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Capillary Behavior Of Viscous Liquids

Marvin De Young
University of the Pacific

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CAPILLARY BEHAVIOR OF
VISCOUS LIQUIDS

A Dissertation
Presented to
the Faculty of the Graduate School
University of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

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by
Marvin De Young
June 1965

This dissertation, written and submitted by

Marvin De Young,

is approved for recommendation to the Graduate Council, University of the Pacific.

Department Chairman or Dean:

Emerson G Cobb

Dissertation Committee:

Howard K Zimmerman, Chairman

Herschel Frye

Carl E. Wulfman

Neil L. Lark

Emerson G Cobb

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CHAPTER I

INTRODUCTION

A major problem confronting every investigator who works with synthetic organic chemistry is that of the crystallization of the products obtained. This problem necessitates extensive attention both on the experimental and on the theoretical level. In order to gain an understanding of the behavior of substances in the liquid state, so as to be better able to manipulate them in procedures intended to induce crystallization from complex mixtures, considerable attention has been given to various models of the liquid state. An understanding of the nature of pure liquids would seem to be an essential prelude to any attempt to understand the behavior of complex mixtures from which one component is to be separated. Since viscous liquids are sometimes in a state of incipient crystallization, or else represent systems which especially resist crystallization (e.g., sirups, glasses, etc.), a study of the capillary behavior of such liquids is of theoretical as well as practical interest.

Aside from the insight into the microscopic structure of liquids which may be gained from theoretical interpretations of viscosity measurements, knowledge of viscous flow properties is important in many hydrodynamic problems.

The viscosities of solutions of high polymers depend upon the sizes and shapes of the molecules in solution and thus provide a useful method for the study of polymer configurations. (33)

FLUID PROPERTIES

Matter may exist in the solid state or in the fluid state. Fluids are divided into liquids and gases, which have many properties that are similar to one another, but certain other properties which are not at all similar. The similarity and lack of similarity among solids, liquids, and gases may be generally traced to the spacing, mobility, and structure of their molecules.

The mobility of the molecules becomes progressively greater as one passes from the solid (in which gross mobility is virtually nonexistent) through the liquid and to the gaseous states. This increase in mobility is caused by the increased kinetic energy of the molecules. The essential difference between a liquid and a gas is that in a liquid the free path does not exist: a molecule is in continual interaction with its neighbors.(13)

The molecular structure of a solid is rigid, and the bonds between the molecules are so strong that the molecules do not readily move relative to each other. A solid does have a certain elasticity, however, which means that, for a given stress, there is a corresponding strain or deformation, regardless of whether the stress is one of compression or of tension.

If a liquid is confined, it will exhibit elastic properties with respect to compression, but only under certain conditions does a liquid withstand tensile stresses. Because of the increased spacing of the molecules in a gas, a gas has much less resistance to compression than either a solid or a liquid, and its tensile strength approximates zero.(2)

Because the molecular structure of a solid is essentially rigid, a force which is applied to the solid is resisted continuously, under static as well as dynamic conditions. In a liquid, the molecules possess a cohesiveness which tends to hold them together. The molecules are not fixed relative to each other, but instead are free to move and slip past one another, despite the fact that the spacing of the molecules is not very different from that in the solid state. This means that, if a force is applied to a free liquid, the liquid will continue to change its shape until the force is relieved. In other words, unless a liquid is confined on all sides, the liquid resistance to a force is a dynamic rather than a static property. This resistance is related to the viscosity and the inertia.

Like molecules of the liquid, the molecules of a gas slip past one another while resisting a force against them only under dynamic conditions of motion. Unlike the liquid molecules, however, the gas molecules are widely spaced and have much more mobility--which results in the gas not only being less dense than the liquid, but also in its having different viscous behavior.

The particular fluid properties of concern in this work are: density (ρ), surface tension (γ), and the viscosity (η).

<u>Density</u>. The density of a fluid is the mass which it possesses per unit volume. Since a molecule of a substance has a certain mass regardless of its state, it follows that the density is proportional to the number of molecules in a unit volume. The density of a substance in the liquid state is approximately the same as that for the solid state and is much greater than the density of the gaseous state. It is significant, however, that the density of a substance (under given conditions of temperature and pressure) is a fixed value, regardless of the gravitational system used. Density is important in any problem of flow in which there is acceleration. (2)

Surface Tension. Surface tension is responsible for the facts that certain insects are able to float on water, that a small drop of liquid assumes a spherical shape, and that liquids move upward in capillaries, or through porous media, for great distances from their source of supply.

The property of surface tension is particularly significant in liquids. This liquid surface phenomenon functions under either static or dynamic conditions. Surface tension arises from relative forces of adhesion and cohesion.

A molecule in the body of a liquid is in continual interaction with its neighbors. Within the body of a liquid the vector sum of these interaction forces is zero. By contrast, a molecule at the surface of a liquid is acted upon by a net inward cohesive force which is perpendicular to the surface. It requires work to move molecules to the surface against this opposing force, and hence the surface molecules have more energy than interior ones.

The surface tension of a liquid is the work that must be done to bring enough molecules from the interior of the liquid to the surface to form one new unit of that surface. By considering a single film it can be seen that the surface tension per unit length is identical with the free surface energy per unit area. (34)

Whenever a liquid surface is in a curved configuration there is a pressure difference between the two sides of the surface. The equation relating the curvature, the pressure difference, and the surface tension forms the basis for many methods of measuring surface tension. This relationship can be derived as follows.

Let ABCD be a small section of a curved liquid surface separating phase α (gas or vapor) from phase β (liquid). If ABCD is not spherical but part of a curved surface, it is always possible to find two lines, AB and BC, at right angles to one another on the surface and such that normals at A and D intersect at point O, while those from C and D intersect at O′. The lines AO and DO′ are called the principal radii of curvature of the surface. In Figure 1 these radii of curvature are denoted by r_1 and r_2. The area of ABCD is given by the product of the two arcs, AB and BC:

$$\text{area} = \Omega = r_1 r_2 \theta_1 \theta_2$$

where θ_1 and θ_2 are the angles formed by the radii at the centers of curvature.

If the area is now moved to a position parallel to its original position, the radii of curvature are increased by an amount dr. This movement can be accomplished by means of a pressure difference $\Delta P = P_\alpha - P_\beta$.

The area of the new surface A'B'C'D' is greater than the original area ABCD, and the change involves work done against the surface tension. The amount of work involved in extending the area must balance the work done by the pressure.

$$\Omega' = A'B'C'D' = (r_1+dr)(r_2+dr)\theta_1\theta_2$$

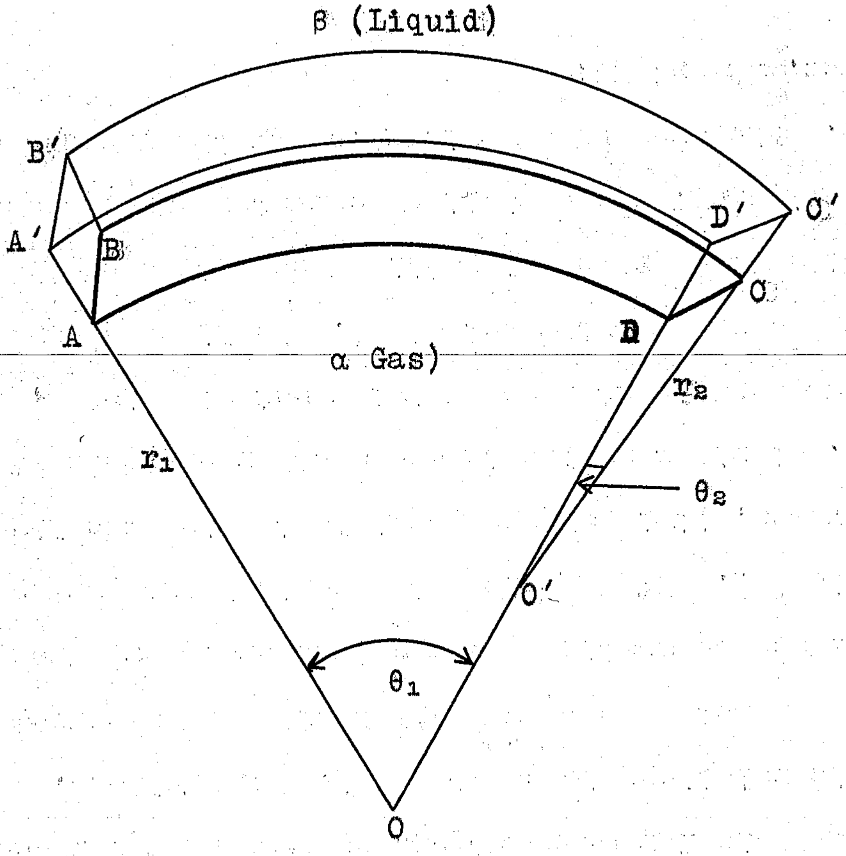

FIGURE 1

SCHEMATIC DRAWING OF A SMALL SECTION OF A CURVED SURFACE SEPARATING A LIQUID FROM ITS VAPOR

Neglecting the product of the differentials one obtains

$$\Omega' = r_1 r_2 \theta_1 \theta_2 + (r_1+r_2)\theta_1\theta_2\ dr.$$

Hence the work done against surface tension is

$$\text{work} = \gamma(\Omega'-\Omega) = \gamma(r_1+r_2)\theta_1\theta_2\ dr.$$

The mechanical work done by the pressure is given essentially as

$$\text{work} = \Delta P(ABCD)dr = \Delta P\ r_1 r_2 \theta_1\theta_2\ dr.$$

Equating these two work terms yields

$$\Delta P\ r_1 r_2 \theta_1\theta_2\ dr = \gamma(r_1+r_2)\theta_1\theta_2\ dr$$

$$\Delta P = \frac{\gamma}{r_1 r_2}(r_1+r_2) = \gamma\left(\frac{1}{r_1}+\frac{1}{r_2}\right).$$

When the curved surface is spherical, the two radii of curvature are identical. In this case the formula simplifies to

$$\Delta P = \frac{2\gamma}{r}.$$

This equation is made the basis of many theorems on surface tension. It states that a liquid under a curved spherical surface of radius r is subject to an excess or deficit of pressure $2\gamma/r$ dynes per cm^2 according as r is positive or negative. When the center of the sphere lies inside the

the liquid (convex liquid surface), r is considered to be positive, and r is negative when the center lies outside the liquid (concave liquid surface).

