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A STUDY OF EMULSION VISCOSITIES

BY

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A THESIS

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ABSTRACT OF THESIS

The apparent viscosity of stable emulsions has been measured and evaluated. The systems studied consisted of various oil in water emulsions, utilizing a series of six n-paraffins from heptane to octadecane. The system was stabilized with a conventional emulsifying agent. The apparent viscosity of these emulsions was studied in relation to (a) the concentration of the disperse phase and, (b) the viscosity of the hydrocarbon used as the continuous phase.

It was established that the volume concentration of the disperse phase had considerable effect on the apparent viscosity of the emulsion. An increase in the concentration of the disperse phase resulted in an increase of the apparent viscosity.

It was also shown that the viscosity of the hydrocarbon comprising the continuous phase had considerable effect upon the apparent viscosity of the emulsion. The increase in apparent viscosity was still greater than the increase in the viscosity of the external phase. This shows that an interaction of effects exists between the concentration of the disperse phase and viscosity of the external phase.

An equation was developed which related apparent emulsion viscosity and concentration of the disperse phase with type and concentration of emulsifier as the correlating parameter.

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

TERMINOLOGY

Because of the wide variation of definitions, it is advisable to define a few terms which are employed in general usage in the remainder of this thesis.

Internal Phase: The medium which is present in the form of small dispersed droplets (also referred to as the dispersed phase).

O/W: Type of emulsion: oil in water; oil being the dispersed phase and the water being the continuous phase.

W/O: Type of emulsion: oil in water; oil being the dispersed phase and water being the continuous phase.

Emulsifier: Surfactants or surface active materials, or other agents which are added to an emulsion in order to increase its stability by interfacial action.

Continuous Phase: Medium in which the internal phase is dispersed (also referred to as the external phase).

INTRODUCTION

The theory of emulsions, a classification of colloids, has grown in a rather haphazard fashion. At present the theory is a mixture of theories of physical properties of matter and structure of matter. Colloid chemistry has been largely an experimental science. The emulsion is partly an outgrowth of classical colloidal chemistry, and partly a development of the ancient arts involved in the production of emulsions. The formulation of exact theories has been hindered by the large number of variables, and the difficulty and complexity of accurate measurements of emulsions. As more knowledge of emulsions and more efficient methods of preparing them have become available, emulsions have found their way into almost every industry, e.g., paint, food, drugs, cosmetics, road, lubricants, and cements.

The earliest emulsion observed was probably milk. An example of a natural application of an emulsion is the absorption of fats in the intestine and the subsequent transport to the living cells in the blood and lymph. Most emulsions today are formulated by man and are tailored for a specific use in the home or industry.

While an emulsion may readily be recognized, there is no universal definition of an emulsion. A wide variety of definitions or comments as to what is an emulsion has been set forth below:

DEFINITIONS

1. Emulsions are mechanical mixtures of liquids that are immiscible under ordinary conditions and which, in turn, may be separated into layers on standing, heating, freezing, by agitation or the addition of other chemicals. (1)
2. An emulsion is a system containing two liquid phases, one of which is dispersed as globules in the other. (2)
3. An emulsion is a very fine dispersion of one liquid in another with which it is immiscible. (3)
4. Emulsions are intimate mixtures of two immiscible liquids, one of them being dispersed in the other in the form of fine droplets. (4)
5. Emulsions are microscopically visible droplets of one liquid suspended in another. (5)
6. An emulsion is a two-phase liquid system consisting of fairly coarse dispersions of one liquid in another with which it is not miscible. (6)
7. An emulsion consists of a stable dispersion of one liquid in another liquid. (7)

Resistance to flow is perhaps one of the more important properties of an emulsion. Sherman (8a) has listed six of the more important factors which affect the viscosity of an emulsion.

1. Viscosity of the external phase

2. Volume concentration of the disperse phase.
3. Viscosity of the internal phase.
4. The nature of the emulsifying agent and the film precipitated at the interface.
5. The electroviscous effect.
6. The particle size and size distribution.

The theory of emulsions has fascinated many scientists,--including Einstein.

Indeed, the usual starting point for such studies is the Einstein equation:

$$\eta_E = \eta_o (1 + 2.5\phi) \qquad (1)$$

wherein
η_E = apparent viscosity of the emulsion;
η_o = viscosity of the continuous phase, &
ϕ = the fraction of the total volume which is the disperse phase.

The apparent viscosity as referred to in this work is the viscosity of an emulsion as measured with a "Lantz-Zeitfuchs" type reverse flow viscometer (described later).

In many emulsions, the emulsifying agent is dispersed or dissolved in the external oil phase and, therefore, η_o is the viscosity of this oil-emulsifier solution rather than of the pure oil.

CONCENTRATION OF INTERNAL PHASE

Many workers in the field of emulsion viscosity have investigated this aspect: Guth, Gold, and Shimha (16); Oliver and Ward (17); Eilers (18); Sherman (19); Richardson (20); Simpson (21); Taylor (10). One of the first equations relating viscosities and the volume of the dispersed material of a two-phase mixture was the Einstein equation:

$$\eta_E = \eta_0 (1 + 2.5\phi) \qquad (1)$$

This equation is only applicable to emulsions having ϕ values of less than 0.05. Emulsions of this type exhibit Newtonian behavior, emulsions containing larger amounts of disperse phase normally exhibit non-Newtonian flow properties. Another limitation is that it applies mainly to mixtures of a liquid with rigid spheres. The Einstein equation, therefore, is of limited utility. It can be seen from the equation (and Fig. 1) that Einstein postulated that the viscosity is a linear function of the concentration of the disperse phase, independent of the size of the dispersed particles and the distance between them.

Generally speaking, emulsions containing more than 50 percent volume disperse phase show considerable non-Newtonian behavior. For such systems, Hatscheck (9) has derived the well-known relationship:

$$\eta_E = \frac{\eta_0}{1 - (h\phi)^{1/3}} \qquad (2)$$

wherein h = constant 1.23

η_E = apparent viscosity of the emulsion

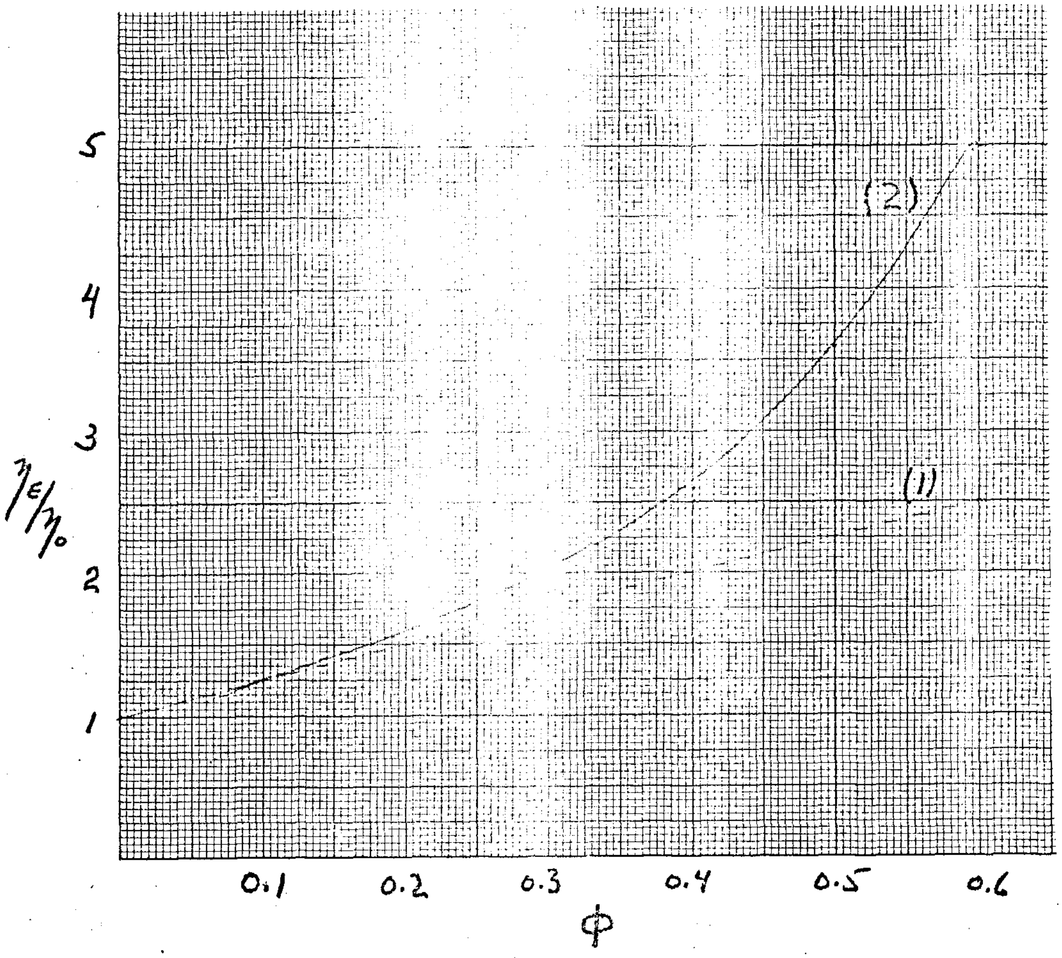

Figure 1 - Viscosity Ratio vs. Concentration of Disperse Phase
(1) Einstein Equation
(2) Hatscheck Equation

η_0 = viscosity of the continuous phase

ϕ = volume concentration of the disperse phase

Hatscheck pointed out that this equation only applies to the linear portion of the shear-flow curves, i.e., at low concentrations of dispersed phase.

Carter (22) maintained that the viscosity of an emulsion is dependent on the viscosity of the internal phase and, to a lesser extent, on the particle size of the dispersed particles. She also stated that as viscosity of both the internal phase and its concentration increases, the resulting emulsion viscosity increases.

More recent approaches to the calculations of emulsion apparent viscosities have been reduced to the following power series:

$$\eta_\epsilon = \eta_o \left(1 + 2.5\phi + a\phi^2 + b\phi^3 + ----\right) \quad (3)$$

Guth, Gold, Shimha (16) calculated the value of "a" to be 14.1, but this only applies to ϕ values of less than 0.06. For high concentrations of disperse phase allowances were made to correct for the influence of "crowding" or close packing of the dispersed globules with increasing concentration. A crowding effect is evident in Monson's (23) work with California crude oils. In this work the viscosity ratio η_ϵ/η_o varied from 1.3 for emulsions with 10 percent volume disperse phase to 4.1 ratio for emulsions having disperse phases of 40 percent volume.

Mooney's (24) equation takes into account the "crowding" factor:

$$\eta_\epsilon = \eta_0 \exp\left(\frac{2.5\phi}{1-S\phi}\right) \qquad (4)$$

wherein S is the crowding factor which depends on the size distribution of spheres. For spheres of a uniform size, the estimated range of S given by Mooney is:

$$1.35 < S < 1.91$$

Another analysis that is applicable to high concentrations of disperse phase was proposed by Vand (25). Vand takes into account both the mutual hydrodynamic interaction between particles and their collisions. This equation for the apparent viscosity of a suspension is:

$$\eta_\epsilon = \eta_0 \exp\left[K_1\phi - \frac{\alpha(K_2-K_1)\phi^2}{1-B\phi}\right] \qquad (5)$$

where, for spherical particles, the values of the constants have been theoretically determined by Vand:

Einstein shape factor of single spheres	$K_1 = 2.5$
Shape factor of collision doublets	$K_2 = 3.175$
Collision time constant	$\alpha = 4$
Hydrodynamic interaction constant	$B = 39/64 = 0.609$

If ϕ is small, then this equation can be reduced to the Einstein equation (via series expansion of the exponential term).

