EMULSIONS AND THE EFFECT OF HYDROGEN ION CONCENTRATION UPON THEIR STABILITY.

By

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Emulsions and the Effect of Hydrogen Ion Concentration upon their Stability.

Introduction.

Since the publication of the work of Harkins (1) and Langmuir (2) on the structure of liquid surfaces at a liquid-liquid surface, the orientation theory of emulsions and emulsification has been the object of much investigation and experimental work. Newman (3) working with Bancroft in 1914 observed that when benzene and water were emulsified using sodium oleate as the emulsifying agent the hydrocarbon formed the inner phase, whereas when oleic acid salts of metals with a higher valence as magnesium oleate were employed, the water becomes dispersed thru the benzene, the latter becoming the continuous phase. These observations were substantiated by Harkins and are in accord with his theoretical deductions of the nature of emulsifying agents.

Harkins and his co-workers believe that the stability of the dispersed particles in an emulsion is accomplished by the orientation of the molecules at the interface with the medium of dispersion. An emulsifying agent in the light of Harkin's theory should be a compound having a polar and non-polar group in the molecule. Hence the alkali salt of a fatty acid such as oleic and stearic acids meet this requirement. As emulsions are systems of two non-soluble liquids, the emulsifying agent must serve to reduce the abruptness of the transition between the two liquids. An emulsion, according to Harkins, is stable when the molecules of the film of the emulsifying agent fit the curvature of the emulsified particle. Accordingly, sodium oleate reduces the free energy between benzene and water and thus induces the emulsification of the benzene in the water, whereas with magnesium oleate the film of the emulsifying agent fits better the water particle and this in turn becomes dispersed in benzene.

In the preparation of medicinal emulsions gum arabic or acacia is the most generally used emulsifying agent and yields very stable milk-like emulsions. Acacia in all of the generally used medicinal emulsions invariably produces an emulsion of the oil-in-water type and as this type of emulsions is the more palatable, this gum serves well for the preparation of medicinal emulsions. In general treatises on Materia Medica and Medicinal Chemistry this gum is referred to as the sodium, potassium and calcium salts of arabic acid. The general texts on pharmacy and pharmaceutical chemistry have assigned the following formulas to this compound arabic acid.

$2(C_6H_{10}O_5)\ H_2O$ (4) $C_{12}H_{22}O_{11}$ (5) and (7)

$C_5H_{10}O_{11}$ (6)

The gum itself contains varying amounts of sodium and potassium and certain samples are practically pure calcium arabate.

Not much work has been done on the determination of the structure of arabic acid and Beilstein gives the following empirical formula for the acid which has been dried at 100°C.

$C_{18}H_{18}O_9$? Neubauer (8) prepared the calcium and potassium salts and found them to have the following compositions $CaO.2C_{12}H_{20}O_{10}$ $K_2O.(C_{12}H_{22}O_{11})_3$? Heckmeyer (9) found the lead, copper and barium salts to have the following compositions $2PbO.3C_{12}H_{20}O_{10}$ $CuO.C_{12}H_{20}O_{10}.C_{12}H_{22}O_{11}$ $BaO.2C_{12}H_{20}O_{10}$. O'Sullivan (10) prepared calcium and barium salts of the acid which he analyzed and assigned to them the following formulas $C_{89}H_{142}O_{74}.Ca$ and $C_{89}H_{142}O_{74}.Ba$. By hydrolyzing arabic acid with diluted sulphuric acid, the same investigator obtained a series of acids having 23 to 71 carbon atoms in the molecule. Bechamp obtained the di and tetra nitro substitution products of arabic acid by treating gum arabic with hot nitric acid. These compounds were amorphous and assigned the compositions $C_{12}H_{18}(NO_2)_2O_{10}$? and $C_{12}H_{16}(NO_2)_4O_{10}$? respectively. Likewise the same investigator succeeded in acetylizing the gum with acetic anhydride at 105°C. and obtained an amorphous insoluble compound of the composition $C_{12}H_{16}(C_2H_3O)_4O_{10}$?

