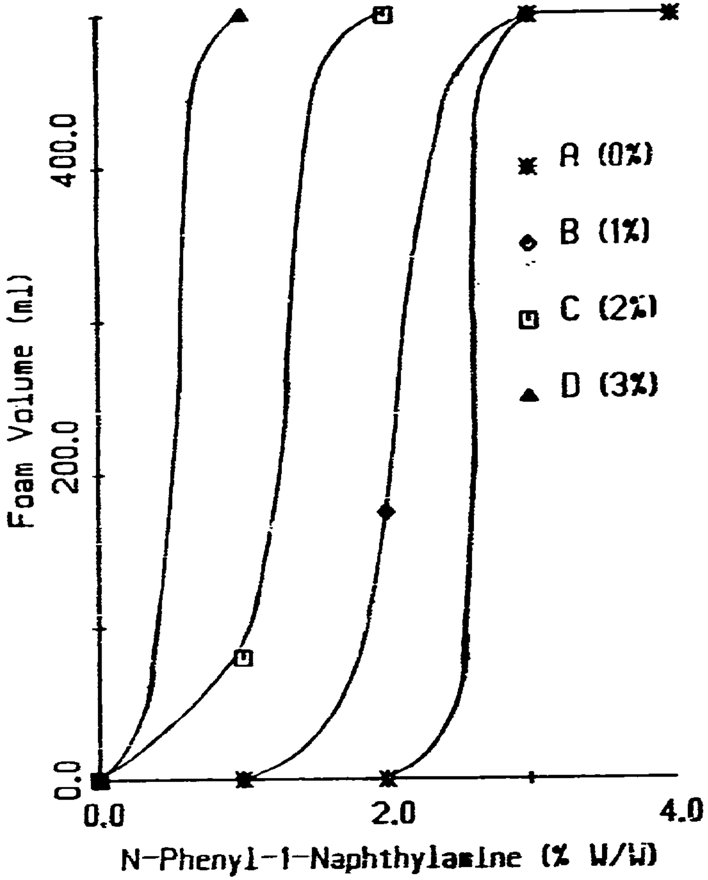


Figure 21a Foaminess measured by Test Method 3213 at 80°C of *N-Phenyl-1-Naphthylamine* dissolved in Tmp-Heptanoate up to a Concentration of 4% (w/w) (A); also Foaminess of Various Concentrations of N-Phenyl-1-Naphthylamine Combined with 1% (B), 2% (C), 3% (D), added Tricresyl Phosphate in Tmp-Heptanoate

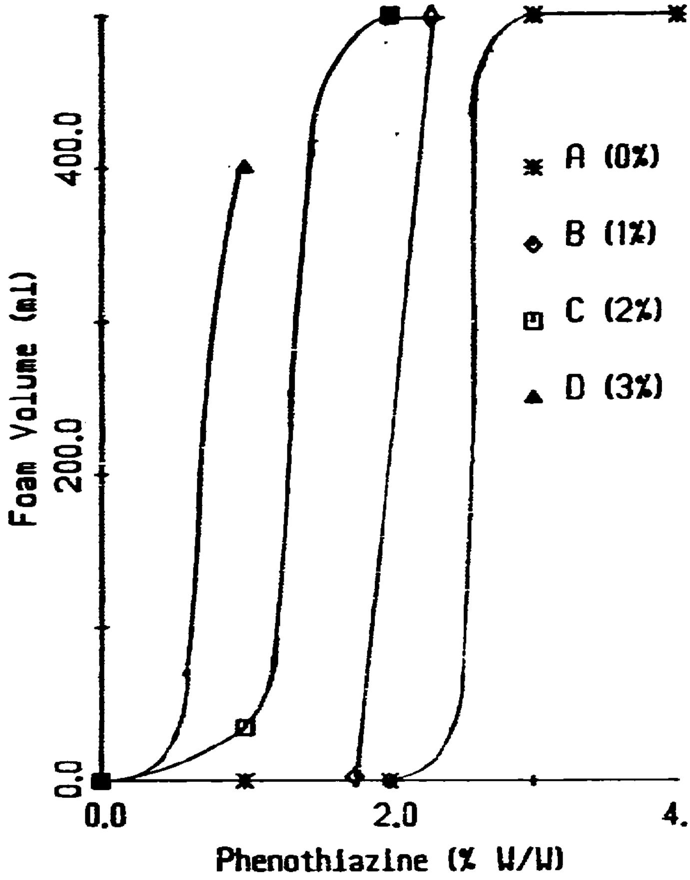


Figure 21b Foaminess measured by Test Method 3213 at 80°C of *Phenothiazine* dissolved in Tmp-Heptanoate up to a Concentration of 4% (w/w) (A); also Foaminess of Various Concentrations of Phenothiazine Combined with 1% (B), 2% (C), and 3% (D) added Tricresyl Phosphate in Tmp-Heptanoate

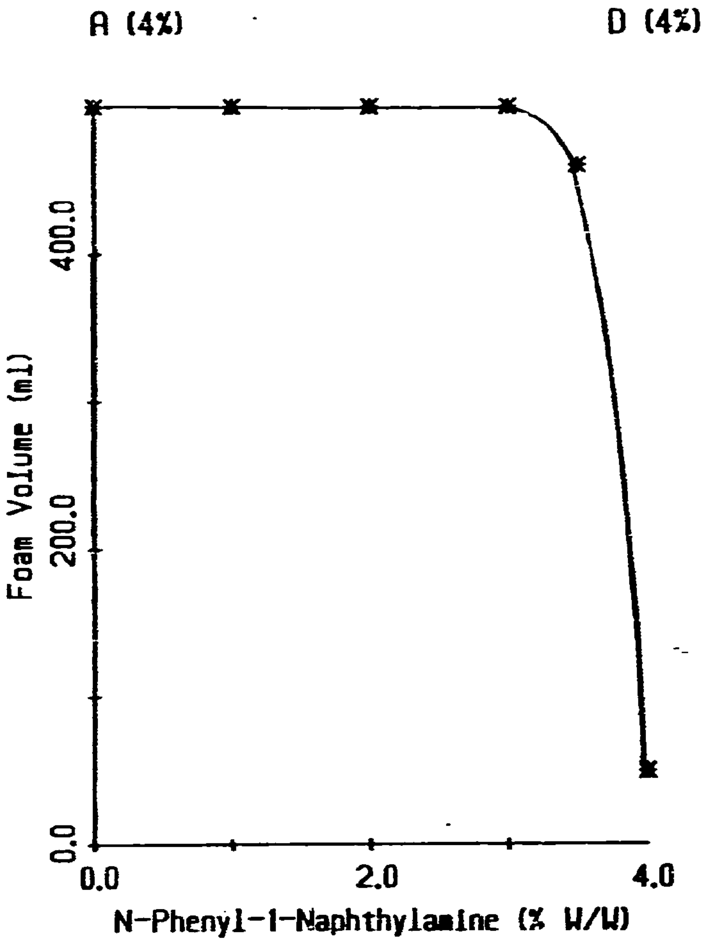


Figure 22a Foaminess of Solutions in Tmp-Heptanoate measured by Test Method 3213 at 80°C as a Function of Mixtures of N-Phenyl-1-naphthylamine (A) Combined with Tricresyl Phosphate (D) at Total Concentrations of 4% (w/w) of each Composition from 4% A to 4% D