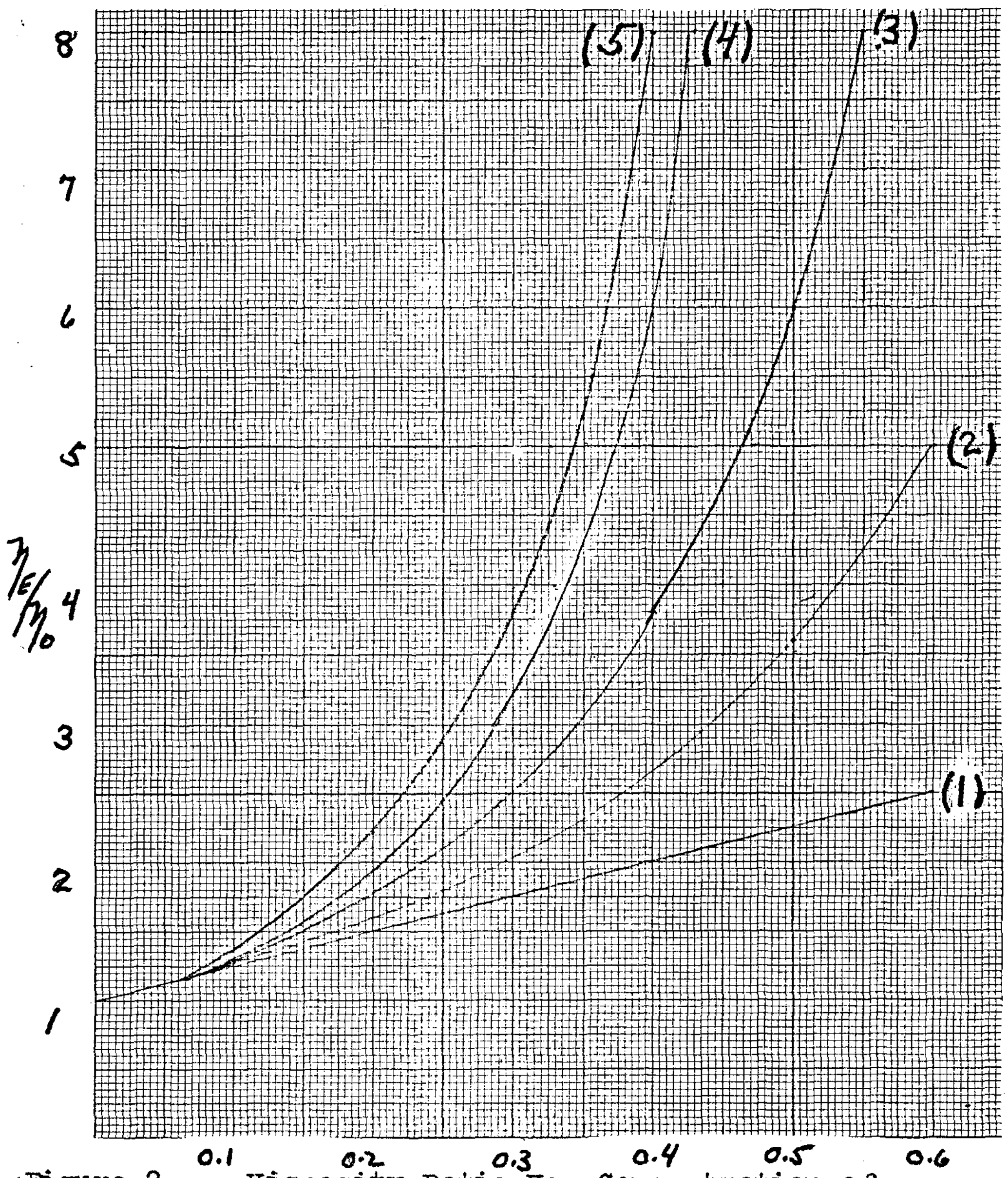

Figure 2 - Viscosity Ratio Vs. Concentration of Disperse Phase (volume percent)

(1) The Einstein Equation
(2) The Hatscheck Equation
(3) The Vand Equation $\alpha = 0$
(4) The Vand Equation $\alpha = 4$
(5) The Mooney Equation

The Einstein, Hatschek, Vand, and Mooney equations are plotted in Figure 2. In order to illustrate the effect of collisions, two curves predicted by Vand are shown: one takes collisions into account ($\alpha = 4$), and the other neglects this effect ($\alpha = 0$).

VISCOSITY OF THE INTERNAL PHASE

The effect of the viscosity of the internal phase was not included in early studies, neither the Einstein equation nor the Hatschek equation take this factor into account. However, many investigators have included this in their results. Taylor (10) modified the Einstein equation to include this as:

$$\eta_E = \eta_o \left[1 + 2.5\phi \left(\frac{\eta_i + 2/5\, \eta_o}{\eta_i + \eta_o} \right) \right] \qquad (6)$$

wherein η_i viscosity of the internal phase.

Leviton and Leighton (11) studied emulsions of milk fat and skim milk and further modified this equation to:

$$\ln \eta_E / \eta_o = 2.5 \left(\frac{\eta_i + 2/5\, \eta_o}{\eta_i + \eta_o} \right) \left(\phi + \phi^{5/3} + \phi^{11/3} \right) \qquad (7)$$

Oldroyd (12) arrived at a more complex equation. He calculated the elastic properties of a dilute emulsion of one incompressible viscous liquid in another liquid, arising from the interfacial tension existing between the two phases. The effect of slip at the interface which might be associated with the presence of an interfacial film of the third component (introduced as a stabilizer) was also calculated.

Bond and Newton (13) proposed that spherical drops behave as rigid spheres provided that the radius of the droplet was less than a certain (undefined) critical value.

Toms (14) studied emulsions and calculated that while the viscosity of the internal phase was of no importance, the chemical nature of the internal phase was quite significant.

The aforementioned investigations used an oil in water (O/W) type emulsions. Sherman (15) was one of the few investigators who used water in oil (W/O) emulsions. He concluded that the viscosity of the internal phase was of little importance but that the chemical nature of the disperse phase could be of considerable significance.

EMULSIFYING AGENT AND THE FILM PRECIPITATED AT THE INTERFACE

Emulsifiers are a broad class of compounds which alter the surface tension of liquids in which they are present. They also alter the interfacial tension between two immiscible liquids which is of importance in emulsion manufacture. As the interfacial tension approaches zero, emulsification is readily affected.

Commercially available emulsifying agents can be classified into five major groups with subdivisions. The classification given below is based on one developed by Schwartz and Perry (27). The agents are classified according to the hydrophilic group in the molecule.

I. ANIONIC

A. Carboxylic Acids
    1. Carboxyl joined directly to the hydrophobic group.
    2. Carboxyl joined through an intermediate linkage.

B. Sulfuric Esters (Sulfates)
    1. Sulfate joined directly to hydrophobic group.
    2. Sulfate group joined through intermediate linkage.

C. Alkene Sulfonic Acids
    1. Sulfonic group directly linked to hydrophobic group.
    2. Sulfonic group joined through intermediate linkage.

D. Alkyl Aromatic Sulfonic Acids
    1. Hydrophobic group joined directly to sulfonated aromatic nucleus.
    2. Hydrophobic group joined to sulfonated aromatic nucleus through intermediate linkage.

E. Miscellaneous Anionic Hydrophylic Groups
    1. Phosphates and phosphonic acids.
    2. Persulfates, thiosulfates, etc.
    3. Sulfonamides.
    4. Sulfamic acids, etc.

II. CATIONIC

A. Amine Salts (Primary, Secondary, and Tertiary)
    1. Amino group joined directly to hydrophobic group.
    2. Amino group joined through intermediate link.
B. Quarternary Ammonium Compounds
    1. Nitrogen joined through an intermediate group.
    2. Nitrogen joined to hydrophilic group.
C. Other Nitrogenous Bases
    1. Nonquarternary bases (e.g., guanidine, thiuronium salts, etc.)
    2. Quarternary bases.
D. Nonnitrogenous Bases
    1. Phosphonium compounds.
    2. Sulfonium compounds, etc.

III. NONIONIC

A. Ether Linkage to Solubilizing Groups
B. Ester Linkage
C. Amide Linkage
D. Miscellaneous Linkages
E. Multiple Linkages

IV. AMPHOLYTIC

A. Amino and Carboxy
    1. Nonquaternary
    2. Quaternary

B. Amino and Sulfuric Ester

  1. Nonquaternary

  2. Quaternary

C. Amino and Alkane Sulfonic Acid

D. Amino and Aromatic Sulfonic Acid

E. Miscellaneous Combination of Basic and Acidic Groups

V. WATER-INSOLUBLE EMULSIFYING AGENTS

A. Ionic Hydrophilic Group

B. Nonionic Hydrophilic Group

The effect of emulsifiers on the surface tension may better be seen in Table 1 set forth below. As may be seen in this table, pure water has a surface tension of 72.3 dynes/cm.^{2} and an interfacial tension with "mineral oil" of 31.0 dynes/cm.^{2}. Addition of various emulsifiers at 1 percent by weight concentration alters the surface tension and interfacial tension significantly. The decrease in the interfacial tension enhances emulsification substantially. When two immiscible liquids are agitated so as to disperse one liquid in the other to form fine globules, the surface of each liquid becomes greatly extended, and a corresponding large quantity of free energy is produced at the interface. This potential energy is measured by the surface produced and the intensity of the interfacial tension acting against it. The potential energy of the surface tends to reduce the surface area to a minimum. This contractile force draws the liquid into a number of spherical droplets and, at the same time, divides an intimate mixture of two immiscible liquids into two phases, separated by a minimum interface. Therefore, if an emulsifying agent reduces the interfacial tension between two immiscible liquids, it decreases the free surface enery of the emulsion and tends to produce a permanent or stable emulsion.

TABLE 1 (Reference 22)

SURFACE AND INTERFACIAL TENSION

COMPOUND (1% wt. aqueous solution)	SURFACE TENSION	INTERFACIAL TENSION* (mineral oil)
Sorbitan monolaurate (Span 20)	28	3.5
Sorbitan monostearate (Span 60)	46	11.0
Sorbitan monooleate (Span 80)	30	2.5
Sorbitan monolaurate (Tween 20)	36	6.0
Sorbitan monostearate (Tween 60)	43	9.0
Sorbitan monooleate (Tween 80)	41	10.0
Sodium oleate	27	
Water	72.3	31**

* dynes/cm.^{2}

** Measured by author for comparison purposes. This is typical for many hydraulic and turbine "mineral oils".

ELECTROVISCOUS EFFECT

The electroviscous effect is an outgrowth of the Helmholtz (28) double layer theory. Helmholtz assumed that the charge on the particles of a lyophobic colloid was due to an unequal distribution of ions at the particle-water interface. He further pointed out that ions of one charge were closely bound to the particle, ions of the opposite charge would line up parallel to them thereby forming a double layer of charges. This situation is presented in Figure 3 as an idealized form for a spherical particle.