This summary indicates that little is known about the structure of arabic acid, but from the work that has been done, the compound seems to be similar to familiar carbohydrates in structure or the carboxylic acids obtained by mild oxidation of the carbohydrates.

Tragacanth, another gum-like substance which is employed to prepare medicinal emulsions, like acacia invariably produces emulsions of the oil-in-water type, although this substance like acacia consists of the calcium salt of a complex organic acid. The principal acid constituent of this gum is bassoric acid, to which Sullivan (12) assigned the formula $H.C_{24}H_{34}O_{20}.H_2O$.

As arabic acid is obtained from acacia in a pure form far more readily than bassoric acid is obtained from tragacanth, this substance was selected as the typical acid for study.

In view of Harkins and Newman's experiences with sodium and magnesium oleates, it was decided to investigate the emulsifying properties of acacia and tragacanth in order to determine the effect of a univalent or divalent metal in the emulsifying agent. It will be recalled that as the oleates of sodium and magnesium have but one polar group in the molecule, namely the respective metallic atoms, the sodium and magnesium salts of bassoric and arabic acids contain the polar hydroxyl groups, in addition to the polar metallic atoms. In addition to investigating the character of the emulsions formed by the univalent and divalent salts of these acids, it was thought necessary to study the influence of changes of hydrogen ion concentration upon the stability of emulsions made with acacia and tragacanth and to determine the influence of this factor upon the two emulsifying agents.

The influence of changes of hydrogen ion concentration upon the emulsions prepared with acacia and tragacanth of the oil-in-water type was interesting enough to warrant studying this influence upon emulsions of the water-in-oil type. It was found impossible, however, to employ the divalent salts of arabic acid for this purpose, as will be observed from the character of these emulsifying agents; therefore to prepare these emulsions magnesium oleate was employed.

Although for years, in medicinal emulsions, the presence of acids was considered detrimental to the stability of emulsions, whereas alkalies (13) have been looked upon as stabilizers, on account of their union with vegetable and animal oils to form soap, little or no work has been done to study the influence of changes of actual hydrogen ion concentration upon emulsions and emulsifying agents. The importance of the stability of emulsions and those agents which influence this cannot be over-estimated; not only has this field an important pharmaceutical significance, but manufacturers of salad dressings and food products in general, many of which are emulsion-like in nature, are calling upon the chemist to interpret and rectify the instability of their products.

The salient problems for study then in this investigation are; first, the study of the type of emulsions produced by salts of arabic acid and related compounds; second, the study of the influence of changes in hydrogen ion concentration upon emulsions prepared with these emulsifying agents of the oil-in-water type; and third, a study of the influence of changes in hydrogen ion concentration upon water-in-oil emulsions.

Experimental.

Materials and Apparatus.

1. Oleates - A sample of C. P. sodium oleate was used as the starting point in the manufacture of the various oleates employed. Each was prepared by double decomposition between sodium oleate and the chlorides of the respective metals. The precipitated oleates were washed free from sodium chloride by repeated decantation. In the case of cobaltous oleate, it was found necessary to use the compound immediately after manufacture, as this compound readily decomposed upon exposure to air and moisture.

2. Arabic Acid - this compound was obtained by slightly acidifying a solution of acacia in water with hydrochloric acid, dialyzing to remove soluble chlorides and precipitating the arabic acid from its aqueous solution by means of alcohol. Merck's Arabin was also employed.

3. Magnesium Arabate - the compound was prepared by boiling a solution of arabic acid in water with an excess of magnesium carbonate, filtering and evaporating the filtrate to dryness over a water-bath.

Upon ignition the compound yielded 2.4 per cent of magnesium oxide.

4. Sodium Arabate - the calcium present in a solution of acacia in water was precipitated by the addition of sodium carbonate and the solution brought to the neutral point. The filtrate was evaporated to dryness over a water-bath.