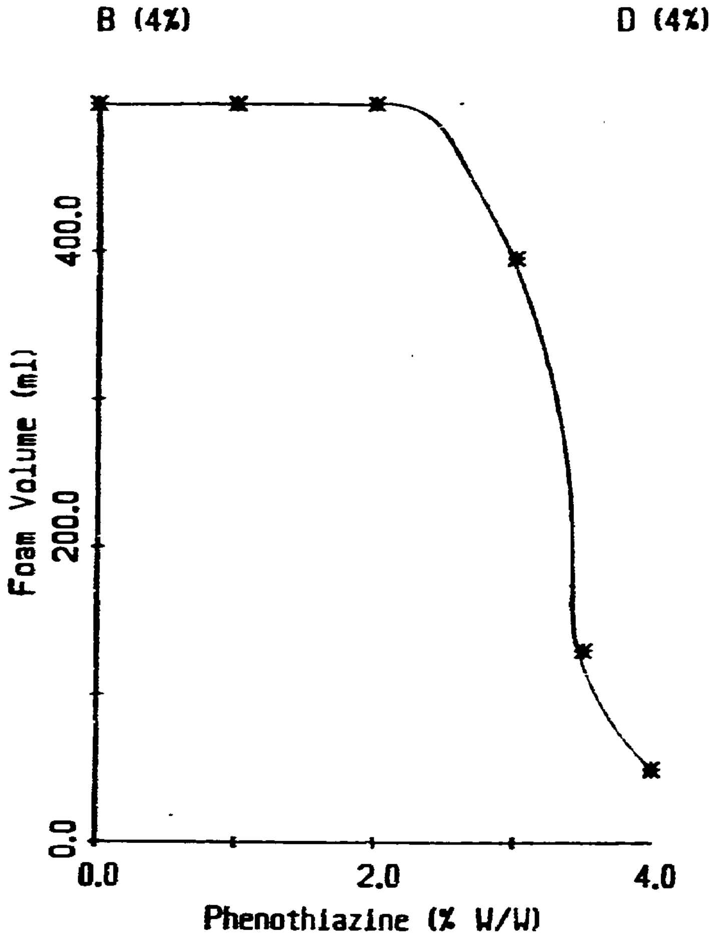


Figure 22b Foaminess of Solutions in Tmp-Heptanoate measured by Test Method 3213 at 80°C as a Function of Mixtures of Phenothiazine (B) Combined with Tricresyl Phosphate (D) at Total Concentrations of 4% (w/w) of each Composition from 4% B to 4% D

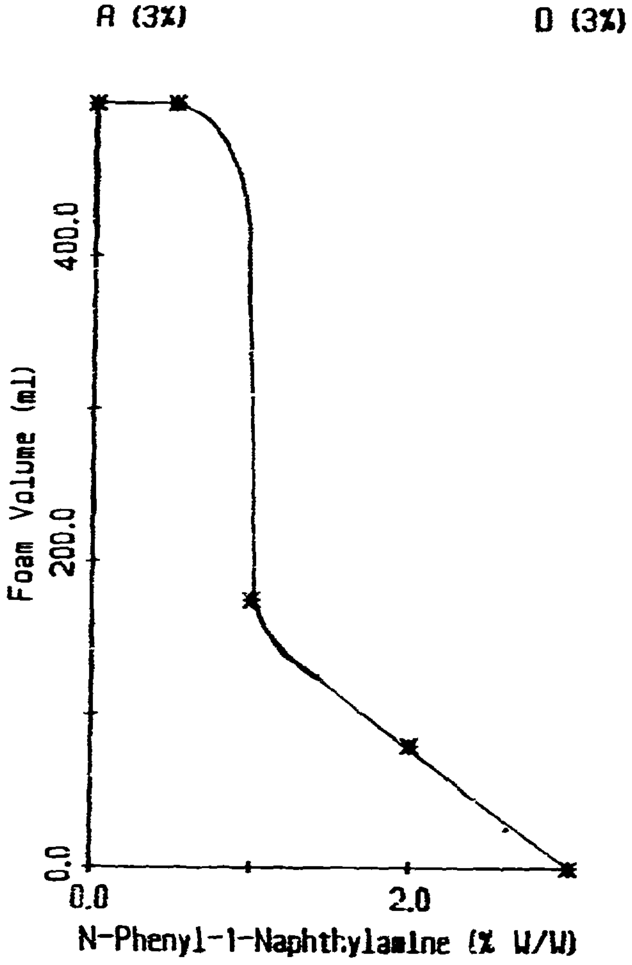


Figure 23a *Foaminess of* Solutions in Tmp-Heptanoate measured by Test Method 3213 at 80°C as a Function of Mixtures of N-Phenyl-1-Naphthylamine (A) *Combined with Tricresyl* Phosphate (D) at Total Concentrations of 3% (w/w) of each Composition from 3% A to 3%D

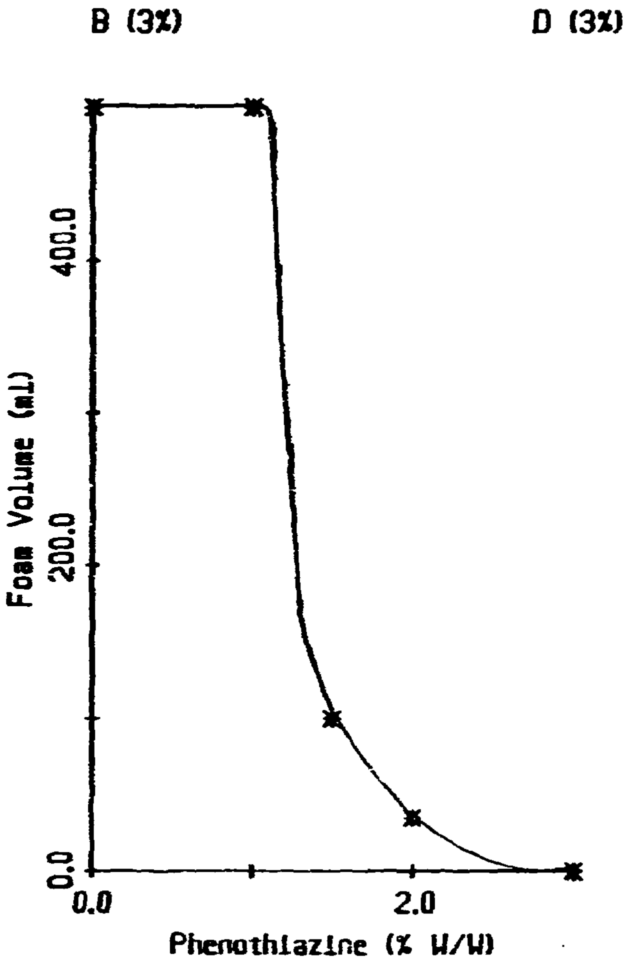


Figure 23b Foaminess of Solutions in Tmp-Heptanoate measured by Test Method 3213 at 80°C as a Function of Mixtures of *Phenothiazine* (B) Combined with Tricresyl Phosphate (D) at Total Concentrations of 3% (w/w) of each Composition from 3% B to 3% D