The Zeta Potential which is an outgrowth of the double layer theory is usually defined in the following way:

> "Most colloidal particles have a negative charge and are surrounded by stationary positive charges, which in turn, are surrounded by a diffuse layer of negative charges. The Zeta Potential is the difference in the charge between the movable layer and that of the bulk suspending liquid." (29)

A recent presentation of this phenomenon is in an article by Schmit (29). However, in regard to emulsions stabilized with nonionic emulsifiers or water in oil emulsions, it is difficult to picture a surface charge arising by this mechanism. Alexander (30) proposes that it is possible to absorb ions from the aqueous phase. Equally possible is the existence of a charge arising from frictional contact between the droplets and the suspension medium, analogous to the frictional electricity generated when an

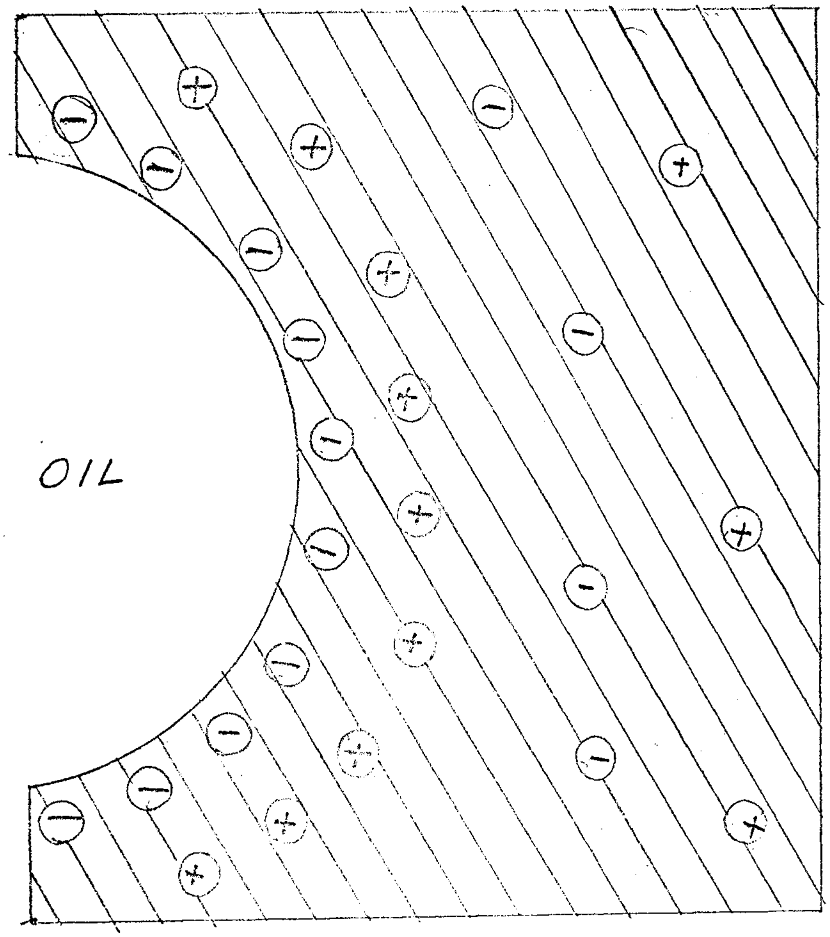

Figure 3 - Double Layer Theory Presentation

amber rod is rubbed with a silk cloth. However, Schulman and Cockbain (31) reject the hypothesis that droplets in water in oil emulsions possess a charge.

PARTICLE SIZE DISTRIBUTION

Particle size is generally expressed as the diameter of the globules in the internal phase. If the size is not uniform, the particle size occurring most frequently is adopted as a designation of particle size of the emulsion. The values of the smallest and the largest particles are indicative of the range of particle size.

The particle size of an emulsion is largely dependent on the type and quantity of emulsifier, the amount of work applied in preparation of emulsion, and the addition order of ingredients. Most commercially available emulsions have a particle size of 0.5 to 2.5 microns. Fine uniform particle size in an emulsion generally indicates good stability. A change in particle size from small to large diameter during storage indicates a breakdown of the emulsion stability. Quantitatively, the particle size of an emulsion can be estimated from a colorimetric observation. (22)

PARTICLE SIZE	APPEARANCE
1 micron	Milky white emulsion
0.1 to 1 micron	Blue white emulsion

0.05 to 0.1 micron	Grey semi-transparent emulsion
0.05 micron and smaller	Transparent emulsions

SCOPE

This present work is a study of the theory of emulsions and, in particular, the factors affecting the apparent viscosity (η_{ε}) of emulsions. This facet has not been investigated thoroughly by previous workers. The work that was carried out involved emulsions of oils or asphalts with water. In the present work, the hydrocarbons employed were pure n-paraffins.

The type system selected was water in oil (W/O) emulsion, sometimes referred to as an "invert" emulsion. These emulsions consisted of water, emulsifier (at two concentrations), and a pure hydrocarbon. The ratio of water to oil was varied and the resulting apparent viscosities of the emulsions were measured. The effect of hydrocarbon chain length of the external phase on the apparent viscosity of the emulsion was also determined.

EXPERIMENTAL EQUIPMENT AND MATERIALS

Emulsions were prepared with a Fischer Scientific hand operated homogenizer (11-504-200) and a single surfactant. Each blend had the same amount of shear and in this manner uniform particle size was obtained. It was predetermined by experiment how much work was needed to produce stable emulsions with disperse particles 1-2 microns in diameter.

PARTICLE SIZE MEASUREMENTS

The particle size was measured with a Bausch & Lomb microscope equipped with a 10 X ocular and 98 X oil immersion lens. In order to stop Brownian movement a drop of the emulsion was dispersed in 100 mls. of a low viscosity mineral oil. The viscosities were measured with a Lantz-Zeitfuchs type reverse flow viscometer. The emulsions were non-transparent, and a straight flow type viscometer could not be utilized.

MATERIALS

Normal paraffins:

Heptane

Decane

Dodecane

Tetradecane

Hexadecane

Octadecane

All paraffins were of 99 percent weight purity and were obtained from Philips Petroleum Company. The water comprising the disperse phase was distilled.

Glycerol mono-oleate was obtained from Emery Industries.

It had the following properties:

GLYCEROL MONOOLEATE PROPERTIES

Saponification Number, mg.KOH/g	152.2
Iodine Number	73.4
Specific Gravity, 60/60°F	0.9516
Total Acid Number, mg.KOH/g	2.0

VISCOSITY MEASUREMENT

The apparent viscosity of the emulsions were determined with a Lantz-Zeitfuchs type reverse flow viscometer conforming to the following characteristics:

VISCOMETER PROPERTIES

Capillary Diameter, mm	2.37
Capillary Length, mm	300
Siphon Diameter, mm	3.00
Bulb Volume, ml	5.0
Constant of Calibration	1.0

EXPERIMENTAL PROCEDURE

The present investigation is centered on pure hydrocarbons. The series of n-paraffins used contain only very small amounts of branched and are devoid of olefinic and aromatic components. Only one emulsifier was employed although emulsifiers are normally used in pairs to facilitate ease of emulsibility. The coupling action of a single emulsifier would be in one direction, i.e., the heads and tails of the compound are all aligned identically. After an examination of a number of emulsifiers and using the "Atlas H L B System", glycerol monooleate was selected. The usual relationship between H L B and end use of surfactants is as follows:

TABLE 2

SURFACTANT APPLICATION

H L B	APPLICATION
4-6	W/O emulsions
7-9	Wetting agents
8-13	O/W emulsions
13-15	Detergents
15-18	Solubilizers

In this work, the emulsifiers examined had H L B numbers from 4-6 because the resultant emulsions were to be

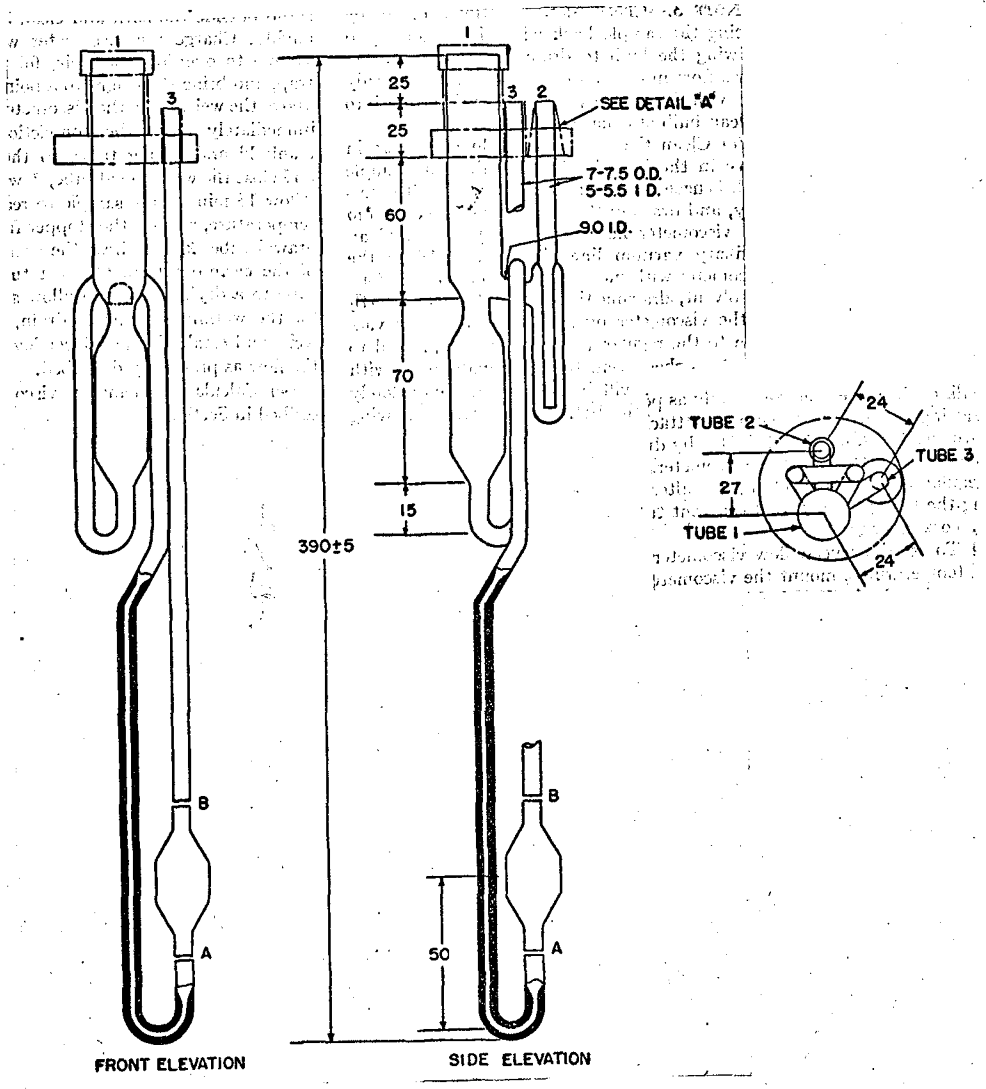

Figure 4 - Lantz-Zeitfuchs Type Reverse-Flow Viscometer
(all Dimensions are in Millimeters)

water in oil type. The H L B number (22) can be calculated (if Atlas compounds are not used) by the following simple formula:

$$H L B = 20 (1 - S/ A) \quad (8)$$

S = saponification no. of the ester.

A = acid no. of the acid.

For the emulsifier chosen (glycerol monooleate) the calculated H L B is:

$$H L B (G M O) = 20 \left(1 - \frac{152.2}{200} \right) = 4.8$$

It might be well to mention that n-paraffins do not emulsify as readily as aromatic hydrocarbons or mixtures of petroleum oils. The H L B system serves as a guide, but in no way guarantees stable emulsions. Of several possibilities, glycerol mono-oleate appeared to be best.

Emulsification was effected by first preparing a coarse emulsion. This coarse emulsion was prepared by mixing the paraffin and emulsifier in a 100 ml. glass stoppered graduate cylinder. Water was added in increments of 3-5 mls. with shaking of the emulsion after each addition. This procedure was repeated until all the water had been added. The addition of water produces an unstable emulsion which may tend to revert to an O/W, oil in water type.

Once the coarse emulsion had been prepared, it was necessary to convert it to a stable emulsion by use of a homogenizer. After each pass through the homogenizer, the particle size was checked with a microscope. It was determined that 4-5 passes gave reproducible emulsions, having the desired particle diameter. The final particle diameter was 1-2 microns. Equally as important as particle diameter was the fact that the apparent viscosity of these emulsions could be reproduced.