When a glass capillary tube of circular cross section is dipped into a liquid, the liquid in general is strongly attracted to (wets) the glass and the liquid surface assumes an approximately spherical shape. The pressure in the liquid under the meniscus is lower than that at the plane surface of the liquid outside the capillary tube. Liquid rises in the capillary until the weight of the liquid column balances the pressure difference. (38)

Consider a cylindrical tube whose radius is small, so that the surface of the meniscus may be considered as a section of a sphere with radius R. Then, since $\cos\theta = r/R$, $\Delta P = (2\gamma \cos\theta)/r$. If the capillary rise is

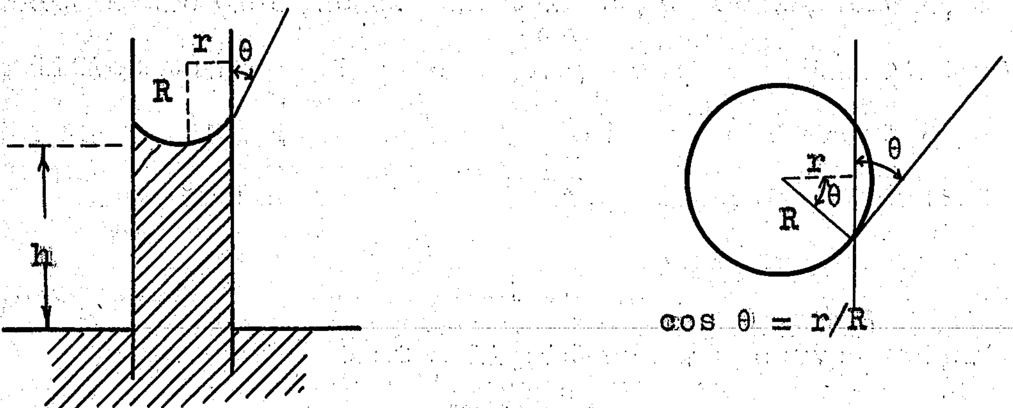

FIGURE 2

CAPILLARY RISE OF A LIQUID THAT

WETS THE WALLS OF A TUBE

h and if ρ and ρ_0 are the densities of the liquid and the surrounding fluid respectively, the weight of the cylindrical liquid column is $\pi r^2 gh(\rho - \rho_0)$, or the force per unit area balancing the pressure difference is $gh(\rho - \rho_0)$. Therefore

$$\frac{2\gamma \cos \theta}{r} = gh(\rho - \rho_0), \quad \gamma = (1/2)gh(\rho - \rho_0)r/\cos \theta.$$

In many cases the contact angle is practically zero, and if the surrounding fluid is a vapor, its density, ρ_0, is negligible compared to ρ. These approximations lead to the frequently used formula $\gamma = (1/2)\rho ghr$. (17)

Viscosity. Viscosity is that property of a fluid which causes resistance to relative motion within a fluid, whereas density and surface tension are properties of a fluid which can be measured under static conditions, viscosity is a property which is exhibited only under dynamic conditions. In other words, a fluid must be in motion for the property of viscosity to be observed.

Viscosity is traceable to the structure of a fluid. In the liquid state, the molecules are packed closely together, and viscosity is apparently due to the cohesiveness of the molecules. Hence, as the temperature increases, the cohesion decreases and the viscosity decreases. In the gaseous state, on the other hand, the molecules are spaced very far apart, and viscosity is due to the mobility of the molecules which leads to intermolecular encounters. As the temperature of the gas is increased, the mobility increases, and the viscosity also increases. The variation of viscosity with the temperature is of great importance. Under ordinary conditions of pressure, viscosity has been found to vary only with the temperature, being virtually independent of pressure.

Viscosity in liquids is only to a very small extent the result of the transfer of momentum by the molecules themselves, though this is the principal mechanism in gases. Instead, liquid viscosity is due mainly to a deformation of the liquid structure by the flow, which produces a dragging action between adjacent layers moving with different velocities, on account of the intermolecular forces.

Newton (31) assumed that the force of friction between neighboring surfaces of a liquid is (a) independent of the pressure, (b) proportional to the area, and (c) proportional to the relative velocity. The frictional force, f, resisting the relative motion of any two adjacent layers is

$$f = \eta S\frac{dv}{dr}$$

where S is the area and dv/dr is the velocity gradient.

This is Newton's law of viscous flow. The proportionality constant, n, is called the viscosity. (The term "coefficient of viscosity" was said by Lord Kelvin to be "illogical" and "vicious," and "a mystery of circumlocution."(38))

An especially important case of viscous flow is that of the flow within a pipe or tube. Consider an incompressible fluid flowing in a tube of circular cross section witn radius R and length l. The fluid at the walls is assumed to be stagnant, and the rate of flow increases to a maximum at the center of the tube. If v is the linear velocity at any distance r from the axis of the tube, a cylinder of radius r experiences a viscous drag given by

$$f = -\eta\frac{dv}{dr}\cdot 2\pi rl.$$

For steady flow, this force must be exactly balanced by the force driving the cylinder through the tube, or

$$f = \pi r^2 \Delta P$$

where ΔP is the difference between the forward pressure and the backward pressure. Thus for steady flow

$$-\eta\frac{dv}{dr}\cdot 2\pi rl = \pi r^2 \Delta P$$

$$dv = -\frac{r}{2\eta l}\,\Delta P\,dr$$

which on integration yields

$$v = -\frac{\Delta p}{4\eta l}\,r^2 + \text{constant.}$$

The constant of integration can be determined by applying the boundary conditions: $v = 0$ when $r = R$. The result is

$$v = \frac{\Delta P}{4\eta l}\,(R^2 - r^2).$$

The total volume of fluid flowing through the tube per second is calculated over each element of cross-sectional area given by $2\pi rv\,dr$.

$$\frac{dV}{dt} = \int_0^R 2\pi vr\,dr = \frac{\pi R^4 \Delta P}{8\eta l}.$$

This is Poiseuille's law, which furnishes a very nice way to determine the viscosity of liquids.

RATE OF CAPILLARY RISE

Considerable theoretical work has been done on the problem of the rate of rise of liquids in capillary tubes. If a vertical capillary is touched to the surface of a liquid which wets the material of the capillary, the liquid is drawn into it by its surface tension. The initial rate of rise is very rapid, and the velocity of flow will be governed by the laws of hydraulics.

The initial velocity soon decreases because of the resistance encountered, and the velocity becomes such that the conditions of flow postulated in Poiseuille's law can be assumed valid and that these conditions thereafter persist.

The distance, l_o, that the meniscus penetrates before the establishment of the Poiseuille's law condition is given by Washburn (41) as

$$l_o = \frac{2\gamma \cos \theta \, r^2 \rho}{4 \times 10^3 \, \eta^2}.$$

For any given viscosity this can be made vanishingly small by choosing a capillary of sufficiently small bore.

Ligenza and Bernstein (23), assuming that the wetting process is very rapid and that Poiseuille's law is valid for the entire flow time, give as the differential equation of motion

$$\frac{d}{dt}\left\{\pi R^2 [\rho h + \rho_o (l - h)] \frac{dh}{dt}\right\} = 2\pi R \gamma \cos \theta -$$

$$8\pi \frac{dh}{dt}[\eta h + \eta_o (l - h)] - \pi R^2 g h (\rho - \rho_o) - \frac{1}{4} \pi R^2 \rho \left(\frac{dh}{dt}\right)^2$$

where h is the height of the liquid column at time t, R and l are the radius and length of the capillary, η and η_o the viscosity of the liquid and air respectively.

The term on the left is the time rate of change of momentum of the contents of the capillary; the terms on the right are, respectively, the forces due to surface tension, viscous resistance, gravity, and the "end drag effect" of Brittin (6).

This equation cannot be solved explicitly. However, several simplifying assumptions can be made. If the radius is small, the momentum term and the end drag term become negligible in comparison with the others. The density of the air may be neglected in comparison with that of the liquid, and the viscosity of the air is negligible compared with that of the liquid. Further, it may be assumed that $\eta h_\infty \gg \eta_0 l$. For liquids which wet the capillary surface, the simplified equation has the form

$$2\pi R\gamma = 8\pi \frac{dh}{dt} \eta h + \pi R^2 \rho g h$$

$$\frac{dh}{dt} = \frac{2\gamma R - R^2 \rho g h}{8\eta h}.$$

The integrated form of this equation is given by Washburn (41) and Ligenza and Bernstein (23) as

$$t = \frac{8\eta}{R^2 \rho g}\left[h_\infty \ln\left(\frac{h_\infty}{h_\infty - h}\right) - h\right],$$

in which $h_\infty = 2\gamma/R\rho g$ and is the final equilibrium height attained by the meniscus.