7. RATE OF RISE OF AIR BUBBLES IN OIL MEDIA

Stokes' law supposes a fluid velocity of zero at the solid-liquid interface.[20] However, this boundary condition of zero velocity at the interface (i.e., no slip) does not hold for the interface of a gas bubble, where direct transfer of momentum across the interface between the phases causes circulation to occur inside the dispersed phase. [21 22] When this occurs, hydrodynamic theory demonstrates[20 23] that the velocity of the bubble should be 1.5 times that predicted by Stokes' law. Experimental values tend, however, toward those predicted by Stokes' law unless care is taken to ensure purity of the liquid, in particular to ensure the absence of even traces of a surface-active contaminant.[24] Adsorption of solute at the liquid-air interface reduces the velocity of the rising bubble and may reduce it all the way to the Stokes'-law value, which is then taken as evidence of the presence of a rigid adsorbed layer that does not deform by viscous drag as the bubble rises.[20 25 26] The measurement of the rate of rise of a bubble provides a sensitive index to the presence of adsorbed films at the oil-air interface. An apparatus that enables us to measure the rate of rise of calibrated bubbles has been completed.

1. EXPERIMENTAL SET-UP

Into oil contained in a graduated cylinder (70 cm height, 26 mm internal diameter) air bubbles are released from an orifice, which is connected to an extended syringe. The diameter of the bubble is calculated by measuring the volume of air in a calibrated capillary. The velocity variations of the rising bubble are measured at three different heights of the liquid-containing column.

2. RATE OF BUBBLE RISE IN MINERAL OIL SOLUTIONS

For calibration and testing of the apparatus, the preliminary work was carried out with dilute solutions of Span 20 (sorbitan monolaurate) in white mineral oil (lubricant laxative grade) and at room temperature.

(a) Viscosity of mineral oil was measured in the temperature range of 19 to 28°C and is reported in Figure 24.

(b) The rate of bubble rise in mineral oil was measured:
K = observed velocity/Stokes' velocity = 1.40 ± 0.03 (uncorrected for wall effects). No variation of velocity with height in the column was observed.

(c) Rate of bubble rise in Span 20 solutions: The results obtained with Span 20 are reported in Figure 25.

The following comments are made relative to these measurements:

1. In the highest concentration of Span 20 in mineral oil (>0.1% w/w) the K value obtained is 0.90 ± 0.04 . No variation of velocity with height on the column was observed, presumably because of the rapid creation of the adsorbed film of solute.

2. In the intermediate range of concentrations (0.005 to 0.05 % w/w) the velocity becomes significantly less as the bubbles rise. This effect could be due to the bubble sweeping up adsorbate as it rises. There is no clear correlation between bubble radius and the change of velocity with height.

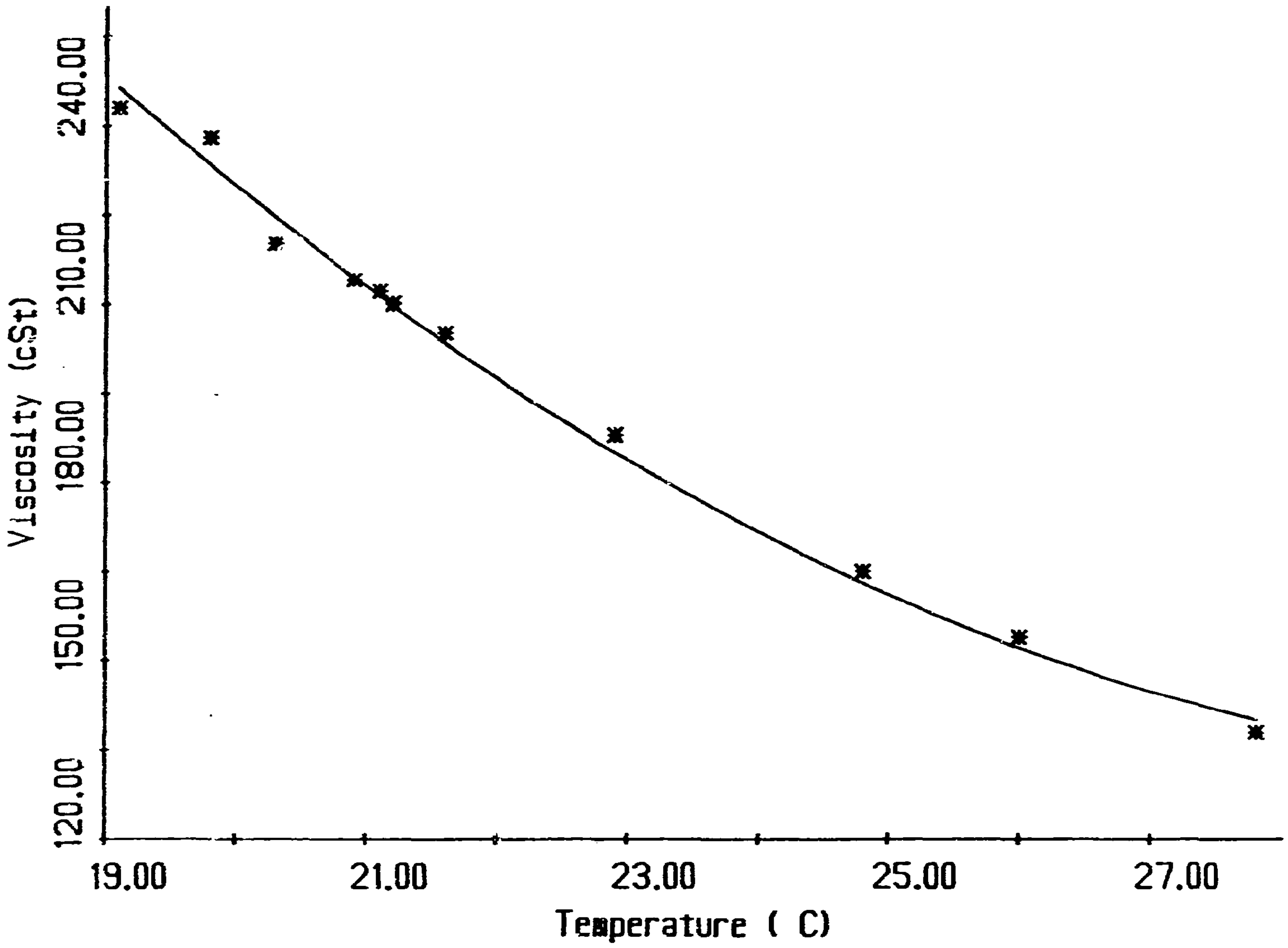


Figure 24 Variation of the Kinematic Viscosity (cSt) with Temperature of Extra-Heavy Mineral Oil, from 19°C to 28°C.