Preliminary work using a Waring Blendor produced emulsions having large particles which evidenced instability and proceeded to "break" before the viscosity values could be determined. An undesirable temperature rise was observed when the Waring Blendor was used. For a one minute mix, temperature rises of 5-10 degrees were observed depending upon the viscosity of the emulsion. Mixes of 3, 5, and 10 minutes duration were prepared; these also exhibited poor stability and had droplet sizes which were large and nonuniform. Some of the materials investigated were quite volatile, and temperature raises enhanced evaporation during emulsifications. Because of these factors, a hand homogenizer was tested. In the hand operated homogenizer, no temperature rise was observed, stability of emulsions was obtained, and particle sizes were in the range of 1-2 microns in diameter. This homogenizer was used throughout the rest of the work.

Homogenization and viscosity determinations were performed at 25° C (77° F) with one exception, octadecane. This material is solid at this temperature, and therefore, was studied at 32.2° C (90° F).

WORKING PROCEDURE

Emulsions were prepared by pipetting 60 mls. of hydrocarbon into a glass stoppered 100 ml. volumetric cylinder. The emulsifier, glycerol monooleate, was added (either 5 ml. or 10 ml.) to the hydrocarbon. This mixture is considered the continuous phase and the viscosity of this material, , in the equations.

Distilled water was added from a burette in 3-5 mls. portions; after each addition, the mixture was vigorously agitated. The resulting mixture, which was a coarse emulsion, was added to the hand homogenizer and "worked". After each pass, the particle size was checked with the Bausch & Lomb microscope. It was found that four or five passes were required to obtain emulsions with droplet sizes of one to two microns in diameter.

The apparent viscosity of the completed water in oil emulsion was determined with a Lantz-Zeitfuchs reverse flow viscometer (see Figure 4). The emulsion sample, after aging for one minute, was poured into the filling tube (1) until the sample overflowed into the trap. The temperature of the continuous phase and the water were adjusted to the proper viscosity temperature (77° or 90° F).

The sample flow was initiated by applying a slight vacuum at the vent (3). The vacuum was maintained until the sample flowed over the siphon to a point opposite the timing mark (A) and thereafter allowed to flow under its own head around the bend in the capillary. (Measured in seconds, the time required for the miniscus to pass from the first timing mark to the second.)

CALCULATION

Kinematic viscosity, cs $=$ CT (9)

C $=$ The calibration constant of the viscometer centistokes per second.

T $=$ The efflux time in seconds.

PRELIMINARY WORK

An examination of previous work showed that a definite relationship existed between the viscosity of the continuous phase and the apparent viscosity of the emulsion. It further appeared that as the viscosity of the continuous phase increased so also did the apparent viscosity of the emulsion. New experiments were made to check these observations. The results may be seen in Table 3 and 4 set forth below. These tables show the viscosity of the continuous phase and the apparent viscosity of an emulsion prepared with these oils. The data in Table 3 were obtained from a family of petroleum oils, all having a low viscosity index, and which were emulsified with a portable hand operated homogenizer. These emulsions contained 60 parts of continuous phase, 40 parts of water, and 3 parts emulsifier (parts by volume). Table 4 is a summary of results obtained with one base oil and shows how the concentration of the disperse phase affects the apparent viscosity of the emulsion.

The emulsion type (O/W or W/O) was determined by the dilution method. This method depends on the fact that an emulsion is readily dilutable by the liquid which constitutes the continuous phase. The emulsions prepared in this investigation were readily extended with the hydrocarbon phase, indicating that these emulsions were water in oil type (W/O).

TABLE 3

THE EFFECT OF OIL VISCOSITY ON EMULSIONS

VISCOSITY OF THE OIL (Centistokes at 100°F)	VISCOSITY OF THE EMULSION (Centistokes at 100°F)
5.2	19.5
23.3	92.8
93.7	541
184	1820
237	3170
343	7030

TABLE 4

THE EFFECT OF THE DISPERSED PHASE
ON THE
APPARENT EMULSION VISCOSITY

		VISCOSITY		Viscosity
H_2O/Oil Ratio	Vol. H_2O%	Base Oil	Emulsion	Ratio
1/10	9.1	23.3	29.2	1/1.2
2/10	16.7	23.3	37.5	1/1.6
3/10	23.1	23.3	50.0	1/2.1
10/15	40	23.3	92.8	1/3.8

These data show that there is a very definite relationship which is nonlinear. It should be remembered, however, that these petroleum oils contain both aromatic and paraffinic type hydrocarbons. N-paraffins, branched chain, olefins and aromatic type hydrocarbons have different emulsification capabilities and different apparent viscosities of the emulsion. N-paraffinic type hydrocarbons were chosen for this work to avoid effects of materials with different emulsification properties.

EXPERIMENTAL RESULTS

Based on the results of preliminary experiments reported in Tables 3 and 4, it was decided to study:

(1) The effect of concentration of the internal phase on the apparent emulsion viscosity.

(2) The effect of the viscosity of the external phase on the apparent emulsion viscosity.

Results of the first part can be summarized in Figures 5 and 6. The effect of viscosity of the continuous phase can be seen in Figures 7 and 8.

The data obtained from these experiments are tabulated in the appendix, Tables 8 to 15. It can be seen from these data and Figures 5 to 8 that there is a definite relationship between:

(1) The concentration of the internal phase, ϕ , and the apparent viscosity of the emulsion, η_E .

(2) The viscosity of the continuous phase, η_o , and η_E .

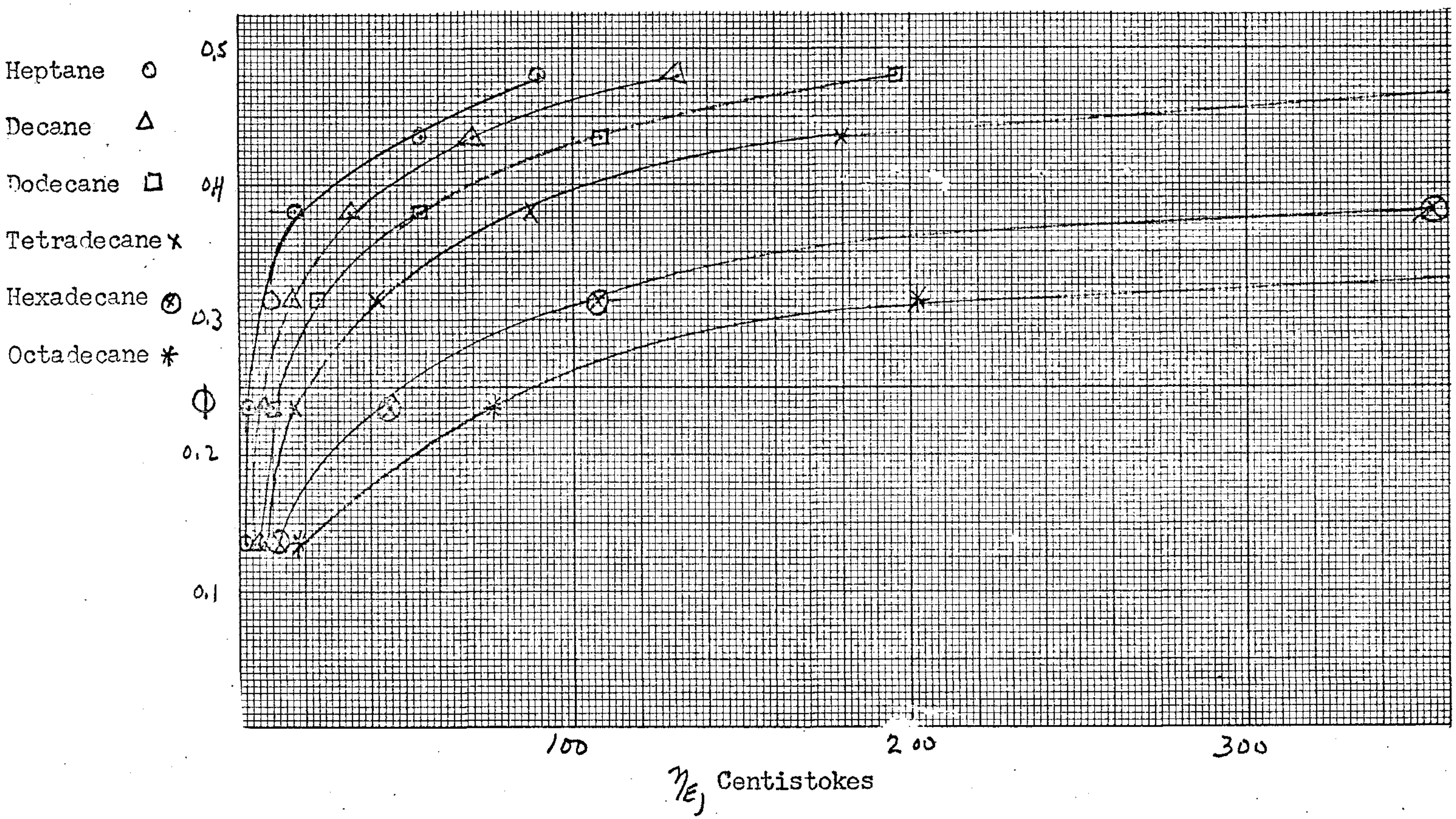

Figure 5 - Apparent Viscosity of the Emulsion vs. Disperse Phase Concentration

(The hydrocarbon phase contains 60 mls. hydrocarbon and 5 mls. emulsifier)

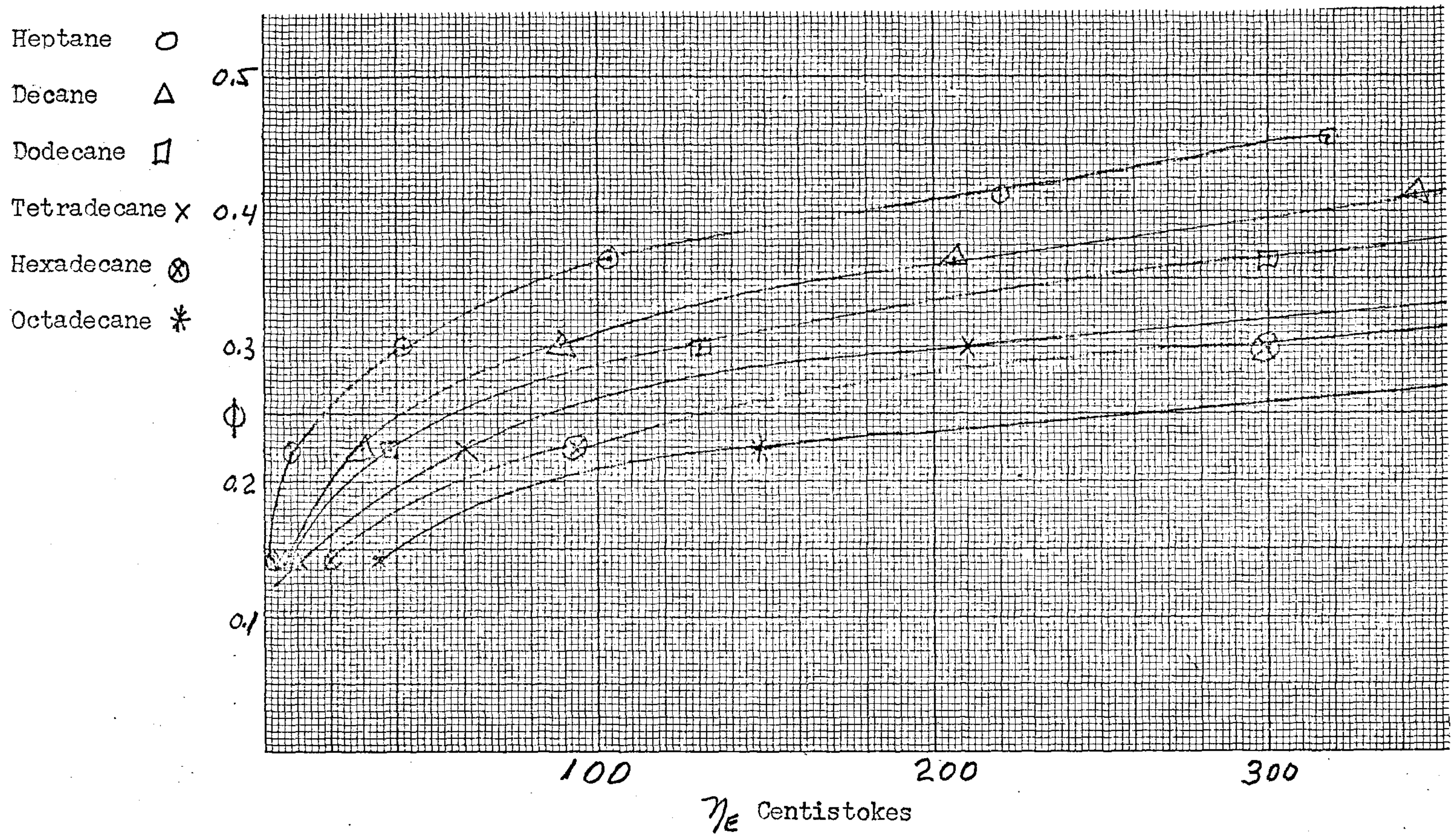

Figure 6 - Apparent Viscosity of the Emulsion vs. Disperse Phase Concentration

(The hydrocarbon phase contains 60 mls. hydrocarbon and 10 mls. emulsifier)