5. Ferric Arabate - a 20 per cent solution of acacia in water was treated with ferric chloride solution, added drop by drop until a gel was obtained of uniform reddish-brown color and a stiff consistency. The iron (Fe) content of the gel was determined by treatment with hydrochloric acid and potassium iodide in the usual manner and titrating the liberated iodine with sodium thiosulphate.

The gel contained 0.39 per cent of iron.

6. Lead Arabate - a solution of acacia in water was treated with a solution of lead subacetate $Pb_2^{=O}$ $(CH_3.COO)_2$ equivalent to 18 per cent of metallic lead, as long as precipitation occurred. The precipitate was washed free of soluble lead salts and dried to a constant weight at 100°C. The lead content was determined by dissolving about one gram of the lead arabate in diluted nitric acid and precipitating the lead as carbonate by means of sodium carbonate, washing, filtering and igniting, weighing the lead as the monoxide.

The compound contained 40.25 per cent PbO.

7. Sodium Valerate - obtained by neutralizing valeric acid with sodium bicarbonate and evaporating the solution to the crystallizing point.

8. Magnesium Valerate - prepared by dissolving magnesium borings (for Grignard reaction) in a mixture of valeric acid and water. After the reaction was complete the solution was evaporated to the crystallizing point.

9. Zinc and Ammonium Valerates - these compounds were used from a supply of the salts of medicinal purity in this laboratory.

10. Calcium Gluconate (14) - prepared by oxidizing glucose with bromine in aqueous solution at room temperature and neutralizing the hydrobromic acid with lead carbonate. The lead was precipitated by passing in a stream of hydrogen sulphide and the filtrate was boiled with an excess of calcium carbonate. The filtrate was then evaporated to the crystallizing point. The sodium salt was obtained by decomposing a solution of the calcium salt by means of sodium carbonate, removing the precipitated calcium carbonate and evaporating the filtrate to dryness.

11. Cadmium i-galactonate (15) - prepared by hydrolyzing lactose with diluted sulphuric acid, removing the sulphuric acid by the addition of barium hydroxide and oxidizing the filtrate with bromine at room temperature. The hydrogen bromide was removed by means of lead carbonate and silver oxide and the lead and silver removed by hydrogen sulphide. The free acid was neutralized with cadmium carbonate and evaporated to dryness. The sodium salt was prepared by neutralization of the free acid with sodium carbonate.

12. Magnesium Dioxystearate (16) - prepared by the oxidation of potassium oleate in alkaline solution by means of potassium permanganate. The acid was precipitated and purified by crystallization from alcohol. The sodium salt was prepared by the addition of a molecular equivalent of sodium hydroxide and the magnesium salt obtained by double decomposition between magnesium chloride and sodium dioxystearate.

13. Calcium Salicylate and Calcium Gallate - these substances were prepared by neutralization of the free acids of a high degree of purity by means of calcium carbonate and crystallizing the salts from water.

14. The acacia and tragacanth employed met the requirements prescribed by the United States Pharmacopoeia for these substances.

15. The mineral oil employed was the commercial "Nujol" and the cottonseed and olive oils met the requirements of the United States Pharmacopoeia. Distilled Water P_H 5.8 to 6.4 was employed.

16. Apparatus - The special apparatus employed in this investigation consisted of a hydrogen ion determination outfit with a type K. potentiometer and a Wilson hydrogen electrode, a Du Noüy Tensiometer and a Donnan pipette which is shown in figure thirteen.

Certain Oleates as Emulsifying Agents:

In alignment with the work of Harkins and Newman several emulsions were prepared of mineral oil using sodium oleate, magnesium oleate, calcium oleate, manganese oleate, cobaltous oleate, nickelous oleate and aluminum oleate as emulsifying agents. Similar to the observations of Newman and Harkins with benzene, the sodium oleate yielded a dispersion of oil in water, whereas the dispersion prepared with the oleates of the divalent metals and aluminum gave emulsions of the water-in-oil type. When sodium oleate was employed one gram of the salt was sufficient to yield 40 cc. of a stable oil-in-water emulsion 25 per cent. The method employed consisted of triturating the oil thoroughly with the sodium oleate and adding 6 cc. of water, in one portion and triturating rapidly until complete emulsification took place; the remainder of the water was added slowly with continued trituration. In each case when an emulsion was prepared by this method dilution with water did not cause a separation, but attempts to dilute with oil failed, illustrating the presence of the oil as the inner phase of the emulsion. With magnesium oleate the following procedure was employed. One gram of magnesium oleate was triturated with 18 cc. of oil and when the mixture was homogeneous, the 10 cc. of water was added in one portion with continuous trituration. The formation of the emulsion nucleus was easily determined by the crackling sound produced when the pestle was rapidly drawn thru the emulsion. This emulsion nucleus was then slowly diluted to 40 cc. with mineral oil. This same procedure was employed in the preparation of the emulsions prepared with calcium, manganese, cobalt, nickel and aluminum oleates. These emulsions were permanent over a period of several months and permitted liberal admixture with oil, but attempts to dilute with water brought about immediate separation. This showed the oil to be the outer phase of the emulsion. Those prepared with magnesium oleate were the most easily prepared and the most stable emulsions of the group. Figure one illustrates the behavior of these emulsions when dilution was attempted with water and oil respectively.

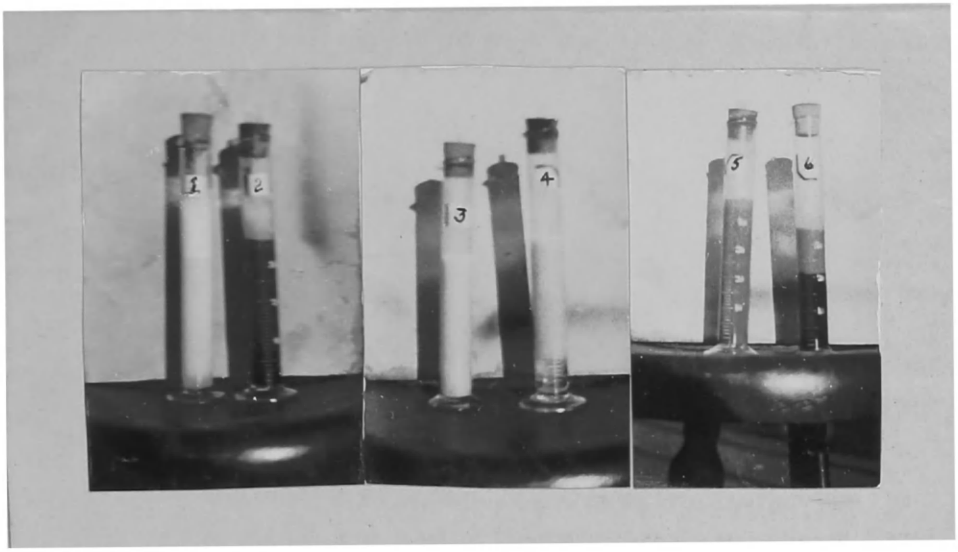


Figure I.

Emulsion #1 - oil-in-water type with sodium oleate.

Emulsion #2 - oil-in-water type with water soluble fluorescein dye - showing continuity of the color and outer phase.

Emulsion #3 - water-in-oil type with magnesium oleate as the emulsifying agent.

Emulsion #4 - shows 30 cc. of emulsion #3 to which 10 cc. of water has been added - note the separation of the water as a layer beneath the emulsion.

Emulsion #5 - water-in-oil type - the water colored with a fluorescein dye - note the discontinuity of the color.

Emulsion #6 - water-in-oil type after an attempt to dilute with water to which a fluorescein dye has been added.

Valerates as Emulsifying Agents.

Considering the simplest formula assigned to arabic acid $C_5H_{10}O_{11}$, five carbon atoms present in the molecule, an acid of the methane series with 5 carbon atoms in the molecule was selected for study. This compound valeric acid is of definite composition and gave an excellent starting point for study. Emulsions of mineral oil prepared with the sodium and ammonium salts of this acid were of the oil-in-water type and permitted slight dilution with water, but could not be diluted with oil at all. The procedure employed was to place 1 Gm. of the salt in a mortar and add 5 cc. of oil and 5 cc. of water and triturate briskly until the mixture was homogeneous. These emulsions were not very stable, and upon standing 12 to 18 hours the oil and water separated, yet upon agitation the oil was again dispersed thru the water.