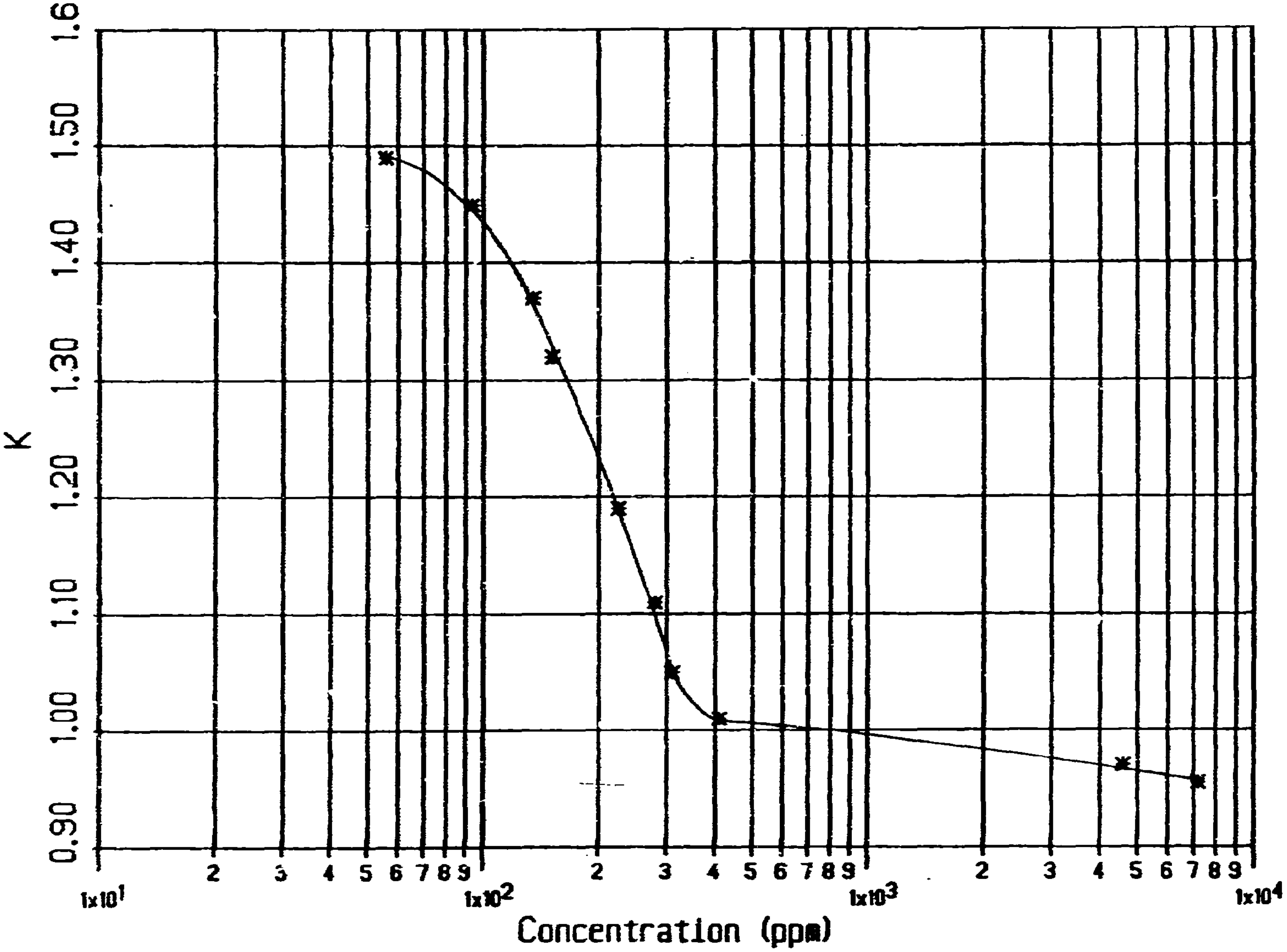


Figure 25 Comparative Rate of Ascension of Air Bubbles in Mineral Oil containing Oil-soluble Detergent Span 20 (Sorbitan Monolaurate), T = 22°C. Values of k are Corrected for the Wall Effect.

3. In the same range of concentration the lowest velocity measured (in the highest part of the column) was used to calculate the values of K reported in Figure 25. We have no assurance, however, that adsorption equilibrium had been attained even then.

4. The values of K vary from 0.9 to 1.4 (Figure 25) instead of the theoretical range of 1.0 to 1.5 . A correction required by the effect of the presence of the confining walls of the tube is provided by the Ladenburg formula[23 25]

$$V_c = V_m\ (1 + 2.1\ d/D) \qquad [5]$$

where V_c = corrected rate of rise;
V_m = measured rate of rise;
d = bubble diameter;
D = tube diameter.

For bubbles of an average diameter of 1.0 mm, rising in a tube of 25 mm diameter, this formula gives a correction factor of 8.4%.

Further experiments on the rate of rise of air bubbles were carried out with dilute solutions of polydimethylsiloxane (1000 centiStokes) in mineral oil and in tmp-heptanoate as solvents. (See Figure 26.) The occurrence of the change in velocity from 1.5 x Stokes' velocity occurs at a concentration of polydimethylsiloxane that is less by a factor of 100 than the corresponding concentration of the hydrocarbon-based oil-soluble detergent Span 20. This change reflects the greater surface activity of the silicone polymer compared to Span 20. But the general effects of the two solutes are similar.

The usual explanation[20 21 27] of the observed effect is that a surface-active species has been adsorbed at the liquid-air interface. As the bubble rises, the adsorbed solute is swept to the rear of the bubble, but the compression generates a back surface-pressure gradient opposing motion. The velocity becomes significantly less as the bubbles rise. Thus, with small bubbles, a stationary state is reached where momentum transfer across the interface decreases and ultimately ceases. Consequently, the fluid velocity at the interface becomes zero and the bubble then rises at a rate predicted for a rigid sphere by Stokes' law.

3. RATE OF BUBBLE RISE IN TMP-HEPTANOATE SOLUTIONS

It seems reasonable to suppose that, if the transition from greater to lower velocities of rise of bubbles in a fluid medium can be traced to the presence of an adsorbed film of solute at the liquid-air interface, then the presence of this layer should be the cause of the stability of a liquid lamella by the Gibbs-Rayleigh theory of foam stability. Yet we have found that there is no appreciable foam stability by the Method 3213 test in the range of concentrations investigated for the effect of solute on the rate of bubble rise. But foaminess by this test method requires a sturdy mechanism of stabilization of the lamellae, and it could well be that a more sensitive probe is required. Significant in this regard is the reported result of Okazaki et al.[28] who found a close parallelism between the stability of single bubbles at the surface of the solution and the ascending velocity of bubbles.