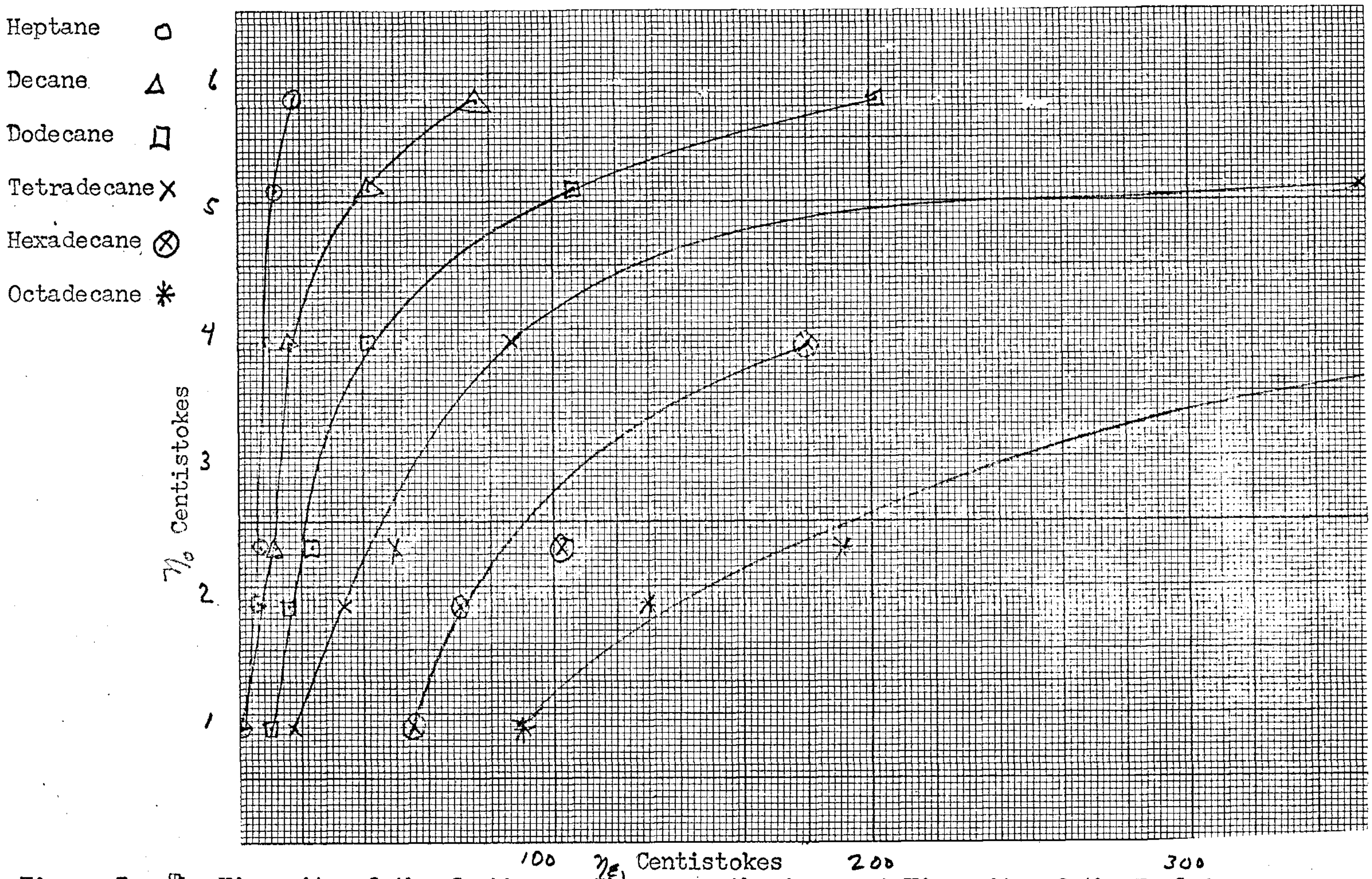

Figure 7 - The Viscosity of the Continuous Phase vs. the Apparent Viscosity of the Emulsion
(These emulsions contained 60 mls. hydrocarbon, 5 mls. emulsifier, and water)

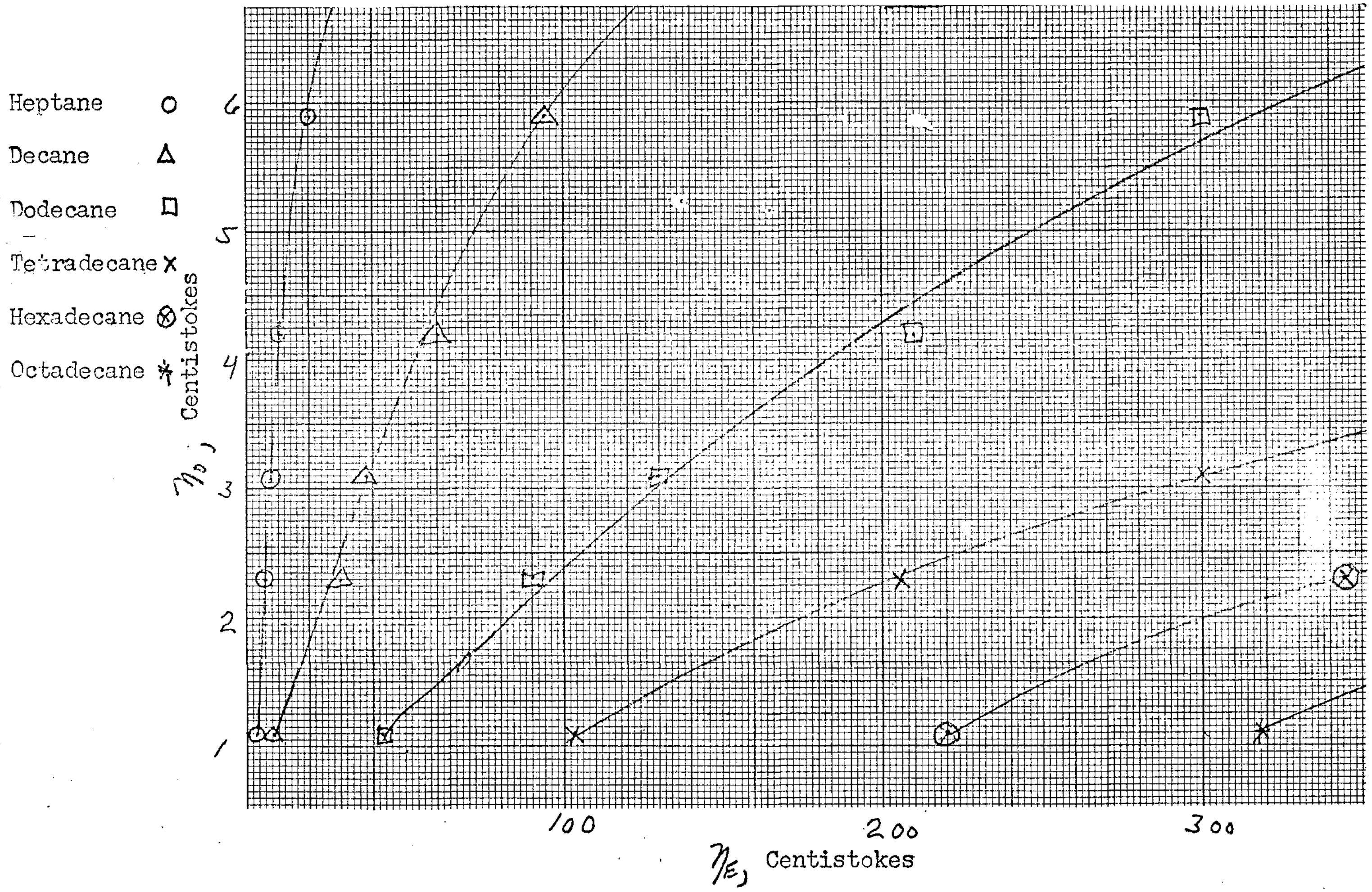

Figure 8 - The Viscosity of the Continuous Phase vs. the Apparent Viscosity of the Emulsion

(These emulsions contained 60 mls. hydrocarbon, 10 mls. emulsifier. and water.)

DISCUSSION

The preliminary work (data presented in Tables 3 and 4) shows that a definite relationship exists between the concentration of the disperse phase and the apparent viscosity of the emulsion. Similar results have been reported before, but these new data more clearly define the magnitude of the effects. However, the oils used in the preliminary work and those previously reported consisted of mixtures of compounds. The physico-chemical properties of such mixtures depend upon their composition. This complicating factor was avoided by using pure n-paraffins as the continuous phase. Pure compounds have consistent properties. The results using a series of n-paraffins are summarized in Tables 8-15 and in Figures 7 and 8 of the appendix. The trends are the same as for oil mixtures, that is:

(a) As the concentration of the disperse phase increases, the apparent viscosity of the emulsion increases.

(b) As the viscosity of the hydrocarbon comprising the external phase increases, the apparent viscosity of the emulsion increases.

The Einstein and Hatscheck curves agree well with experimental data up to a ϕ of 0.2. Beyond this value of the discrepancies become increasingly great. The Vand equation is applicable up to a ϕ of 0.3. The Mooney equation using crowding factors of 1.6 and 1.8 bracket the experimental data up to a ϕ of 0.4. Beyond this point large variations are evident. Therefore, it can be said that these equations apply only to a limited range of ϕ .

These equations have certain factors in common which have been examined in detail. The principle ones are the viscosity of the external phase and the concentration of the internal phase.

Considering first the viscosity of the external phase, it can be seen in Figure 10 how the viscosity of the pure paraffin increases with molecular weight. A study of Figures 7, 8, 9, and 10, shows that all these curves have a similar shape. The increase in the apparent viscosity for a given ϕ was approximately 5 times the change of the pure hydrocarbon viscosity. The similarity in the shape of the curves suggest that the viscosity of the external phase is part of the answer. The difference in the shapes of the curves show that the external phase viscosity is not the only cause of the apparent viscosity of the emulsion. Figures 7 and 8 show the increase of the apparent viscosity of the emulsion as the viscosity of the continuous phase increases.

In the Einstein Equation the relationship between η_E and ϕ has a linear form. The resulting curve does not agree with experimental data at high concentrations. In the Hatscheck Equation ϕ is in a power form. The shape of this curve approaches the one obtained from experimental data, but the similarity is only in the shape. The Vand Equation which takes into account the shape factor, the collision factor (or time between collisions), and the hydrodynamic interaction constant is much better than either the Einstein or the Hatscheck Equations. However, this equation still shows rather poor correlation with experimental data. With the Mooney Equation, an exponental relationship with two constants is used. The curve of the Mooney Equation matches the experimental data better than the other equations. However, the factor for S is chosen as a constant depending on the particle size of the disperse phase. This is apparently so for solids dispersed in a liquid (10), but as can be seen in Tables 18 and 18A of the appendix, S varies with ϕ . This is shown on Figure 11 of the next page. The points in Figure 11 were obtained with different hydrocarbons as the external phase.