From this the viscosity is obtained by the relation

$$\eta = \frac{R^2\rho g t}{8h_\infty}\left[\ln\left(\frac{1}{1-\ell}\right) - \ell\right]^{-1}, \ \ell = h/h_\infty.$$

Ligenza and Bernstein examined the validity of these equations experimentally using very fine bore capillaries and liquids of low viscosity. They reported an average deviation in the time required to reach a given height to be less than ±1% except toward the end of the ascent where deviations rose to about ±2%.

Levitt (22) defines a half-time of rise as the time required for a liquid to rise to a distance $h_\infty/2$ in the capillary. This half-time, $t_{1/2}$, is given by the equation

$$t_{1/2} = \frac{8\eta h_\infty}{R^2\rho g}\left(\ln 2 - \frac{1}{2}\right) = \frac{8\eta h_\infty}{R^2\rho g}(0.193).$$

The viscosity then is

$$\eta = \frac{0.647R^2\rho g}{h_\infty}\, t_{1/2}.$$

The experimental procedure for the determination of viscosity by this relationship was to determine $\underline{h_\infty}$ for a given capillary and liquid, mark off the distance $\underline{h_\infty/2}$ and accurately to determine the time required for the liquid to rise to this mark.

This method of viscosity determination has the disadvantage that an experiment must be performed to determine the parameter $\underline{h_\infty}$ before the measurement of the viscosity can be made. Since the cleaning and drying of the capillary is a time consuming and not always reproducible operation, we propose the following method of viscosity determination.

The rise of the liquid in the capillary can be followed with a cathetometer. The height of the meniscus can be recorded as a function of the time. If a plot of the function $\{\ln[1/(1 - \ell)] - \ell\}$ against the time of rise is made, a straight line should result, with a slope equal to $R^2\rho g/8\eta h_\infty$. From this slope one can then determine the viscosity. This method would have the advantage of permitting the determination of viscosities of very small amounts of liquid in a single experiment and would minimize the deviations observed by Ligenza and Bernstein.

CHAPTER II

EXPERIMENTAL PROCEDURES AND RESULTS

The general method used in this project was as follows. A carefully cleaned and dried capillary was touched to the surface of the liquid whose capillary behavior was being investigated. The rise of the meniscus in the capillary was followed with the aid of a cathetometer and a stopwatch. The height of the meniscus was recorded as a function of the time of rise. When the rate of rise became extremely slow, the liquid was drawn up into the capillary under slight suction, and the meniscus allowed to descend to its equilibrium position. Then the liquid was forced down under slight pressure and the meniscus allowed to rise to its equilibrium position. These two positions should be very nearly the same if the capillary is thoroughly cleaned. The average equilibrium position was used as the value of h_∞.

From the tabulated rate of rise data, and the values of h_∞, p, and R, it is possible to determine the surface tension and the viscosity of the liquid. By determining these values at a series of temperatures, it was possible to obtain some information on the temperature dependence of these quantities.

I. APPARATUS USED

The major pieces of apparatus used in this project were the following: a cathetometer manufactured by the Gaertner Scientific Corporation, serial number 1925A; a circulating type constant-temperature bath manufactured by Lab-Line, catalog number 3052, serial number 0264; and a stopwatch.

The capillaries used were of flint glass and were 0.5 mm in nominal diameter, although the range was given as 0.25 mm-0.75 mm.

II. LIQUIDS USED

Three liquids were studied, representing a wide range of viscosities. These liquids were: monolene (N-[2-hydroxypropyl] ethylenediamine) and quadrol (N, N, N′, N′-tetrakis [2-hydroxypropyl] ethylenediamine), both supplied by Wyandotte Chemical Corporation, and glycerol, Eastman Kodak number 339. The liquids were distilled before use.

Monolene. Monolene was distilled under atmospheric pressure in an ordinary distillation apparatus. The boiling point range was 232-235°C. After distillation the liquids were stored in glass-stoppered flasks in a desiccator over concentrated sulfuric acid until used.

Quadrol. Quadrol was distilled first under vacuum of a water aspirator. The first material to distill was slightly yellow. When the temperature reached 270°C the material beimg distilled was colorless. The vacuum was broken to change receivers. When the distillation was resumed, the first material to distill was again slightly discolored. The distillation was continued until most of the quadrol had distilled. The boiling point range was 270-275°C.

The apparatus was then rearranged to make it possible to change receivers without breaking the vacuum. The quadrol was redistilled, this time using a vacuum pump. The boiling point range of the collected material was 213-215°C. The material was not colored.

Glycerol. The glycerol was distilled first under atmospheric pressure. The boiling point range was 292-293°C. It was then redistilled using the vacuum distillation apparatus with the vacuum pump. The boiling point range of the collected material was 150-151°C.

Refractive Index. The liquids were further characterized by taking the refractive index of each at a series of temperatures. The refractive indices are tabulated in Table I, page 22.

Densities. The liquids were also characterized by determining their densities. The densities were determined by the pyonometer method. The pyonometers were cleaned with cleaning solution, followed by a rinse with phosphoric acid, and then by rincing in distilled water. They were dried by placing them in an evacuated desiccator until constant weight was obtained. The pyonometer was calibrated at each temperature at which densities were obtained. The data for the densities of the liquids are tabulated in Table II, page 22.

The balance weights were checked against each other by the Kohlraush method. (4) The weights were not checked against any other standard.

III. CLEANING THE CAPILLARY TUBES

For reproducible results in the measurement of the rate of rise of liquids in capillaries, the capillary surface must be scrupulously clean. Several methods were tried.

The cleaning procedure finally adopted was that given by Davis and Rideal (11) as the method to be used for cleaning glass surfaces for monolayer studies. In this method, the glass surface to be cleaned is soaked in warm chromic acid cleaning solution until the solution drains uniformly. The surface is then soaked in syrupy

TABLE I

REFRACTIVE INDEX OF LIQUIDS

Temperature °C	Monolene Index	Glycerol Index	Quadrol Index
20	1.4767	1.4730	1.4809
25	1.4746	1.4719	1.4794
30	1.4726	1.4708	1.4778
35	1.4705	1.4698	1.4764
40	1.4684	1.4687	1.4749
45	1.4663	1.4676	1.4734
50	1.4642	1.4665	1.4719

TABLE II

DENSITIES OF LIQUIDS

Temperature °C	Monolene ρ(gm/ml)	Glycerol ρ(gm/ml)	Quadrol ρ(gm/ml)
20	0.993	1.267	1.042
25	0.988	1.261	1.038
30	0.982	1.256	1.033
35	0.976	1.250	1.028
40		1.245	1.022
45		1.240	1.106
50			1.011
65			0.997

phosphoric acid to remove any adhering chromium ions. This is followed by thorough washing in distilled water to remove the phosphoric acid. The capillaries were finally dried by passing a stream of dry gas (hydrogen) through the tube for ten minutes.

Several other methods of cleaning the capillary surfaces were tried. Ligenza and Bernstein (23) reported using 1:1 nitric acid and water. Reproducible results were not obtained when this was used. Since the project was started in the summer when "Stockton peat dust" abounds, it may be that peat dust got into the capillaries and that the nitric acid did not oxidize this in the time that it was in contact.

Levitt (22) used cleaning solution followed by water. When this method was tried the rising and falling final positions of the meniscus did not agree. It was noticed on several occasions that, in determining the equilibrium position, the meniscus would drop to a minimum and then, overnight, would rise slightly. This change in surface tension may have been due to diffusion of adhering chromium ions into the liquid. This same effect could also be explained by assuming that the molecules of the liquid near the capillary wall orient themselves and thus cause an apparent decrease in capillary diameter. This has been observed in other polar liquids. (18).

IV. DETAILED PROCEDURE

The detailed procedure for obtaining data on the rate of rise of liquids in capillary tubes is described below.

A three inch test tube was cleaned by the procedure given by Davis and Rideal (11). About one milliliter of the liquid to be studied was placed in the clean dry test tube. This test tube, with the liquid, was placed in a Liebig condenser which was supported vertically and attached to the circulating constant temperature bath. The lip of the test tube just fit the neck of the condenser so as not to fall through. The condenser was supported in a vertical position by means of two adjustible clamps. The capillary tube was held in a buret clamp above the condenser, and the condenser's position was adjusted so that the capillary would be centered in the test tube. The vertical position of the condenser was such that the level of the liquid in the test tube was at a convienient height for oberving the rise of the liquid in the capillary through the telescope of the cathetometer. To make the calculations easier the position was made to be some even number of centimeters, e.g., 40.000 cm on the cathetometer scale.

A table for data was outlined with a column of time intervals of ten seconds for the early rise period.

The clean dry capillary was placed in the buret clamp so that the lower end of the capillary was just above the surface of the liquid. The stopwatch was hung on the cathetometer so that the time could be watched with one eye, while the level of the meniscus was watched through the telescope with the other eye.

While observing through the telescope of the cathetometer, the capillary was inserted into the liquid, and the stopwatch started simultaneously. The level of the lower end of the dry capillary was adjusted to exactly 40.000 cm., i.e., the depth of immersion was essentially zero, so that there was no hydrostatic head of pressure.

The position of the meniscus was recorded at each ten-second interval. Perhaps this was the most difficult technique to master. To get the cathetometer focused on the moving meniscus while watching the time, and obtaining the reading of the cathetometer's vernier scale to an accuracy of 0.005 cm. and recording this height of the meniscus all in the ten-second time interval required much practice. As the rate of rise of the liquid in the capillary became slower, readings were obtained at longer time intervals.

When the rate of rise became very slow, a slight vacuum was applied to the contents of the capillary, causing the meniscus to rise above its final equilibrium position. The vacuum was then released and the meniscus descended to its equilibrium position. This position was recorded. A slight pressure was then applied to the liquid in the capillary to force the meniscus below its final equilibrium position. This pressure was then released and the meniscus rose in the capillary to its equilibrium position. If the capillary was thoroughly clean, the descending and ascending equilibrium positions were practically identical. The average of the two positions was recorded as the final height attained by the meniscus.