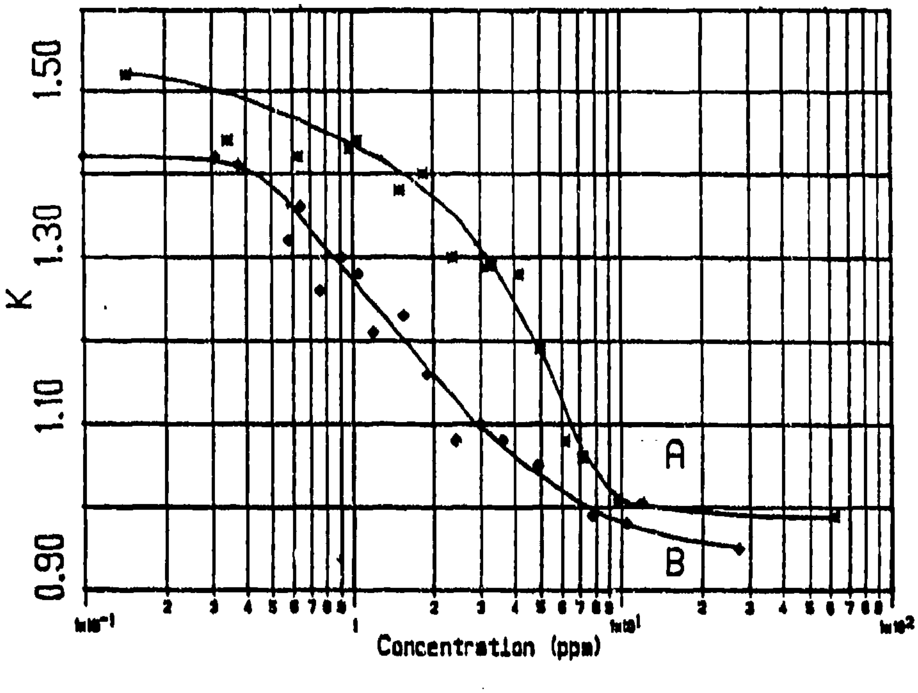


Figure 26 Comparative Rate of Ascension of Air Bubbles in Oils containing Polydimethylsiloxane (1000 cSt), T = 22°C. Values of K are Corrected for the Wall Effect.
A is Mineral Oil; B is Tmp-Heptanoate.

We therefore expect that we shall yet demonstrate such a relation with our own systems of present interest. Even more significant than this correlation would be the discovery of the common cause of the two phenomena; whether it is the result of non-Newtonian viscosity confined to a surface layer (or flow resistance near the bubble surface) which sensitively affects the ascending velocity of the bubble, as is the conclusion reached by Okazaki _et_ _al_.; or whether it is a Marangoni effect caused by dynamic surface tension. We have apparatus designed to measure both these effects independently, and so plan to obtain a definitive answer to this question.

8. ELECTRICAL PROPERTIES OF TMP-HEPTANOATE AND ITS SOLUTIONS

1. ELECTRICAL CONDUCTIVITY

In connection with the possibility that electrical effects in lubricating oils may influence foam stabilities, we have assembled equipment to measure the extremely low electrical conductivity of lubricating oils, with and without additives. The following Table reports our results for tmp-heptanoate and a few typical additives that might be present in a formulated lubricating oil (Table 2.)

TABLE 2. SPECIFIC CONDUCTIVITY OF TMP-HEPTANOATE AND ITS SOLUTIONS

Name of sample	Specific conductivity at 20°C in $ohms^{-1}$ cm^{-1} x 10^{14}
Solvent alone (tmp-heptanoate)	66
+ 0.2 % L5720 (Union Carbide Corporation)	95
+ 0.2 % L5303 (U.C.C.)	130
+ 0.2 % L6202 (U.C.C.)	810
+ 0.2 % L548 (U.C.C.)	150
+ 0.15% L540 (U.C.C.)	160
+ 0.14% silicone oil (50 cSt)	65
+ 0.14% polypropylene (Triol)	77
+ 0.15% polypropylene (Diol)	100
+ 0.17% carbon black	32
+ 1.0 % chloroform	90
+ 0.85% o-tritolyl phosphate	51
+ 0.77% phenyl naphthylamine	67
+ 1.0 % phenothiazine	2300
+ 1.1 % dihydroxy anthraquinone	46

One of our objectives is to see if foaminess can be correlated with proton or electron transfer between species in the solution. So far we can say that changes in the electrical conductivity do not necessarily attend foaminess, but we are still to determine whether in some cases such changes act to augment foaminess.

The specific electrical conductivity in $ohms^{-1}$ cm^{-1} was measured on a number of samples of oils, with and without additives, and both used and unused as lubricants in aircraft engines (Table 3.)

TABLE 3. SPECIFIC CONDUCTIVITY OF USED AND REGENERATED LUBRICATING OILS

Code number	Description (provided by H.A.Smith in letter of 9/11/81)	$ohms^{-1}\ cm^{-1} \times 10^{14}$
L-1	Basestock Esters treated with 5% calcium hydroxide at 25°c	5.0
L-2	Basestock Esters treated with 2% wt. calcium hydroxide at 40°C.	51.1
L-3	Basestock Esters treated with 0.3% wt. calcium hydroxide at 40°C.	40.8
L-4	Basestock Esters treated with 0.3% wt. calcium hydroxide at 25°C	57.5
L-5	New Formulated Ester Lubricant	16.8
L-6	Used Lubricant MIL-L-23699	4600
L-7	Used Lubricant MIL-L-23699	131
L-8	Used Lubricant MIL-L-23699	562
L-9	Used Lubricant MIL-L-7808	877
L-10	New MIL-L-7808	16.1
L-11	Basestock Esters prior to calcium hydroxide treatment	212

The results show that new and regenerated oils have lower electrical conductivities than used oils.