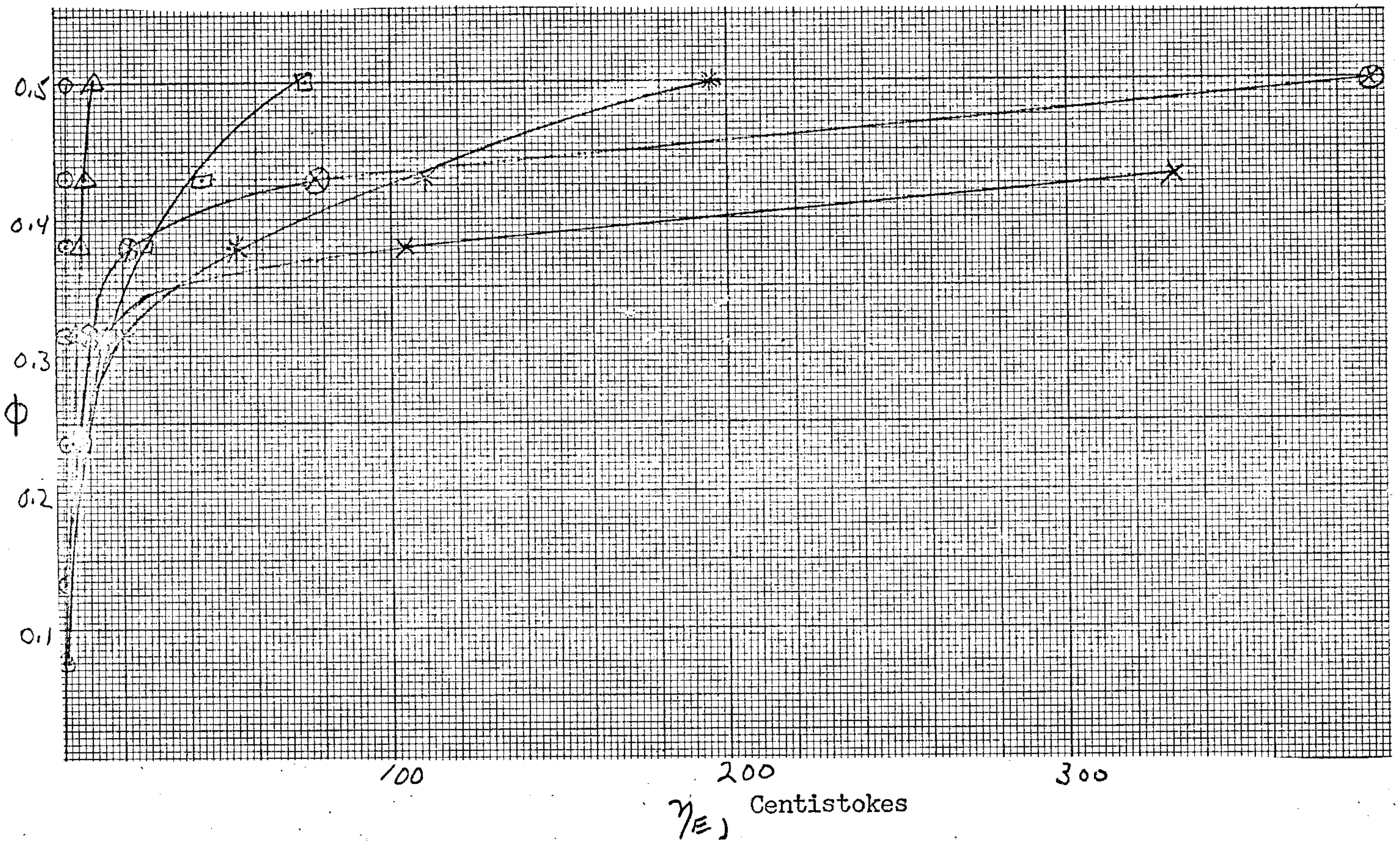

Figure 9 - Theoretical Emulsion Curves vs. Experimental
(60 mls. Decane- 5 mls. G M O)

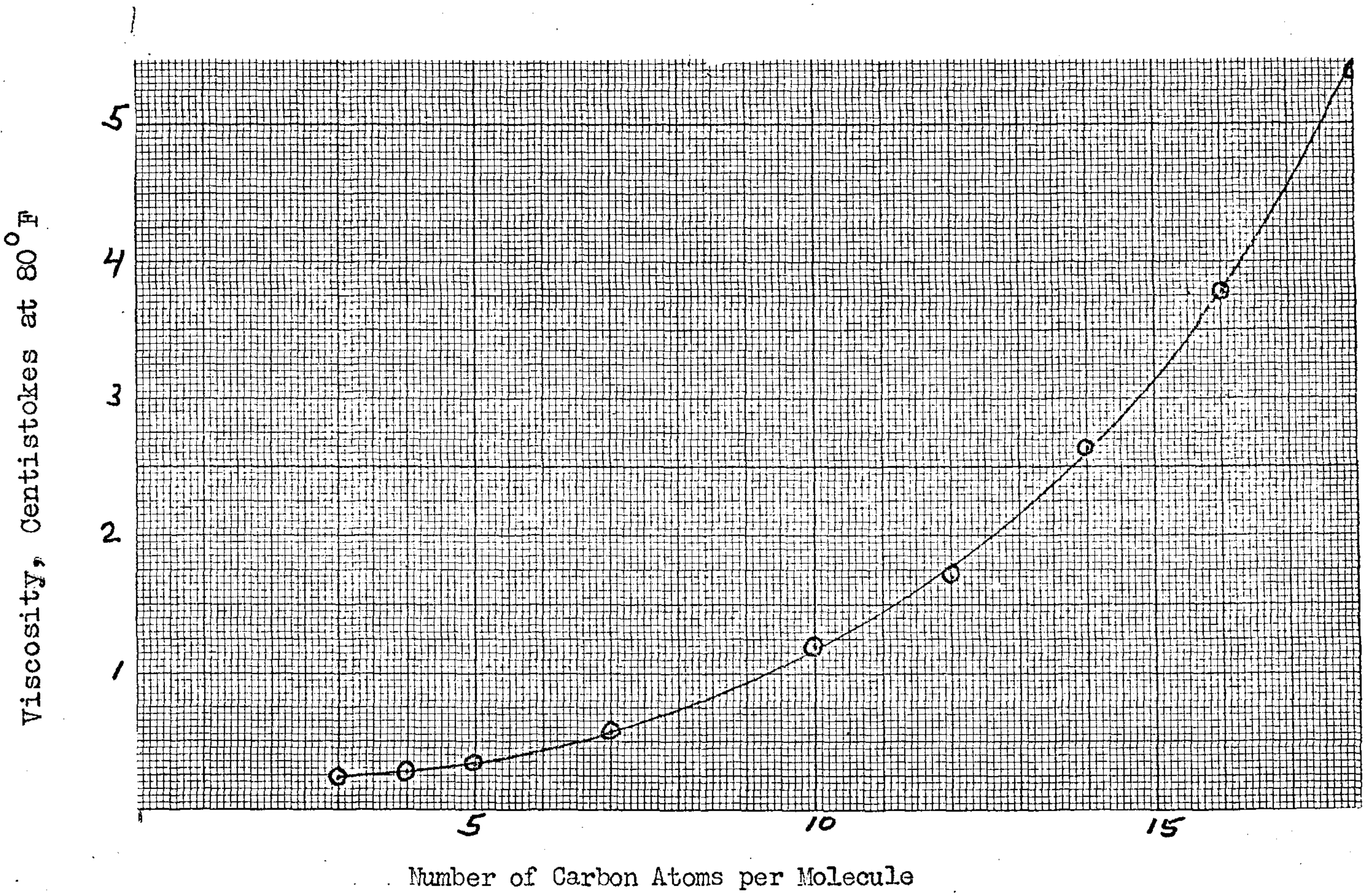

Figure 10 - Viscosity of Pure Hydrocarbons vs. the Number of Carbon Atoms per Molecule

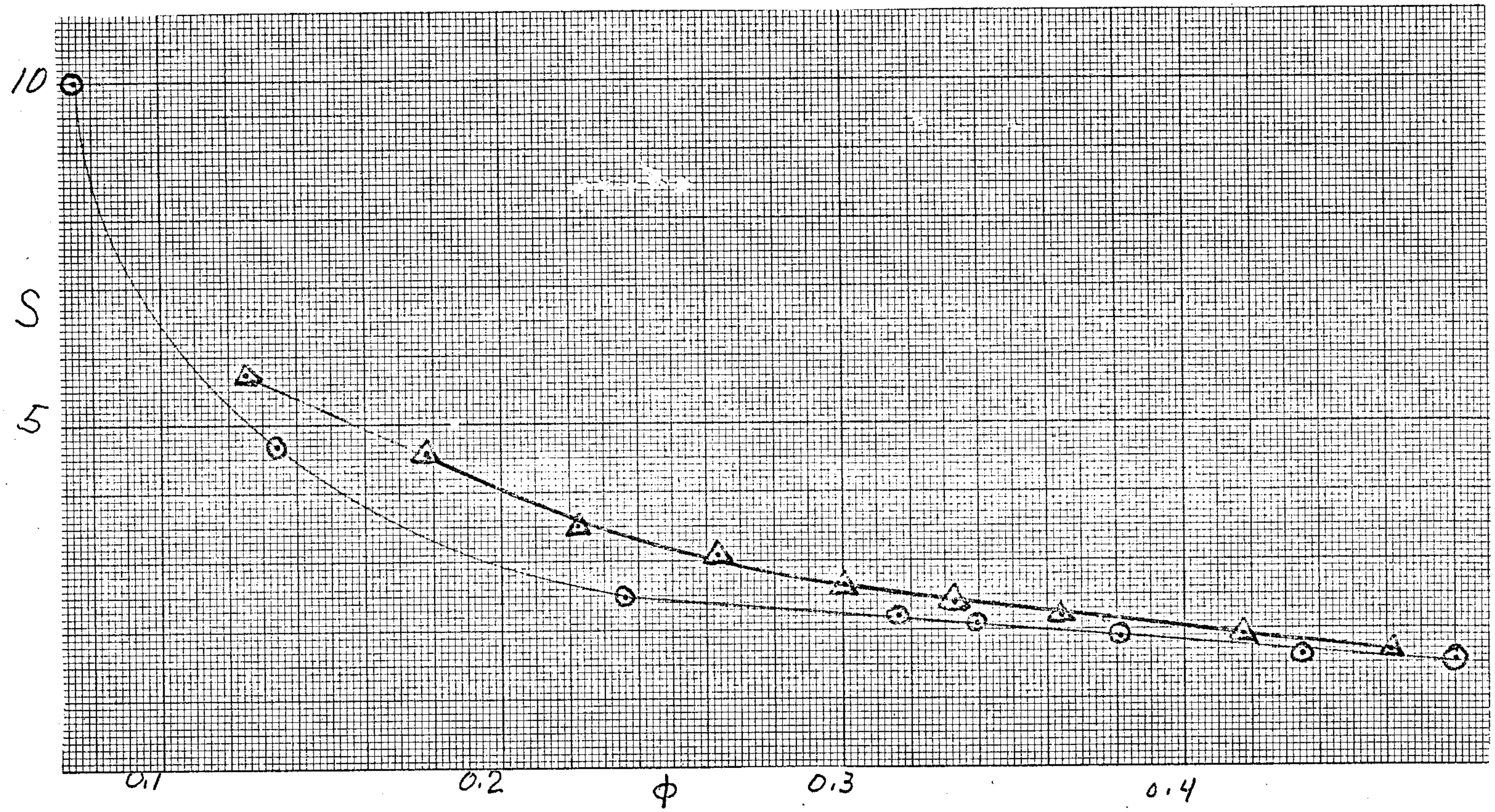

Figure 11 - Crowding Factor (S) vs. Disperse Phase Concentration (○)