V. TREATMENT OF DATA

From the recorded data it was possible to obtain the surface tension and the viscosity

Surface Tension. From the final height attained by the meniscus, the surface tension of each liquid was calculated from the relationship $\gamma = (1/2)\rho g h_\infty R$. The surface tensions at various temperatures are summarized in Table III, page 2 . The surface tension is a linear function of the temperature over the range studied. The temperature coefficient of the surface tension is -0.040 for monolene, -0.060 for glycerine, and -0/036 for quadrol.

Viscosity. The height, h, attained by the meniscus at time t for the liquids studied is tabulated in Tables XI-XIII, pages 49-51. In order to make a linear function from which to calculate the viscosity, the values of h and h_∞ were used in the function $[\ln\{1/(1-\ell)\} - \ell]$ in which $\ell = h/h_\infty$. The value of this function at time t is given in Tables XIV-XVI, pages 52-54.

Near room temperature, the plot of this function of the height against the time of rise is linear, and, from the slope, m, the viscosity can be calculated from the relationship

$$\eta = \frac{R^2 \rho g}{8 h_\infty m}.$$

At higher temperature the plot of this function of the height against the time of rise is linear during the early rise time when the ascent is fairly rapid. From the linear portion of the plot, the viscosity is calculated by the above relationship. Because of a temperature gradient within the apparatus, when the rate of rise slows, the upper portion of the liquid cools and there is a systematic deviation from the straight line. To correct for this deviation, the values of h from the relationship

$$\frac{R^2 \rho g t}{8 \eta h_\infty} = \ln\left(\frac{1}{1-\ell}\right) - \ell$$

were taken as the corrected points which take into account the variation in surface tension, density, and viscosity which arise because of the temperature gradient. These linear plots are shown in Figures 1-3, pages 55-57.

The calculated viscosities of the liquids at various temperatures are summarized in Table IV, page 29.

A well known relationship between temperature and viscosity is given by the Andrade (3) equation:

$$\eta v^{1/3} = Ae^{c/vT}$$

where v is the specific volume, and A and c are constants. A plot of log η vs 1/T for each liquid is shown in Figures 4-6, pages 58-60. On these plots are also shown the viscosities at two temperatures obtained by a Brookfield viscometer. It can be seen that the Andrade relationship is essentially linear over the range of temperatures studied.

TABLE III

SURFACE TENSIONS OF LIQUIDS BY THE CAPILLARY TUBE METHOD

Temperature °C	Monolene γ(dynes/cm)	Glycerol γ(dynes/cm)	Quadrol γ(dynes/cm)
20	42.6		
25	42.4	63.8	31.9
30	42.2	63.5	
35	42.0	63.2	31.6
45		62.6	
50			31.0
65			30.5

TABLE IV

VISCOSITIES OF LIQUIDS AS MEASURED BY RATE OF CAPILLARY RISE

Temperature °C	Monolene η(cp)	Glycerol η(cp)	Quadrol η(cp)
20	132		
25	94.4	940	68700
30	67.8	623	
35	50.2	415	24600
45		245	
50			6070
65			1990

CHAPTER III

DISCUSSION OF RESULTS

The liquid state shows a transition condition between gases and solids. That it is more closely related to the solid than to the gaseous state appears from several lines of evidence. In this chapter a model of the liquid state developed in this laboratory is applied to the viscous organic liquids studied.

I. SURFACE TENSION

The surface tension of all liquids decreases with an increase in temperature. The decrease is nearly linear with rise of temperature; thus, to a fair approximation

$$\gamma_t = \gamma_0(1 - kt),$$

and Laplace showed that the coefficient k is approximately equal to the rate of decrease of the density of the liquid with rise of temperature (38),

$$\rho_t = \rho_0(1 - kt).$$

These relationships hold for the liquids studied using the values for the respective parameters as given in Table V, page 31.

Macleod (24) found empirically that the relationship

$$\gamma^{1/4}/(\rho_l - \rho_g) = \gamma^{1/4}/\rho_l = \text{constant} = C$$

holds for many organic liquids nearly up to the critical temperature. Sugden (39) multiplied both sides of this equation by the molecular weight, M, and called the constant, CM, the parachor, P. This is primarily an additive property, the parachor of a compound being the sum of the atomic parachors, with some additional terms where certain structures such as double and triple bonds and cyclic structures are present. The additivity of parachors is thus equivalent to that of atomic volumes measured under unit surface tension, which is regarded as approximately the same as under equal internal pressures. For most unassociated liquids the parachor is subject to only a minor temperature coefficient (29).

TABLE V

PARAMETERS FOR CALCULATING SURFACE TENSIONS AND DENSITIES AT ANY TEMPERATURE

Liquid	γ_0 dynes/cm	ρ_0 gm/ml	k x10^4
Monolene	43.4	1.012	9.22
Glycerol	65.8	1.292	9.97
Quadrol	32.8	1.066	10.8

In order to obtain a check on the measured surface tensions, the parachors were obtained from the experimental surface tension data and compared with the calculated parachors, using the atomic constants given by Quayle (35). The experimental and calculated parachors are summarized in Table VI. The increase in the parachor with an increase in temperature is a characteristic of associated liquids.

TABLE VI

EXPERIMENTAL AND CALCULATED VALUES OF PARACHORS OF LIQUIDS

Temperature °C	Monolene ml/mole	Glycerol ml/mole	Quadrol ml/mole
20	304		
25	305	206	661
30	306	207	
35	308	208	673
45		209	
50			682
65			688
Calculated	302	194	678

The molar refraction, R, is defined as

$$R = \left(\frac{n^2 - 1}{n^2 + 2}\right)\left(\frac{M}{\rho}\right)$$

where n is the refractive index. R is to a first approximation independent of temperature or physical state, and it provides an approximate measure of the actual total volume (without free space) of the molecules in one mole of substance. For a very large number of compounds R is approximately additive for the atoms present in the molecule. The molar refraction can be combined with the parachor equation giving

$$\frac{(n^2 - 1)}{(n^2 + 2)} = \frac{R\gamma^{1/4}}{P}.$$

Since R and P can be calculated from atomic constants a knowledge of the surface tension will give the refractive index, and vice versa (38). The observed molar refractions and those calculated from atomic constants for the liquids studied are given in Table VII.

TABLE VII

OBSERVED AND CALCULATED VALUES OF MOLAR REFRACTIONS OF LIQUIDS

Liquid	Observed ml/mole	Calculated ml/mole
Monolene	33.62	33.83
Glycerol	20.84	20.57
Quadrol	79.73	81.01

II. VISCOSITY

The effect of temperature on viscosity has been extensively investigated. The viscosity of a liquid always falls with increasing temperature, and many empirical formulas representing this depemdence have been proposed (7).

A theory of the liquid state developed in this laboratory, which has led to a new general equation (14, 15, 16) describing the variation of liquid viscosities with temperature over the entire normal liquid range was applied to the liquids studied. This theory concerning the nature of a generalized liquid is based on a modified cluster model of the liquid state (14). As in many other theories, it is assumed that the liquid consists of two classes of molecules, active and inactive.

Two lines of evidence lead to the assumption that the activated molecules are not arranged in the liquid according to purely statistical considerations. If a liquid is regarded as a very poorly organized crystal in which the activated molecules or dislocations are statistically distributed, a quite unsatisfactory quantitative explanation of the melting-point phenomena follows, since from such a model one would expect that the discontinuity of properties observed at that point would correspond to a qualitative structural difference. Further, it is known from studies of crystal formation that strongly disordered lattices are unstable, so that there is a preference for the elaboration of plane crystal surfaces through an equilibrium with the "activated" molecules in the fluid or molten state.

In analogy to such an equilibrium, it is assumed that the molecules in a liquid become communally activated in layers, rather than individually or statistically. In addition, it is known that the liquid structure can undergo extraordinarily rapid changes in orientation. This circumstance is introduced into the calculations in terms of organized groups of molecules in activated and inactive layers, so that the transition from one category to the other can occur without gross rearrangements of the molecules from place to place.

In order to express viscosity in terms of this model of the liquid state, it is convienient to express the viscosity as a function of a parameter a, the number of molecules on the edge of an assumed cubic domain of ordered inactive molecules. The parameter a is defined by the relationship

$$a = n \frac{(1 - e^{-E_a/RT})^{1/3}}{1 - (1 - e^{-E_a/RT})^{1/3}}$$

in which E_a is the energy of activation and n is the thickness (in molecules) of the active layer surrounding the cube of inactive molecules. The value of n is unity (within the limits of experimental error), and a is independent of the flow process. The flow process must occur through the medium of "glide planes" constituted by the activated-molecule regions between inactive clusters. Lamella which arise in the liquid in consequence of the flow process must at the least possess a thickness the width of one unit cell in order to allow the inactive zones to flow past one another. As a consequence of the onterlocking effect of the disordered arrangement, it is to be expected that an increase in a will lead to an increase in viscosity.

In this model, the viscosity can be expressed (15) in terms of the density, independently of the temperature as

$$\eta V^{1/3} = \eta N^{1/3} d + \zeta q,$$

or in logarithmic form as

$$\log \left(\eta + \frac{\zeta q}{N^{1/3} d}\right) = \frac{a}{2.303} + \log \frac{q}{N^{1/3} d},$$

in which $V^{1/3}$ is the cubic root of the molar volume, $N^{1/3}$ is the cubic root of Avogadro's number, d is the average molecular diameter, ζ is the number of molecules that must be imagined to be withdrawn to produce the "zone of disengagement" between lamella, and q is a characteristic constant.