2. SURFACE POTENTIALS

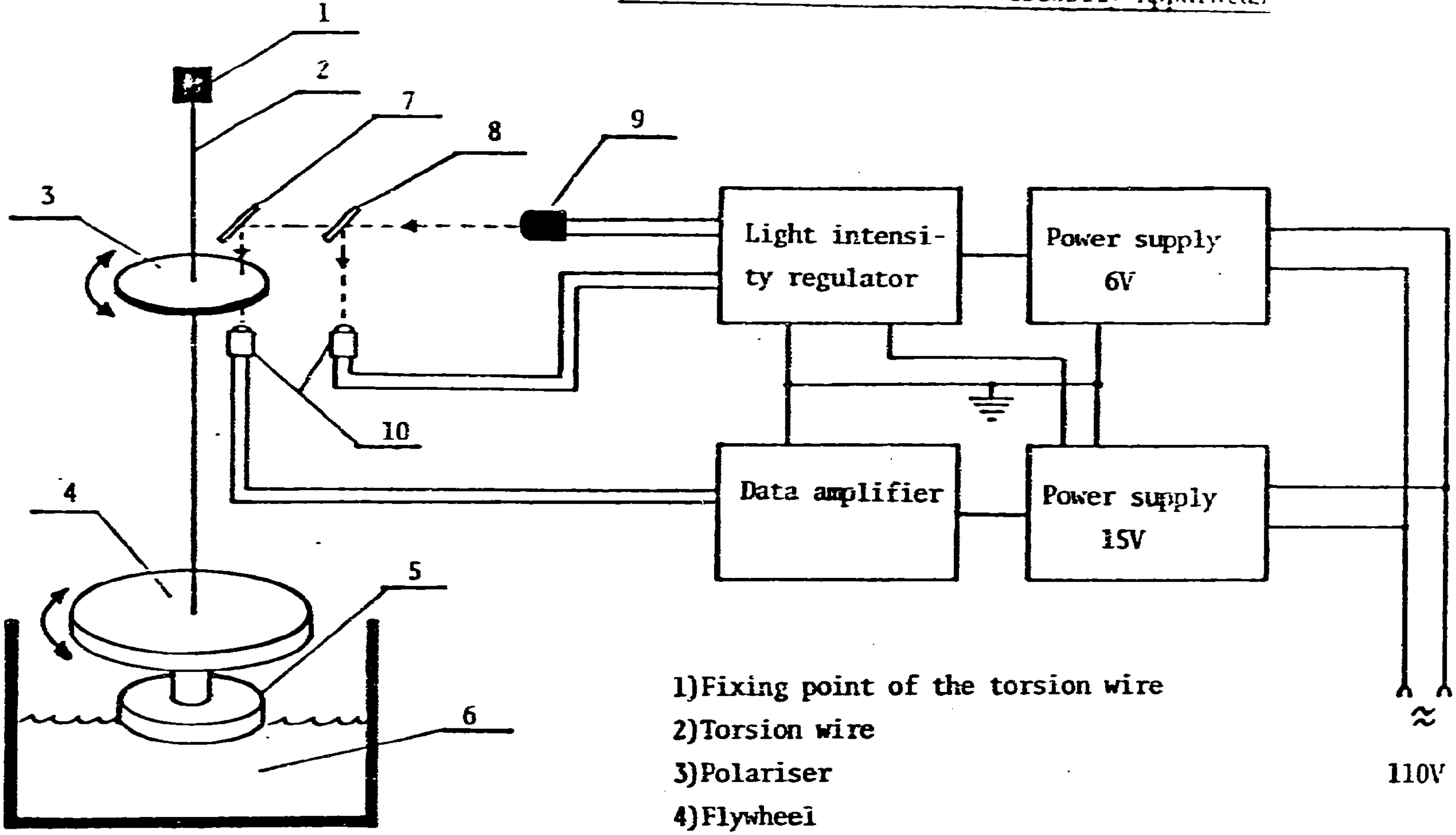
The theory of Derjaguin that foam may be stabilized by charges of like sign on opposite sides of the liquid lamellae, requires us to address that question for oils susceptible to foam formation. Although measurements of electrical conductivity give general information about charge separation in the liquid, they do not give direct evidence of the presence or absence of adsorbed electrical double layers at the liquid surfaces. The measurement of the Volta (or contact) potential change that occurs when a charged solute segregates at the surface of the solution gives a definitive answer to this question. To date, however, we have no more to report than our progress in the construction of a suitable instrument to measure surface potentials by the vibrating condenser method of Yamins and Zisman.[29] If a difference in electrostatic potential exists between the two plates of the condenser, a current will flow in an external circuit when one plate is moved with respect to the other. An amplifier possessing high-gain is used to detect the alternating signal generated when the plate vibrates. The electric field produced by oriented dipoles at the surface of the liquid can be detected by the vibrating-plate technique, and its magnitude determined by cancelling the dipole field with a produced field.

9. SURFACE VISCOSITY MEASUREMENTS

J.A.F. Plateau introduced the concept of surface viscosity, and referred the stability of foam lamellae to its influence. This property is the two-dimensional analog of ordinary viscosity and its coefficient is analogously defined and determined. The coefficient of surface viscosity is the force in dynes that must be applied per cm. of length along a surface to maintain a gradient of surface flow (between two parallel lines 1 cm. apart) of 1 cm. $sec.^{-1}$. The unit is the surface poise with dimensions MT^{-1}. Weakly foaming solutions have little surface viscosity, soap solutions a moderate amount, and some solutions of proteins, saponin, etc., a high surface viscosity amounting to a non-Newtonian plasticity.

The simplest instrument to detect surface viscosity is the oscillating- disc viscosimeter.[30] The logarithmic decrement of its torsional oscillations is determined with and without the surface film of adsorbed solute. Figure 27 shows the details of the apparatus. The torsion wire is supported at the end of a shaft that can be given a rotational twist by means of an external lever. The damping of the oscillations is measured by a light beam whose intensity varies as it passes across a polariser that is attached to, and moves with, the torsion wire. The source of the light beam is a red light-emitting-diode. The intensity of the light is regulated and stabilized by a feed-back mechanism. The variation of the light intensity is transferred to a receiving photo-diode that is connected to a recorder through a variable-gain amplifier. The electronic circuit diagram is shown on Figure 28, and a record of the output is shown on Figure 29 (surface damping of tmp-heptanoate.) The damping curve shown in Figure 29 is typical of a perfectly Newtonian liquid surface, inasmuch as the logarithmic decrement is linear with time (Figure 30). The effects of surface-active solutes on the surface viscosity of this solvent are yet to be investigated.

Schematics of the Surface Viscosity Apparatus



1)Fixing point of the torsion wire
2)Torsion wire
3)Polariser
4)Flywheel
5)Circular Knife-edge
6)Probe
7)Mirror
8)Beam Split
9)Light Source (LED-Diode)
10)Photodiodes