○ Emulsions with 5 mls. G M O
△ Emulsions with 10 mls. G M O

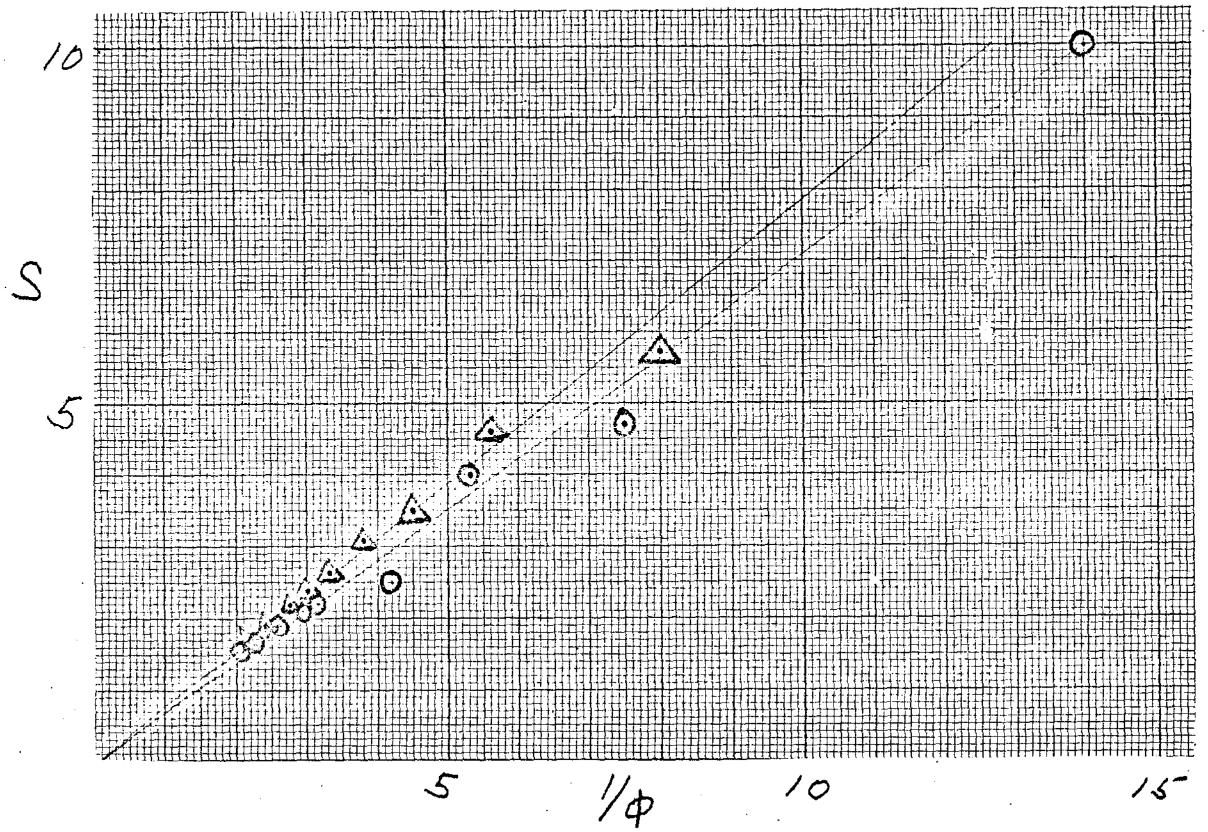

Figure 12 - Crowding Factor (s) vs. the Reciprocal of the Disperse Phase Concentration (1/φ)

○ Emulsions with 5 mls G M O

△ Emulsions with 10 mls. G M O

This graph shows that S is a function of $1/\phi$ with the emulsifier concentration as a parameter. Evidently, and as should be expected, the amount of emulsifier is an important factor. The curves can be represented in the slope-intercept form:

$$S = \frac{m}{\phi} + b \qquad (10)$$

Where m is the slope and b is the intercept. The slopes and intercepts are found tabulated below in Table 16.

TABLE 5

CONSTANTS FOR NEW EQUATION

m	b	Continuous Phase Composition
0.685	0.016	60 mls. hydrocarbon - 5 mls. G M O
0.795	0.010	60 mls. hydrocarbon - 10 mls. G M O

The slope-intercept form is substituted into the Mooney Equation starting with:

$$\ln \eta_\epsilon/\eta_0 = \frac{2.5\,\phi}{1 - S\,\phi} \qquad (4)$$

We get:

$$\ln \eta_\epsilon/\eta_0 = \frac{2.5\,\phi}{1 - \phi\left(\frac{m}{\phi} + b\right)} \qquad (11)$$

and in final form:

$$\ln \eta_\epsilon/\eta_0 = \frac{2.5\,\phi}{1 - m - b\,\phi} \qquad (12)$$

Table 16 shows m is a function of the emulsifier concentration but data are insufficient to determine the form of the function. It can be seen in Figure 12 that the curves almost go through the origin. In Table 16, b can be seen to be very small and b ϕ therefore is much smaller. For all general purposes b ϕ may be taken as a constant because of its numerical size in comparison to the term (1 - m).

From Figures 13 and 14 it is seen that the suggested equation correlation is superior to the Mooney form and hence to the other suggested equations. The equation data agree in the overall sense. There is considerable scatter which perhaps could be reduced by further determinations. The agreement is best for materials comprising the continuous phase which are liquids at 77°F. The data obtained with octadecane vary considerably from the derived equation, and tend to follow a Mooney form. This can also be seen in Figures 13 and 14.

The new equation may be used in two forms,

$$\ln \eta_\epsilon/\eta_0 = \frac{2.5\phi}{1 - m - b\phi} \qquad (12)$$

or if b ϕ is considered insignificant

$$\ln \eta_\epsilon/\eta_0 = \frac{2.5\phi}{1 - m} = M\phi \qquad (13)$$

Figure 13 and 14 are in effect plots of equation (13) at two different emulsifier concentrations. This form seems most applicable since b is a small number for the emulsions studied. If b ϕ is not considered a constant (or negligible) then a log - log plot is necessary and the slope of the line will have the form:

$$M = \frac{A}{B + C\phi}$$

This equation suggests that the constant 2.5 may not always apply.

The emulsifier composition was not varied in this work. Experience suggests that the composition is very important. At least, the magnitudes of m, M, and b can be expected to change. The effects of other emulsifier types and the effects of mixed emulsifiers requires further study.

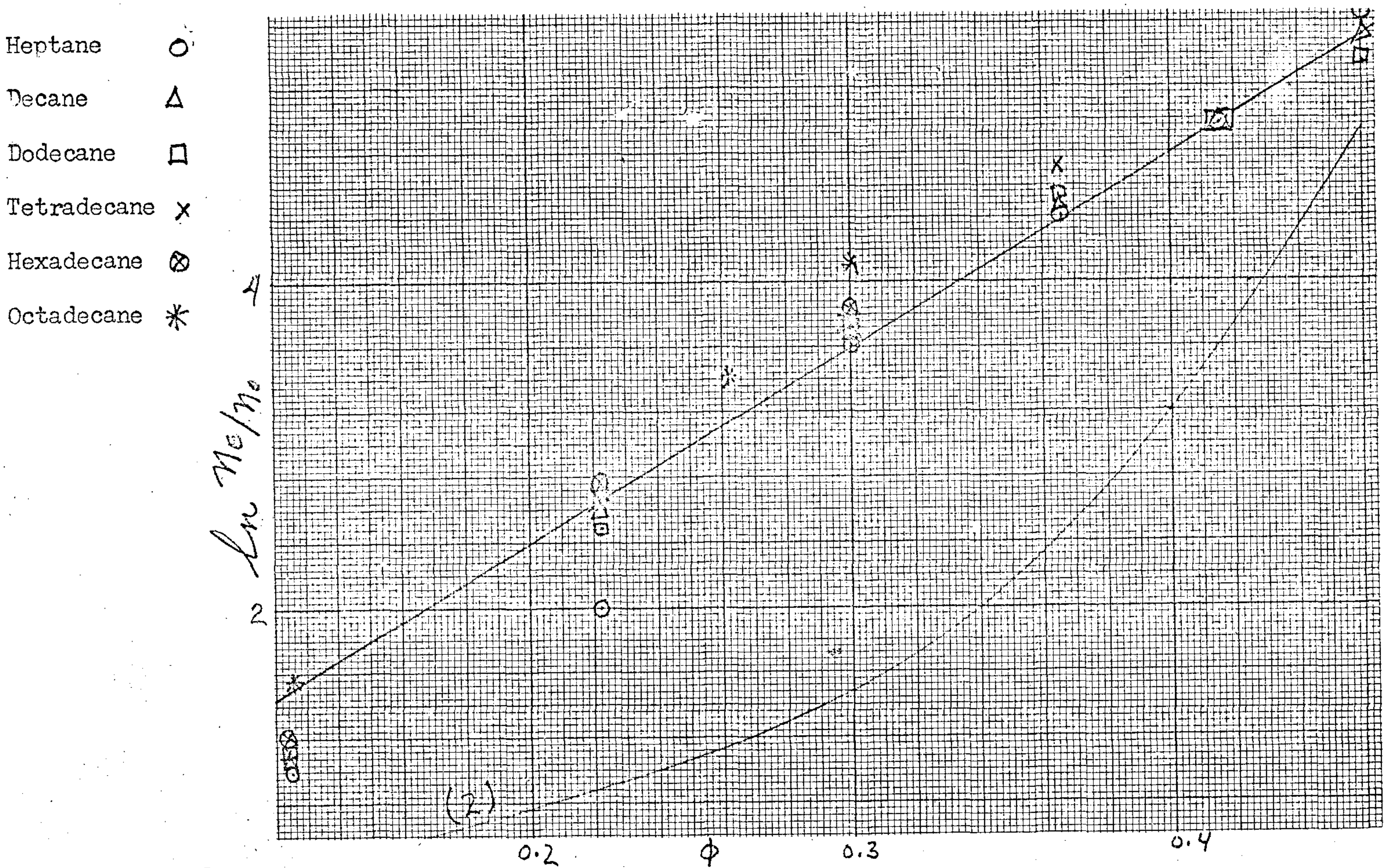

Figure 13 - ln η_E/η_o vs. ϕ Compared with the New Equation (1) and the Mooney Equation (2) S ≃ 1.7
(Emulsions contained 10 mls. G M O)