An analytical solution is not practical, so that a numerical method must be used (15). To evaluate $\underline{E_a}$, $\underline{\zeta}$, $\underline{q}$, and $\underline{d}$ one makes use of experimental values of $\underline{\eta}$ and $\underline{V^{1/3}}$ at two temperatures in the first of these equations. Solving these equations simultaneously gives the value for $N^{1/3}d$ and hence the value of $\underline{d}$. Making use of this value for $N^{1/3}d$ in the original equation gives the value of ζq.

It is noted that $\log \frac{\eta_2^\circ}{\eta_1^\circ} = \frac{1}{2.303}(a_2 - a_1)$, where $\eta^\circ = \eta + \frac{\zeta q}{N^{1/3}d}$. Table VIII gives the values of a/2.303 determined from the defining equation. This table extends one previously published (15). This extension of the table was necessary for use in the range of viscosities and temperatures studied here.

TABLE VIII

VALUES OF a/2.303 FOR VARIOUS VALUES OF THE ARGUMENT, E_a/RT

E_a/RT	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
1.3	3.8815	3.9299	3.9788	4.0282	4.0781	4.1285	4.1794	4.2308	4.2827	4.3351
1.4	4.3880	4.4415	4.4955	4.5500	4.6050	4.6605	4.7165	4.7730	4.8301	4.8877
1.5	4.9459	5.0047	5.0640	5.1239	5.1844	5.2455	5.3073	5.3697	5.4328	5.4966
1.6	5.5611	5.6263	5.6922	5.7588	5.8261	5.8941	5.9627	6.0320	6.1020	6.1727
1.7	6.2441	6.3162	6.3889	6.4622	6.5362	6.6108	6.6860	6.7619	6.8385	6.9158
1.8	6.9938	7.0726	7.1522	7.2327	7.3142	7.3967	7.4803	7.5651	7.6501	7.7365

The value of E_a/RT (= x) is found by trial and error. First compute $T_1/T_2 = \theta$ for the two temperatures for which the viscosity is known. For $a_1/2.303$ a value is found from the table, using a trial value of x_1, and the associated value of $x_2 = \theta x_1$ is simalarly introduced into the table to obtain a value of $a_2/2.303$. The difference between these values should yield the experimental quantity log (η_2^o/η_1^o). By trial and error the correct choice is made.

When the value of a/2.303 is known, it is introduced into the logarithimic form of the equation in order to determine $q/N^{1/3}d$, which when multiplied by the previously found value of $N^{1/3}d$, yields the value of q, and when divided into the previously computed value of $\zeta q/N^{1/3}d$, yields the value of ζ.

Table IX gives the values of the constants d, E_a, ζ, and q for the liquids studied.

TABLE IX

LIQUID STATE PARAMETERS DETERMINED FROM DENSITY AND VISCOSITY DATA

Liquid	d Angstroms	E_a cal/mole	ζ	q Centipoise-cm.
Monolene	5.796	877.4	462.5	0.006486
Glycerol	4.924	957.0	1656.8	0.8450
Quadrol	7.754	1070.6	4973.8	0.04021

III. NEWTONIAN AND NON-NEWTONIAN LIQUIDS

The theory of flow of liquids whose behavior in shear is describable in terms of a single constant viscosity coefficient is usually referred to as Newtonian flow. The behavior of liquids which appear to have different viscosities when observed in different types of apparatus, or at differentrates of flow in the same apparatus, under uniform temperature conditions is described as non-Newtonian.

The present theory appears to offer a basis for a theoretical distinction between Newtonian and non-Newtonian flow in capillaries. If the thickness of a lamina exceeds the size of the capillary, the flow process will be non-Newtonian, while a lamina smaller than the capillary size will permit Newtonian flow.

The approximate laminar size can be calculated as follows (16). If in traversing one lamina, z molecules are encountered, each having an average diameter d, the laminar thickness will be zd when there is no free space between the molecules in the lamina. However, if the actual average diameter of the molecules in the liquid as a whole is δ and ζ is the number of molecules which must be imagined to be withdrawn from a lamina to produce the imaginary "zone of disengagement" between lamina, then the width of such a zone is $\zeta\delta$. In these terms, the distance from the beginning of one lamina to the beginning of the next must be

$$z\delta = zd + \zeta\delta.$$

In terms of the molar volume, V, the overall average intermolecular distance is given by $\delta = (V/N)^{1/3}$. From the average values of d in Table IX, page 38, it is possible to approximate a diameter for each temperature, and to extrapolate to nearby temperatures.

When this calculation is performed using the data available for the liquids studied in the present work, the results are as shown in Table X.

TABLE X

LAMINAR THICKNESSES OF LIQUIDS FROM LIQUID STATE THEORY

Temperature °C	Monolene cm	Glycerol cm	Quadrol cm
20	0.00654	0.0372	0.396
25	0.00542	0.0290	0.166
30	0.00395	0.0226	
35	0.00324	0.0177	0.0973
45		0.0132	
50			0.0396
65			0.0281

Although these values of laminar thicknesses are undoubtedly accurate only as to orders of magnitude, it can be seen that at 20° the laminar thickness of quadrol greatly exceeds the diameter of the capillary (0.07 cm). It was found experimentally that at 20° the quadrol meniscus had penetrated the capillary only three millimeters in two hours. On calculating the viscosity at 20° by extrapolation and calculating the expected rate of rise, it was found that the three millimeter penetration should have occured in about three minutes, and that in one hour the penetration should have been about ten millimeters if the flow process were Newtonian. Thus, it appears that, in the 0.07 cm capillary, while the laminar thickness for quadrol at 20° is much too large to permit free Newtonian flow, at temperatures in the range from 25°-35°, the laminar thickness is of the same order of magnitude as the capillary diameter, therefore just barely permitting laminar Newtonian flow. On the other hand, the laminar thicknesses of both glycerol and monolene clearly lead to fully Newtonian flow in all the observations.

The results noted with quadrol are of special interest and value, not only in affording a direct experimental confirmation of a crucial prediction of the theory of the liquid state derived from the Gross model (14), but also in providing, hopefully, a system which may be amenable to future detailed experimental studies of flow mechanism, slip processes, wetting and adhesion, etc., and of the fundamental nature of the transition between Newtonian and non-Newtonian flow behavior in a system of constant composition comprising just one chemical species.

CHAPTER IV

SUMMARY

The differential equation of motion of a liquid rising in a vertical capillary includes terms for the time rate of change of momentum of the contents of the capillary, the forces due to surface tension, viscous resistance, gravity, and end drag. If the motion is slow because of small diameter or high viscosity, only the terms involving surface tension and viscosity are important. The solution relating viscosity and the height attained at any time is

$$t = \frac{8\eta}{R^2\rho g}\left[h_\infty \ln\left(\frac{h_\infty}{h_\infty - h}\right) - h\right].$$

A plot of the function $\{\ln[1/(1 - \ell)] - \ell\}$, in which $\ell = h/h_\infty$, against the time of rise is linear, with a slope equal to $R^2\rho g/8\eta h_\infty$. From this slope the viscosity can be determined.

Based on this relationship a new experimental method for finding viscosities of small amounts of viscous liquids has been developed.

Three liquids, representing a very wide range of viscosities were studied over a range of temperatures. These liquids were glycerol, monolene (N-[2-hydroxypropyl]-ethylenediamine), and quadrol (N, N, N′, N′-tetrakis[2-

hydroxypropyl] ethylenediamine). Each substance was characterized by measuring the density, refractive index, surface tension, and viscosity at a series of temperatures, and the temperature dependence of each was calculated. The parachor and molar refraction of each material was calculated in order to give a check on the general reliability of the experimental data.

By applying a theory of the liquid state developed in this laboratory, the energy of activation for viscous flow, E_a, the intrinsic molecular diameter, d, and the thickness of a flowing lamina of each was calculated. These calculations required a numerical method of solution. For this purpose a previously published table of values of the function

$$\frac{a}{2.303} = \frac{(1 - e^{-E_a/RT})^{1/3}}{2.303[1 - (1 - e^{-E_a/RT})^{1/3}]}$$

for various values of the argument, E_a/RT, was extended.

The theory of the liquid state was extended to suggest a theoretical distinction between Newtonian and non-Newtonian behavior in capillaries.

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APPENDIX

TABLE XI

RATE OF CAPILLARY RISE

OF MONOLENE

	Height in mm. at			
Time	20°C	25°C	30°C	35°C
Seconds				
10	6.80	7.95	9.10	10.25
20	9.25	10.60	12.10	13.05
30	10.95	12.50	13.10	15.65
40	12.30	13.90	15.05	17.20
50	13.35	15.10	16.70	18.40
60	14.30	16.10	17.80	19.40
70	15.15	16.90	18.65	20.20
80	15.85	17.60	19.35	20.90
90	16.45	18.25	20.00	21.45
100	17.05	18.85	20.50	21.70
110	17.55	19.35	21.00	22.05
120	18.05	19.80	21.40	22.65
130	18.50	20.20	21.75	23.00
140	18.95	20.55	22.10	23.20
150	19.25	20.95	22.35	23.40
160	19.55	21.25	22.60	
170	19.90	21.50	22.85	
180	20.20	21.75	23.10	
Minutes				
3.5	21.00	22.40	23.55	
4.0	21.40	22.90		
4.5	22.10	23.30		
5.0	22.90			
h_∞	25.00	25.00	24.95	24.95

R = 0.349 mm.