Figure 27 Schematics of the Oscillating-Disc Surface

Electronic Circuits of the Surface Viscosity Apparatus

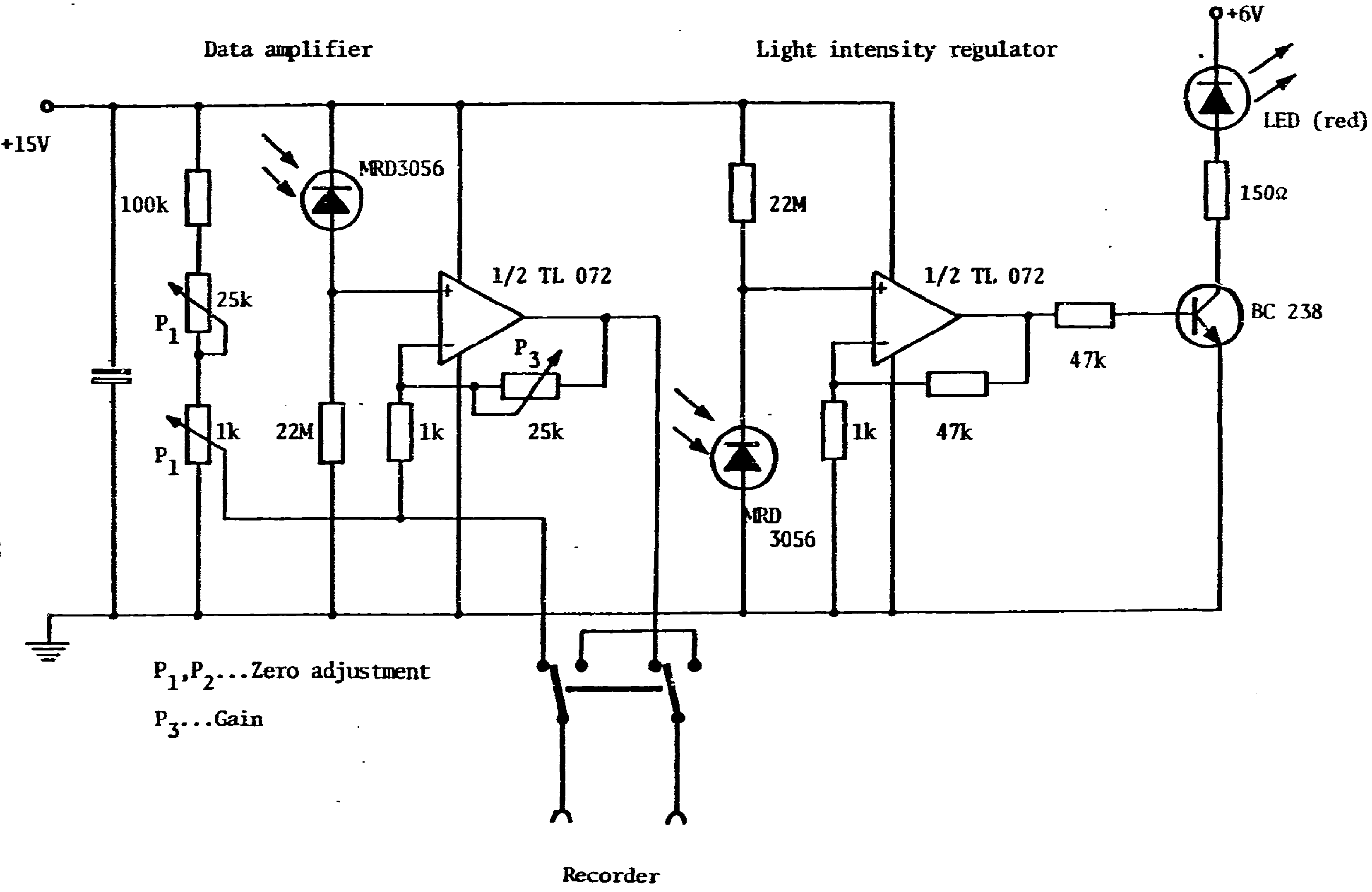


Figure 28 Electronic Circuits of the Oscillating-Disc Surface Viscosimeter

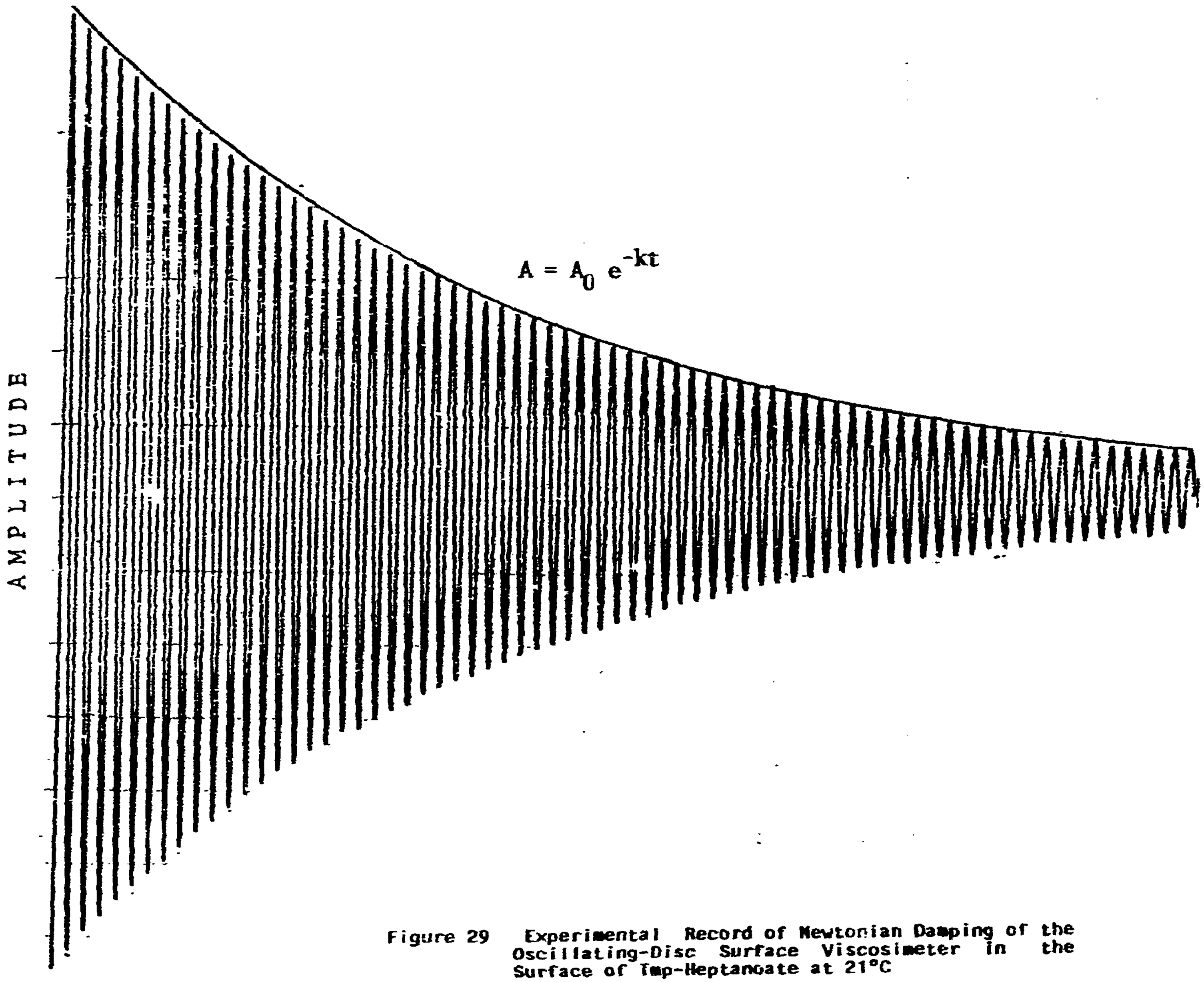


Figure 29 Experimental Record of Newtonian Damping of the Oscillating-Disc Surface Viscosimeter in the Surface of Tmp-Heptanoate at 21°C