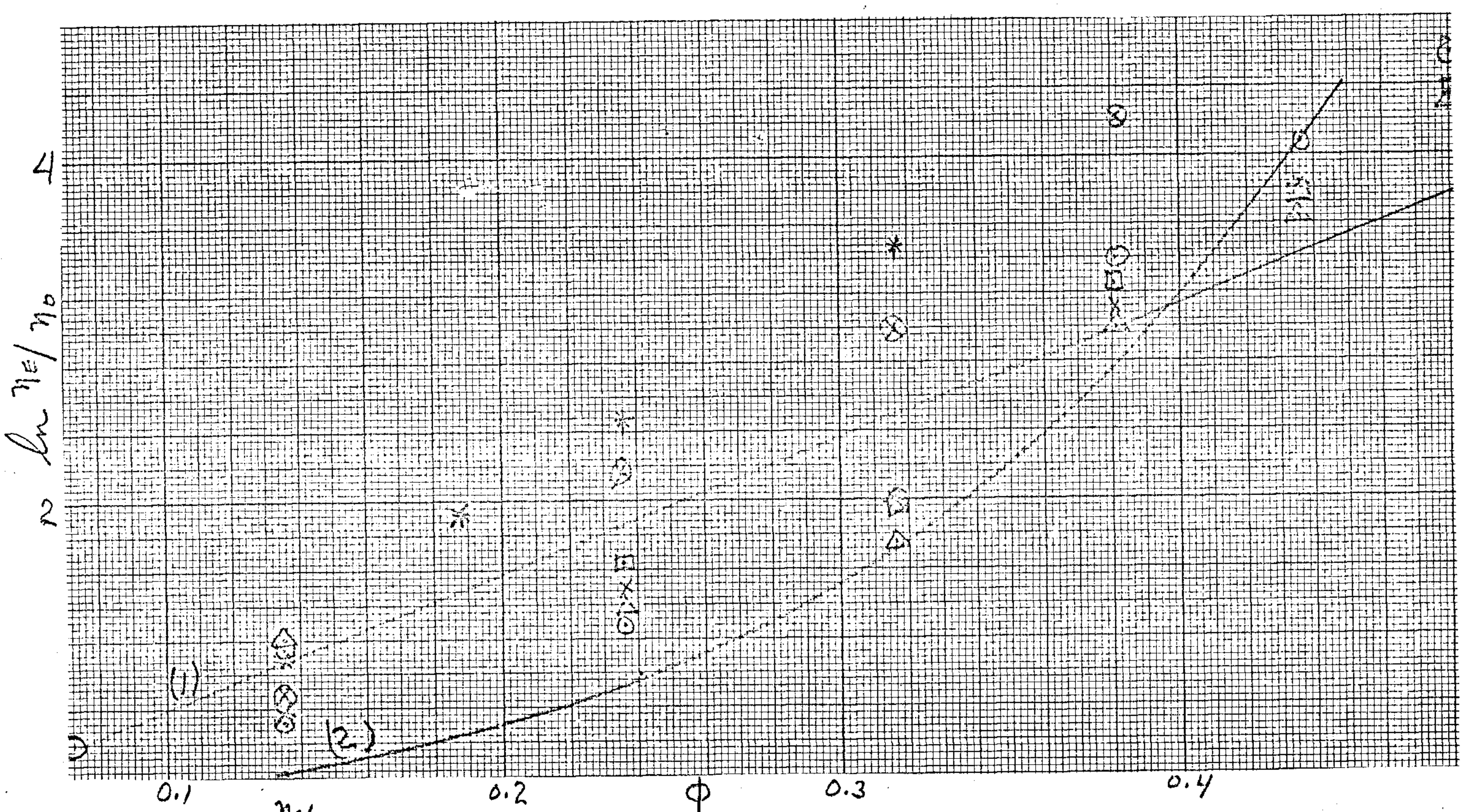

Figure 14 - ln η_E/η_0 vs. ϕ Compared with the New Equation (1) and the Mooney Equation (2) S = 1.7

(Emulsions contained 5 mls. G M O)

Heptane	○	Tetradecane	×
Decane	△	Hexadecane	⊗
Dodecane	□	Octadecane	✳

CONCLUSION

It was found that the apparent viscosity of the emulsion was dependent upon a number of factors:

(1) The concentration of the disperse phase.

(2) The viscosity of the continuous phase.

(3) The crowding factor, which is dependent upon the emulsifier content.

It was established that the crowding factor was dependent upon the concentration of the disperse phase. An equation for S in terms of the disperse phase concentration was determined. This expression for S when substituted into the Mooney Equation resulted in a new equation without a crowding factor term. This new equation takes into account η_E, η_0, ϕ, and one or two constants. The constants may be evaluated from a suitable plot of the data or via the crowding factor and the Mooney Equation. The equations for the apparent viscosity of a water in oil emulsion are:

$$\ln \eta_E/\eta_0 = \frac{2.5\phi}{1-m-b\phi} \qquad (12)$$

or since $b\phi$ is small

$$\ln \eta_E/\eta_0 = \frac{2.5\phi}{1-m} = M\phi \qquad (13)$$

M is a function of emulsifier concentration and very likely also a function of emulsifier composition.

NOMENCLATURE

B	Hydrodynamic interaction constant, Vand Equation
C	Calibration constant for viscometer
h	Constant in the Hatscheck Equation
K_1	Einstein shape factor, Vand Equation
K_2	Shape factor of collision doublets, Vand Equation
S	Mooney's crowding factor
T	Efflux time for viscometer
α	Collision time constant, Vand Equation
ϕ	Volume fraction of disperse phase
η_E	Apparent viscosity of the emulsion, centistokes
η_o	Viscosity of the external phase, Centistokes
η_i	Viscosity of the internal phase, centistokes

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TABLE 6

HEPTANE

Effect of Disperse Phase Concentration on η_E

(60 mls. heptane, 5 mls. G M O)

Water, % Vol.	η_E
0	0.91
7.17	1.7
13.35	1.8
23.60	2.8
31.60	10.1
38.10	27.2
43.5	55.3
48.0	89.5

(60 mls. heptane, 10 mls. G M O)

Water, % Vol.	η_E
0	1.1
14.3	3.0
22.2	5.1
30.0	42.0
36.4	103
41.7	220
46.2	318

TABLE 7

DECANE

Effect of Disperse Phase Concentration on η_E

(60 mls. decane, 5 mls. G M O) (60 mls. decane, 10 mls. G M O)

Water, % Vol.	η_E	Water, % Vol.	η_E
0	1.77	0	2.3
13.4	6.1	14.3	6.1
23.6	7.5	18.3	12.0
31.6	16.0	22.2	30.1
38.1	33.8	30.0	89.7
43.5	70.5	36.4	206.0
48.0	130.0	41.7	344

TABLE 8

DODECANE

Effect of Disperse Phase Concentration on

(60 mls. dodecane, 5 mls. G M O) (60 mls. dodecane, 10 mls. G M O)

Water, % Vol.	η_E	Water, % Vol.	η_E
0	2.34	0	3.1
13.4	7.4	14.3	8.5
23.6	12.0	22.2	38.0
31.6	24.3	30.0	130.2
38.1	55.5	36.4	296.6
43.5	108.1	41.7	674
48.0	196.5		

TABLE 9

TETRADECANE

Effect of Disperse Phase Concentration on η_E

(60 mls. tetradecane,
5 mls. G M O)

Water, % vol.	η_E
0	3.9
13.4	8.7
23.6	16.7
31.6	42.1
38.1	87.2
43.5	180.0
48.0	431.3

(60 mls. tetradecane,
10 mls. G M O)

Water, % vol.	η_E
0	4.2
14.3	10.8
22.2	60.1
30.0	210.0
26.4	474.2
41.7	Too viscous

TABLE 10

HEXADECANE

Effect of Disperse Phase Concentration on η_E

(60 mls. hexadecane,
5 mls. G M O)

Water, % vol.	η_E
0	5.1
13.4	12.1
23.6	45.1
31.6	107.5
38.1	355.5

(60 mls. hexadecane,
10 mls. G M O)

Water, % vol.	η_E
0	5.9
14.3	20.0
22.2	94.1
26.1	160.0
30.0	298.0
33.2	520

TABLE 11

OCTADECANE

Effect of Disperse Phase Concentration on η_ϵ

(60 mls. octadecane, 5 mls. G M O)		(60 mls. octadecane, 10 mls. G M O)	
Water, % vol.	η_ϵ	Water, % vol.	η_ϵ
0	5.8	0	7.25
13.4	18.	14.3	35.0
18.5	41.0	18.3	90.5
23.6	76.0	22.2	148.0
31.6	202.0	26.1	250
38.1	1130	30.0	460

TABLE 12

HYDROCARBON AND EMULSION DATA

	Mol. Wt.	Density	VISCOSITY Hydrocarbon*	η_E **		η_o **	
				A	B	A	B
Heptane	100.20	0.6828	0.56	27.2	103	0.91	1.10
Decane	142.28	0.7301	1.18	33.8	206	1.77	2.30
Dodecane	170.33	0.7470	1.81	55.5	297	2.34	3.10
Tetradecane	198.38	0.7650	2.64	87.2	474	3.90	4.20
Hexadecane	226.44	0.7751	3.85	356		5.10	5.90
Octadecane	254.49	0.7768	5.40	1130		5.80	7.25

(η_E) A 60 ml. hydrocarbon, 40 ml. water, 5 ml. G M O

(η_o) B 60 ml. hydrocarbon, 40 ml. water, 10 ml. G M O

Density at 20/4° C

* Centistokes at 80° F

** Centistokes at 77° F except octadecane viscosity which was at 90° F

TABLE 13

EMULSIFIER, VISCOSITY DATA

HYDROCARBON CC	G M O CC	WATER CC	VISCOSITY centistokes
Heptane			
60	5.0	40	27.2
60	7.5	40	50.0
60	10	40	103.1
Decane			
60	1.0	40	20.0
60	3.3	40	24.0
60	5.0	40	33.8
60	10	40	206.0
Dodecane			
60	3.0	40	26.1
60	5.0	40	55.5
60	10	40	296.6
Tetradecane			
60	3.0	40	30.0
60	5.0	40	87.2
60	10	40	474.2
Hexadecane			
60	0.7	40	28.0
60	2.0	40	100.0
60	5.0	40	355.5

Octadecane

60	0.5	40	40.0
60	2.0	40	208.0
60	2.5	40	553.0
60	5.0	40	1130

TABLE 14

HYDROCARBON VISCOSITY DATA

	η_E/η_o			
WATER, CC.	10	20	30	40
HEPTANE	1.98/1	3.08/1	11.1/1	29.9/1
DECANE	2.45/1	4.23/1	9.6/1	19.8/1
DODECANE	3.16/1	5.12/1	10.4/1	23.7/1
TETRADECANE	2.23/1	4.28/1	10.8/1	26.4/1
HEXADECANE	2.37/1	8.90/1	21.2/1	70.2/1
OCTADECANE	3.12/1	13.1/1	34.8/1	195/1

These emulsions contained 60 ml. hydrocarbon, 5 ml. emulsifier, and water.

TABLE 15

HYDROCARBON VISCOSITY DATA

	η_E/η_o			
HEPTANE	2.73/1	7.35/1	38.2/1	93.7/1
DECANE	2.67/1	13.1/1	38.9/1	89.6/1
DODECANE	2.74/1	12.2/1	42.1/1	95.7/1
TETRADECANE	2.57/1	14.3/1	50.0/1	113/1
HEXADECANE	3.31/1	15.5/1	49.3/1	-----
OCTADECANE	4.83/1	20.4/1	63.4/1	-----

These emulsions contained 60 ml. hydrocarbon, 10 ml. emulsifier, and water.

TABLE 16

S-VALUES

φ	C7	C10	C12	C14	C16	C18
.0715	10	-	-	-	-	-
.1335	3.8	4.7	5.4	4.4	4.6	5.3
.188	-	-	-	-	-	4.0
.236	2.0	2.5	2.7	2.5	3.1	3.3
.316	2.1	2.0	2.2	2.1	2.3	2.6
.339	-	-	-	-	-	2.3
.381	1.9	1.8	1.8	1.8	2.0	2.1
.435	1.7	1.6	1.7	1.6	-	-
.480	1.5	1.5	1.6	1.6	-	-

TABLE 17

.125	5.5	5.4	5.5	5.4	6.3	6.4
.178	-	-	-	-	-	4.6
.222	3.3	3.5	3.5	3.6	3.6	3.7
.263	-	-	-	-	-	3.1
.300	2.6	2.6	2.7	2.7	2.6	2.7
.333	-	-	-	-	2.4	-
.364	2.2	2.2	2.2	2.2	-	-
.417	1.9	1.9	1.9	-	-	-
.461	1.7	-	1.7	-	-	-

Table 16 Blends cont'd. 60 ml. hydrocarbon, 40 ml. water, & 5 ml. G M O

Table 17 Blends contained 60 ml. hydrocarbon, 40 ml. water,
& 10 ml. G M O