TABLE XII

RATE OF CAPILLARY RISE OF GLYCEROL

Time	Height in mm. at 25°C	30°C	35°C	45°C
Seconds				
10	3.25	4.00	4.35	6.10
20	4.65	5.60	6.15	8.50
30	5.60	6.80	7.30	10.10
40	6.45	7.65	8.30	11.45
50	7.10	8.55	9.20	12.55
60	7.65	9.25	9.85	13.50
70	8.25	9.80	10.60	14.35
80	8.75	10.40	11.25	15.00
90	9.20	10.95	11.70	15.90
100	9.60	11.45	12.30	16.35
110	10.00	11.95	12.75	17.10
120	10.40	12.30	13.20	17.55
Minutes				
2.5	11.40	13.45	14.50	18.95
3.0	12.30	14.50	15.60	20.10
4.0	13.80	16.25	17.35	21.90
5.0	15.10	17.55	18.60	23.25
7.5	17.35	20.20	21.20	
10.0	19.30	21.80	22.95	
12.5	20.75	23.20	24.30	
15.0	21.80	24.30		
17.5	22.75	25.00		
20.0	23.60			
22.5	24.30			
25.0	24.90			
h_∞	29.40	29.40	29.40	29.35

R = 0.349 mm.

TABLE XIII

RATE OF CAPILLARY RISE

OF QUADROL

	Height in mm. at			
Time	30°C	35°C	50°C	65°C
Minutes				
0.5	1.40	2.45	4.70	7.55
1.0	2.10	3.35	6.35	9.90
1.5	2.45	4.10	7.55	11.40
2.0	2.90	4.65	8.45	12.50
2.5	3.20	5.20	9.25	13.35
3.0	3.35	5.60	9.90	14.05
3.5	3.80	6.05	10.45	14.60
4.0	4.00	6.35	11.00	15.10
4.5	4.25	6.65	11.40	15.40
5.0	4.45	7.00	11.75	15.75
6.0	4.85	7.50	12.50	16.00
7.0	5.20	8.05	13.10	16.85
8.0	5.50	8.45	13.60	
9.0	5.80	8.85	14.05	
10.0	6.00	9.20	14.40	
15.0	7.20	10.70	15.75	
20.0	8.10	11.80	16.40	
25.0	8.85	12.65		
30.0	9.50	13.35		
45.0	11.00	14.85		
60.0	12.10	15.70		
h_∞	17.85	17.85	17.80	17.80

$R = 0.351$ mm.

TABLE XIV

VALUES OF THE FUNCTION

$\mathrm{Ln}[1/(1 - t)] - t$

FOR MONOLENE

Time	20°C	25°C	30°C	35°C
Seconds				
10	0.045	0.071	0.087	0.117
20	.092	.128	.179	.218
30	.138	.193	.219	.358
40	.185	.256	.319	.481
50	.230	.322	.435	.599
60	.251	.389	.535	.727
70	.325	.451	.630	.851
80	.371	.513	.717	0.982
90	.415	.579	.809	1.11
100	.464	.648	.904	1.24
110	.490	.713	0.998	1.27
120	.558	.741	1.11	1.47
130	.607	.877	1.17	1.64
140	.661	.891	1.27	1.73
150	.700	0.982	1.36	1.84
160	.737	1.04	1.44	
170	.794	1.10	1.55	
180	.842	1.17	1.68	
Minutes				
3.5	0.993	1.36		
4.0	1.70	1.55		
4.5	1.27	1.75		
5.0	1.56			

TABLE XV

VALUES OF THE FUNCTION

$\mathrm{Ln}[1/(1 - t)] - t$

FOR GLYCEROL

Time	25°C	30°C	35°C	45°C
Seconds				
10	0.007	0.010	0.012	0.025
20	.014	.021	.025	.052
30	.021	.032	.037	.078
40	.028	.041	.049	.104
50	.035	.054	.062	.131
60	.041	.063	.073	.156
70	.049	.072	.087	.182
80	.056	.083	.100	.204
90	.062	.093	.110	.239
100	.069	.104	.123	.257
110	.076	.115	.135	.292
120	.083	.123	.147	.313
Minutes				
2.5	.103	.154	.186	.392
3.0	.123	.186	.226	.470
4.0	.164	.252	.302	.624
5.0	.208	.312	.368	0.778
7.5	.302	.475	.556	
10.0	.411	.610	.738	
12.5	.518	.767	0.927	
15.0	.610	0.927		
17.5	.718	1.05		
20.0	.822			
22.5	0.927			
25.0	1.03			

TABLE XVI

VALUES OF THE FUNCTION

$$\mathrm{Ln}[1/(1 - t)] - t$$

FOR QUADROL

Time	25°C	35°C	50°C	65°C
Minutes				
0.5	0.004	0.011	0.043	0.128
1.0	.008	.021	.085	.256
1.5	.011	.032	.128	.384
2.0	.015	.042	.170	.511
2.5	.019	.053	.213	.640
3.0	.023	.063	.255	.766
3.5	.027	.074	.298	0.895
4.0	.030	.084	.340	1.02
4.5	.034	.095	.383	1.15
5.0	.038	.106	.425	1.28
6.0	.045	.127	.510	1.54
7.0	.053	.148	.595	1.79
8.0	.061	.169	.680	
9.0	.068	.190	.765	
10.0	.076	.211	0.850	
15.0	.114	.319	1.27	
20.0	.152	.524	1.70	
25.0	.190	.528		
30.0	.229	.634		
45.0	.343	0.952		
60.0	0.457	1.27		

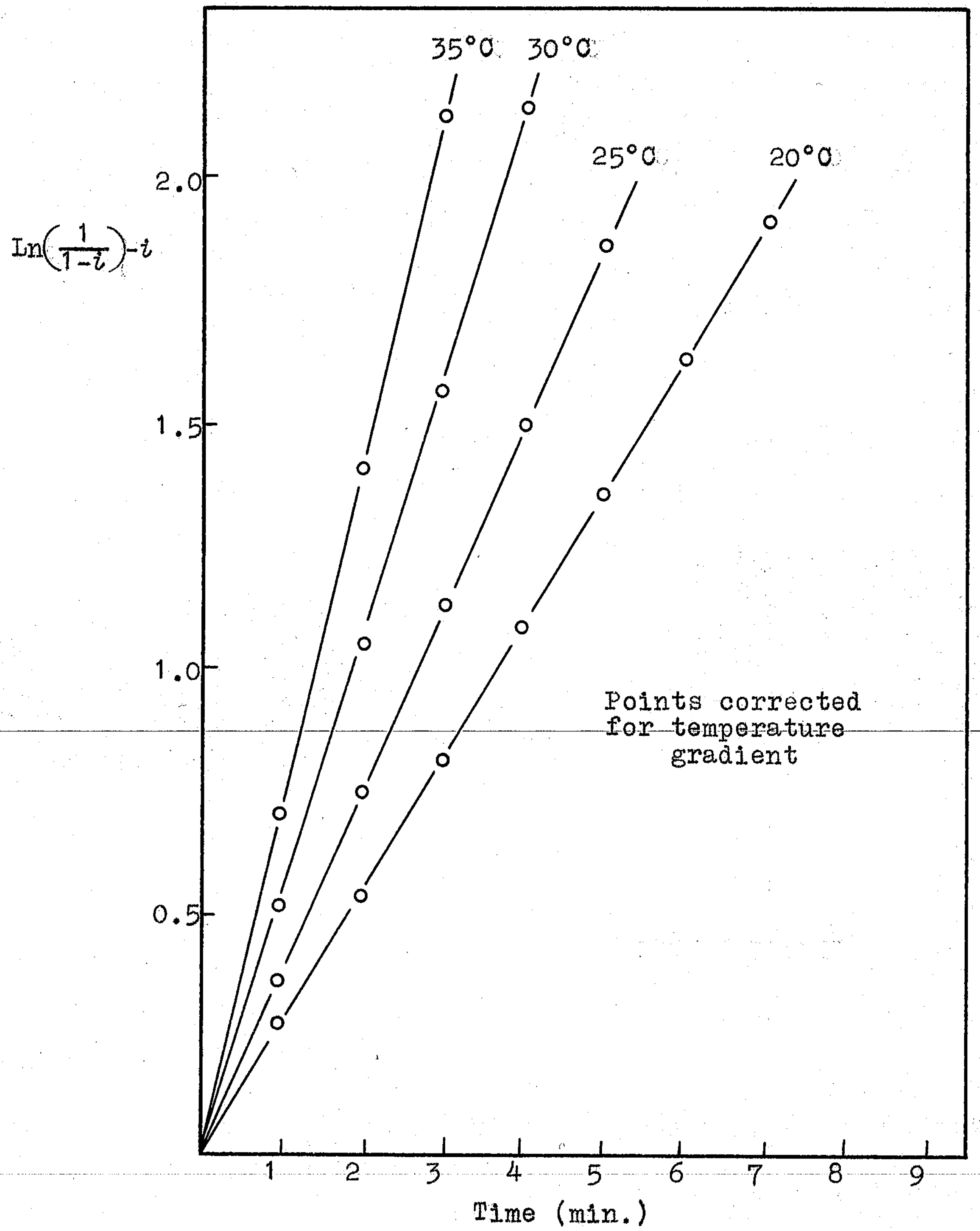

FIGURE 3

VARIATION WITH TIME OF $\mathrm{Ln}\left(\frac{1}{1-i}\right)-i$
FOR MONOLENE (cf. TABLE XI)