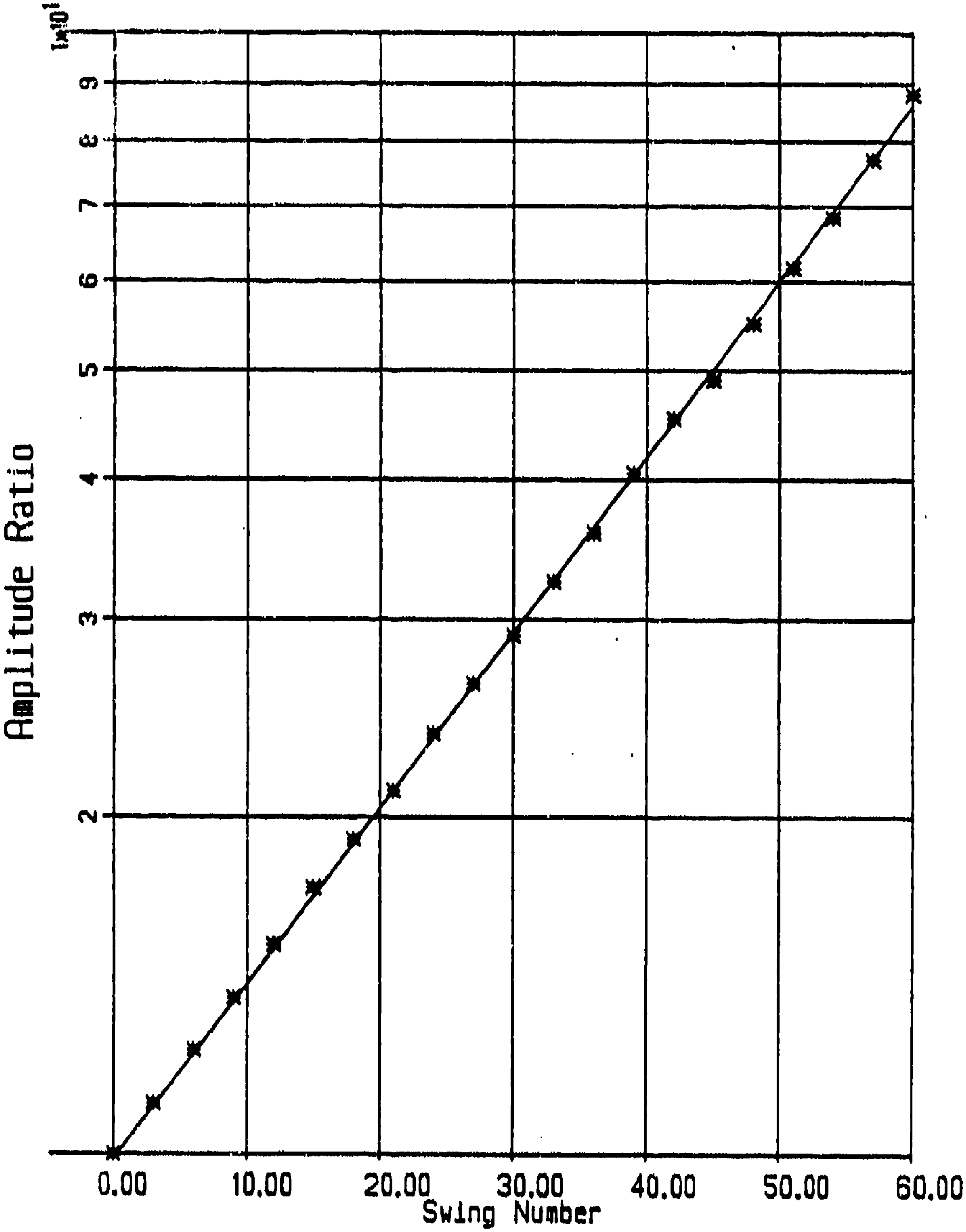


Figure 30 Linear Logarithmic Decrement of Amplitude with Time(measured by Swing Number,) calculated from the Experimental Record shown in Figure 29.

10. CONCLUSIONS

1 When dissolved in tmp-heptanoate, polydimethylsiloxanes of molecular weights less than 26,000 are surface active solutes and promote foaminess of the solution.

2 Oil additives such as N-phenyl-1-naphthylamine, phenothiazine, and tricresyl phosphate also cause the solution to foam at certain combinations and concentrations.

3 By itself when dissolved in tmp-heptanoate, tricresyl phosphate does not promote foam, even at concentrations as high as 4.0%; but when combined with either N-phenyl-1-naphthylamine or phenothiazine in solution in tmp-heptanoate, it behaves, as far as foam is concerned, as if it were additional N-phenyl-1-naphthylamine or phenothiazine; and so brings the concentration of the combined solutes into the range where foam is promoted. When the total concentration of these combinations of two additives is raised to levels above 2.5% (w/w) copious foam is produced.

4 Aeration of oil refers to how long tiny gas bubbles remain dispersed in oil before they rise to the surface and disappear. The rate of rise of a single air bubble of known diameter is our current index of aeration. The rate of rise of a bubble in oil is reduced by one-third or more by the presence of surface-active additives at low concentrations. These concentrations, however, are still too low to cause the oil to foam. Thus aeration and foaminess are two distinct phenomena, although both are ultimate effects of the surface activity of the solute present.

11. PLANS FOR FURTHER WORK

We plan further work as follows:

1. To test suggested improvements in the measurement of foaminess by Method 3213 of Federal Test Method Standard 791.

2. To continue to extend measurements on the effects of common oil additives and combinations thereof on aeration and foaming.

3. To confirm by finding more examples the relation we have recently found (subsequent to the date of the present Interim Report) between foaminess of certain oil additives and their property of forming a plastic surface layer, or "skin."

4. To determine whether the above correlation holds in all cases, or whether foaminess can occur in the absence of altered surface viscosity.

5. To determine whether synergestic effects on the foam and on the surface viscosity between certain pairs of additives result from the forming of molecular complexes between them.

6. To test the chemical stability of tmp-heptanoate and solutions therein of various additives by accelerated aging.

7. To compare the results of a standard aeration test with the measured rate of rise of a single bubble.

8. To determine whether the aeration effects introduced by additives are due to altered surface viscosity or to a Marangoni effect of dynamic surface tension.

9. To continue our current measurements on electrical properties of oil solutions, which have recently included the Hall effect, to investigate their possible connection with enhanced foaminess.

10. To measure gas solubilities in oil and in solutions thereof, and the effect of gas solubility on aeration and foaming.

11. To consider, in the light of all our findings, what properties of the solute with respect to its interaction with the oil medium lead to enhanced aeration and/or foam production.

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