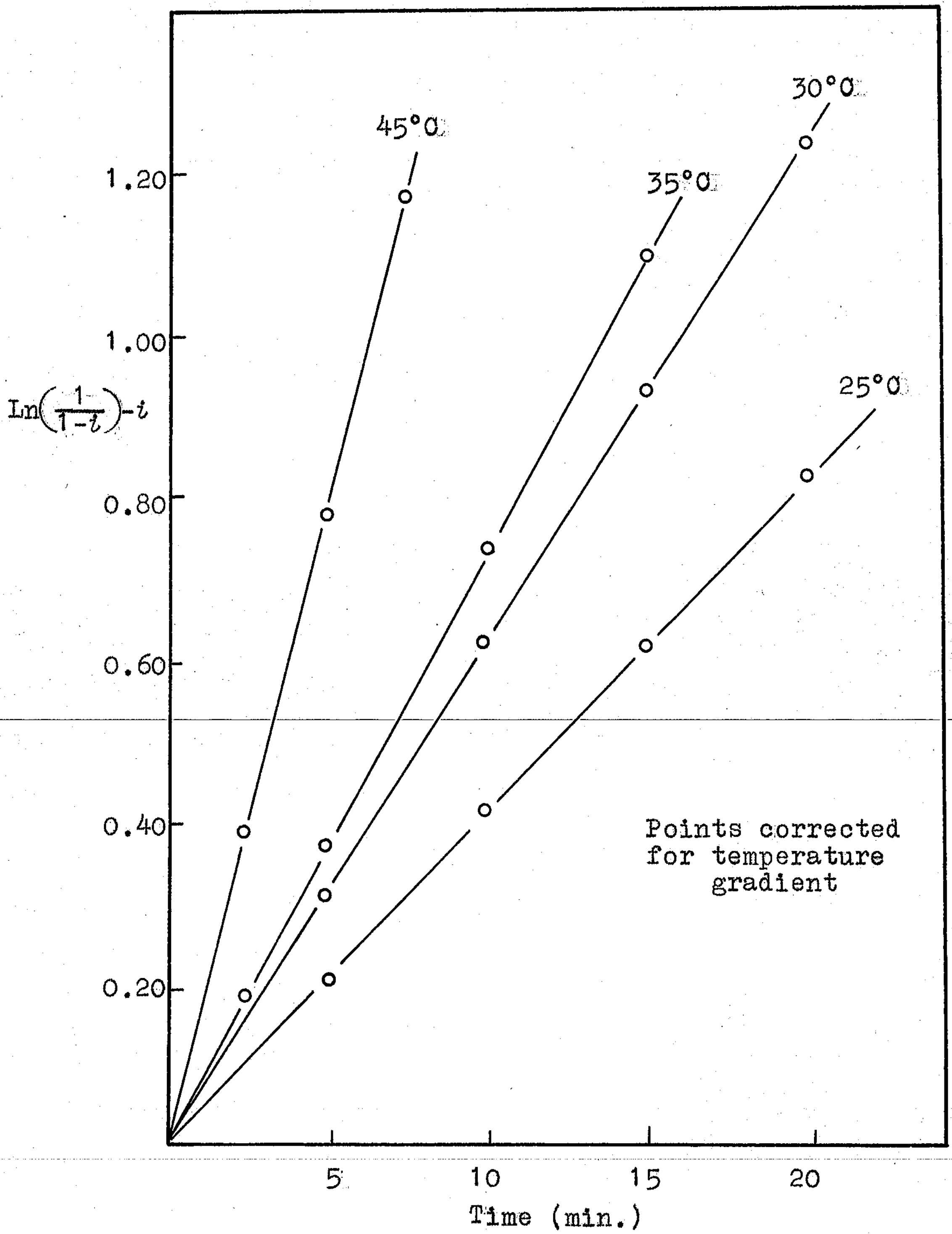

FIGURE 4

VARIATION WITH TIME OF $\mathrm{Ln}\left(\frac{1}{1-i}\right)-i$ FOR GLYCEROL (cf. TABLE XII)

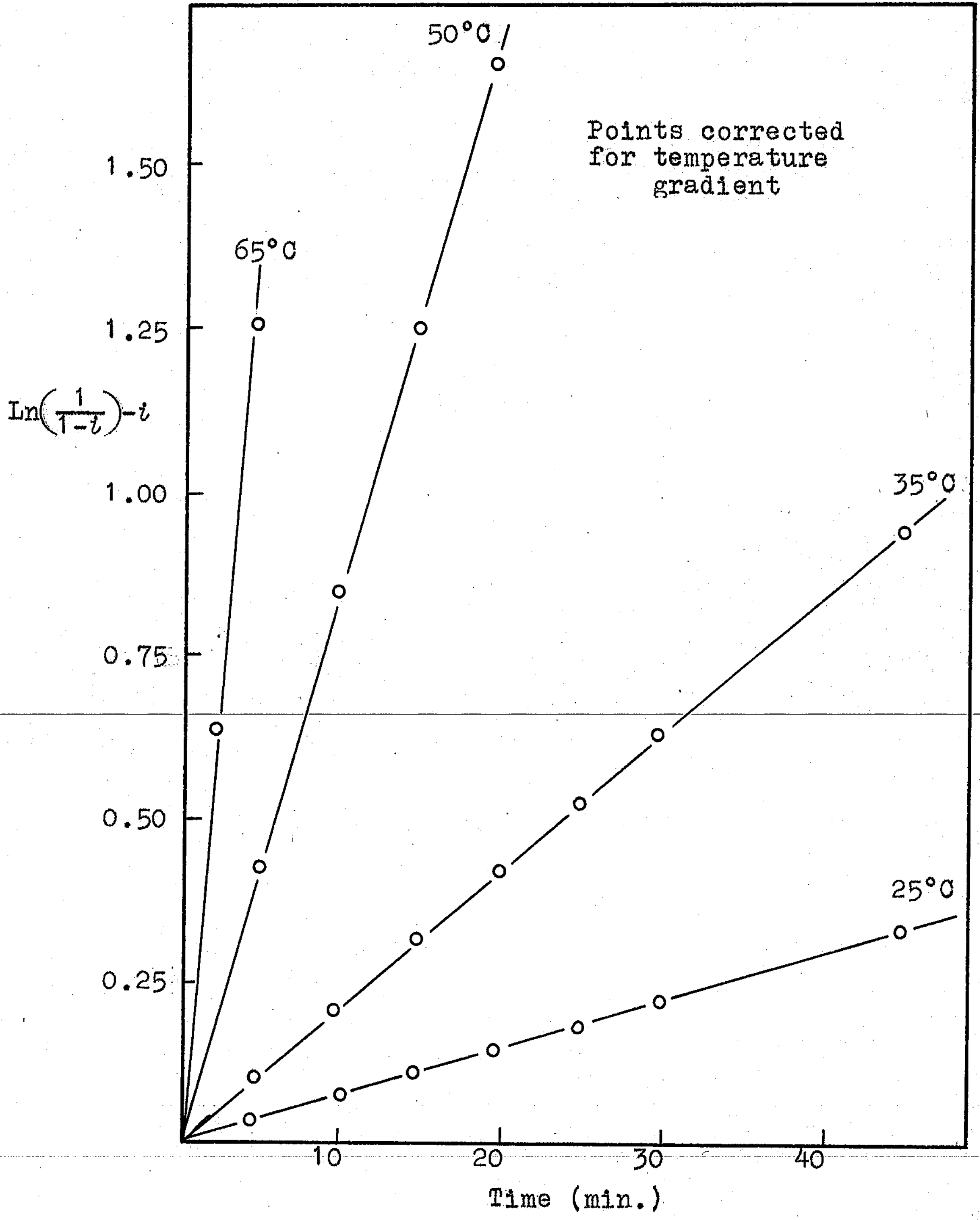

FIGURE 5

VARIATION WITH TIME OF $\ln\left(\frac{1}{1-i}\right)-i$
FOR QUADROL (cf. TABLE XIII)

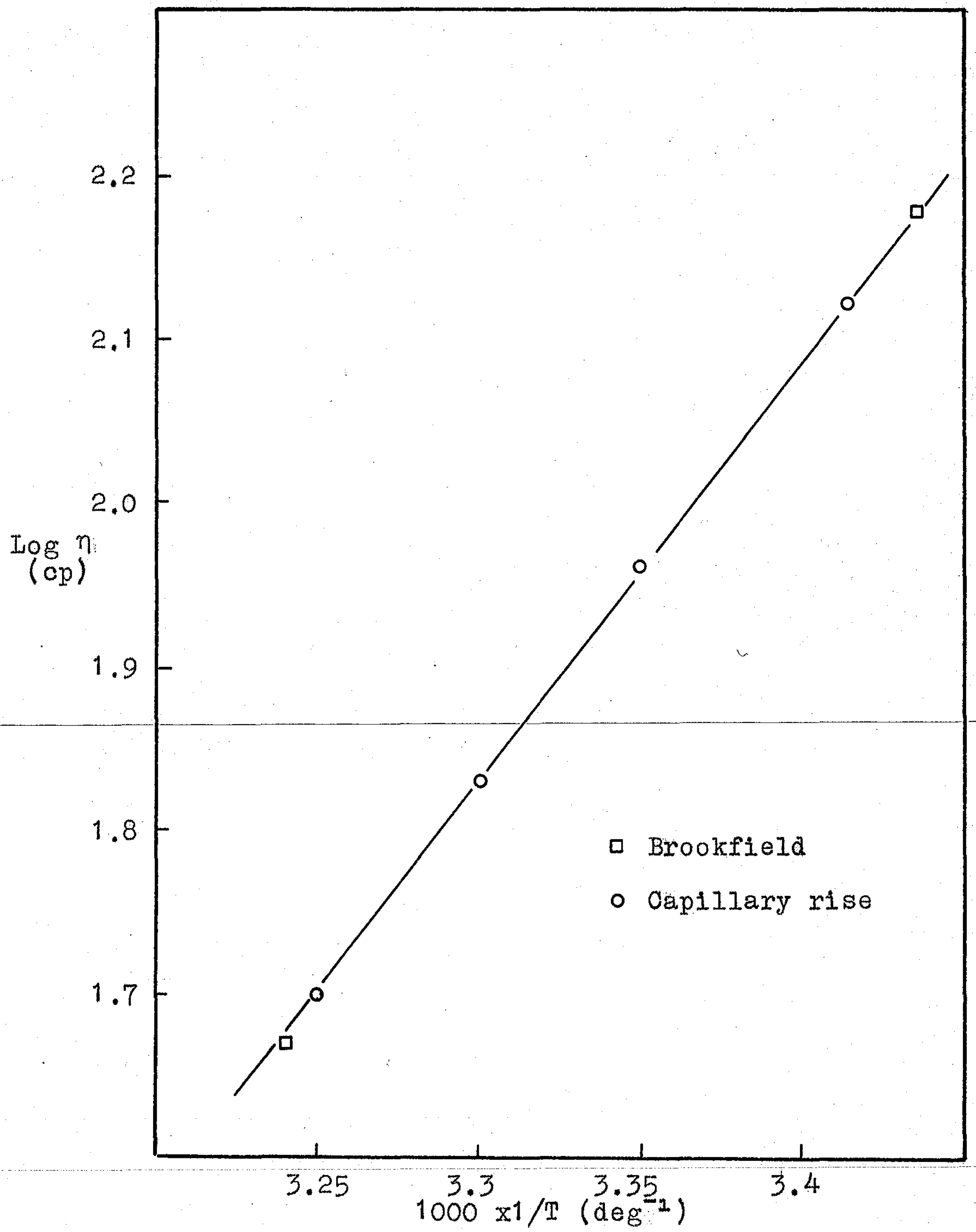

FIGURE 6

VARIATION WITH TEMPERATURE OF LOG η
FOR MONOLENE (cf. TABLE IV)

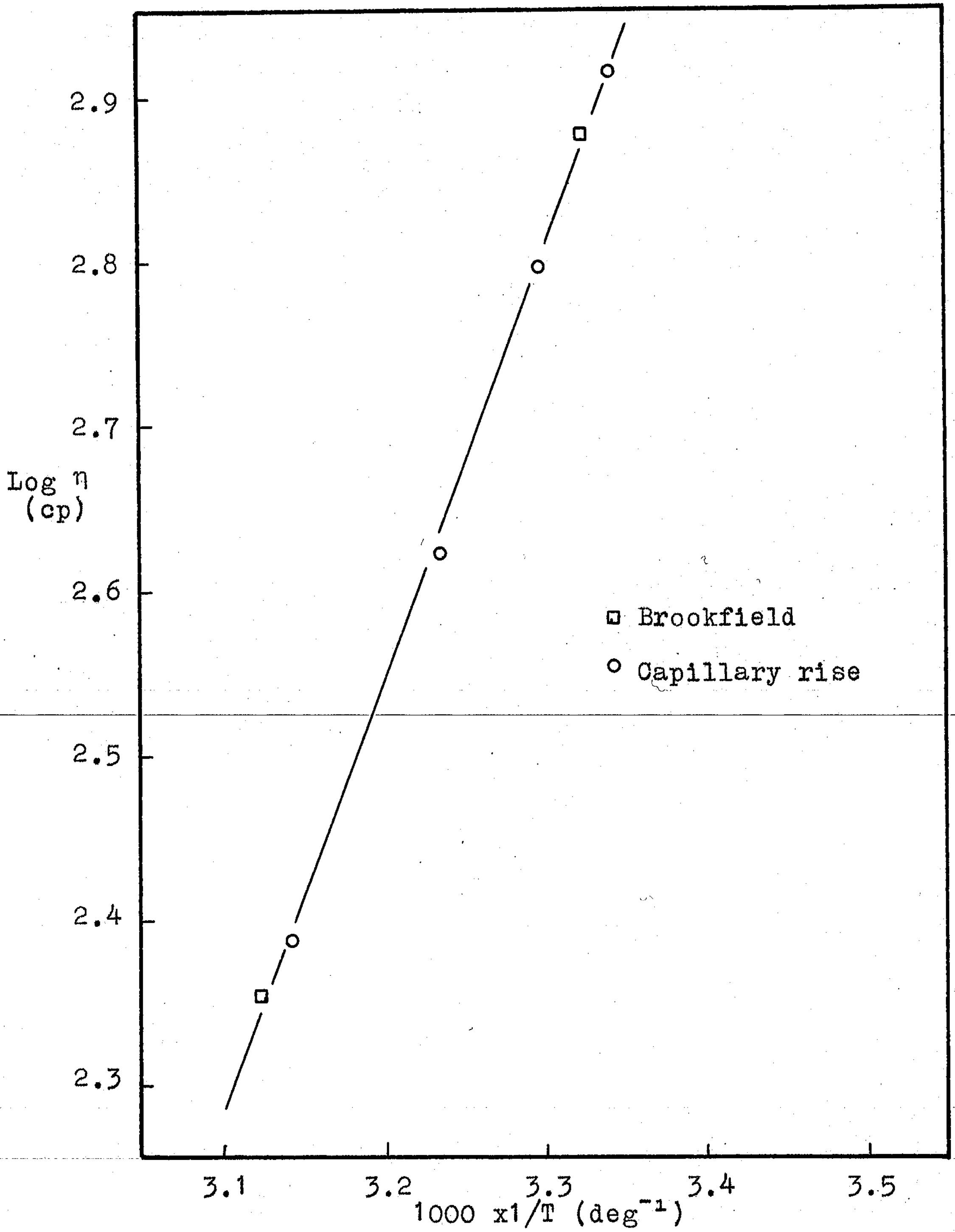

FIGURE 7

VARIATION WITH TEMPERATURE OF LOG η
FOR GLYCEROL (cf. TABLE IV)

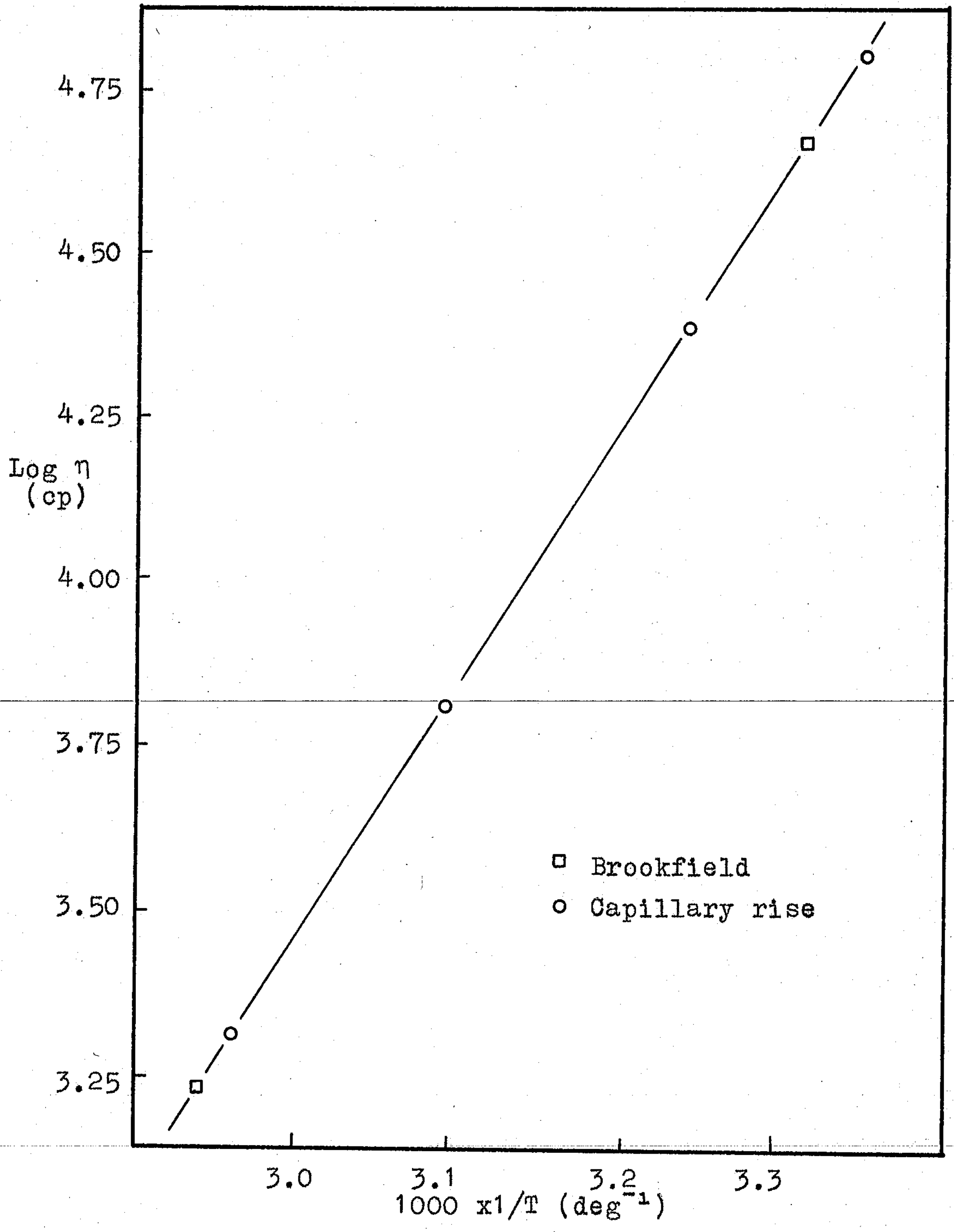

FIGURE 8

VARIATION WITH TEMPERATURE OF LOG η
FOR QUADROL (cf. TABLE IV)