The magnesium and zinc salts of valeric acid, using the same quantities and procedure as directed in the foregoing experiment, yielded emulsions of the water in oil type. As the salts of valeric acid were found to possess far less emulsifying power than the salts of oleic acid, more difficulty was experienced in determining whether the emulsion was of the oil in water type or vice versa. In order to overcome this difficulty the water was colored slightly by an organic pigment cudbear, which is insoluble in the oil. The continuity of this pigment in the emulsion indicated that water was the outer or continuous phase, whereas the discontinuity of the red color showed that the water was dispersed in the oil.

Arabates as Emulsifying Agents.

Having demonstrated the capacity of divalent metals when combined with the five carbon atom valeric acid to form water-in-oil emulsions, several emulsions were prepared using different salts of arabic acid. Arabic acid, sodium and magnesium arabates gave stable emulsions of the oil-in-water type. The procedure employed was to triturate 10 cc. of the oil with 2.5 Gm. of the emulsifying agent and add in one portion 5 cc. of water, then after brisk trituration and the formation of the emulsion nucleus, the remainder of the water was added slowly with continued trituration until 40 cc. volume was obtained. Thus in each case a 25% oil in water emulsion was prepared.

The iron gel prepared with arabic acid gave an emulsion of the oil-in-water type, by using 15 Gm. of the gel, 5 cc. of water and 10 cc. of oil and briskly triturating until emulsification occurred. This then was diluted with water until 40 cc. was obtained. These emulsions were stable over several weeks but separated a creamy layer upon the surface as do typical emulsions prepared with gum arabic.

With lead arabate as an emulsifying agent, the oil could not be emulsified in water, and likewise it was impossible to prepare an inverted emulsion using this emulsifying agent. When 1.5 Gm. of the salt was briskly triturated with 5 cc. of oil and 5 cc. of water, the oil quickly separated to the surface of the mixture. Lead arabate was practically insoluble in water and in oil.

These experiments indicate that although the magnesium and zinc salts of valeric acid yield emulsions of the water-in-oil type, the magnesium and iron salts of arabic acid gave the normal oil-in-water emulsion.

Compounds Related to Arabic Acid as Emulsifying Agents.

Having shown that the divalent and trivalent salts of arabic acid produce emulsions of the oil-in-water type, the next step in experimental work was to select a number of acids of definite structure having hydroxyl groups in the molecule and determine the nature of the emulsions prepared with their divalent salts.

The salts of the following acids were employed:

$OH.CH_2(CH.OH)_4.COOH$

i-Galactonic Acid

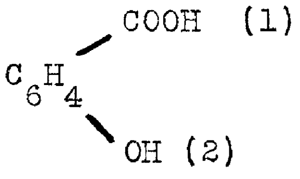
a mixture of d and l-Galactonic acids.

$OH.CH_2(CH.OH)_4.COOH$

d-Gluconic Acid.

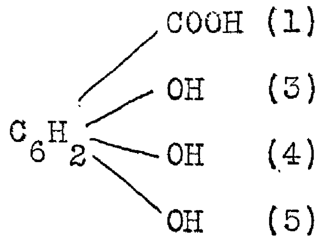
$CH_3(CH_2)_7.\ CH.OH.CH.OH.(CH_2)_7.COOH$

Dihydroxystearic Acid



$$C_6H_4 \begin{cases} COOH\ (1) \\ OH\ (2) \end{cases}$$

Salicylic Acid



Gallic Acid

The sodium salts and also a salt of a divalent metal were prepared from each of these acids and when employed as emulsifying agents the following observations were made.

1. <u>Gluconic Acid.</u> The sodium salt of gluconic acid like the sodium salt of valeric acid produced emulsions with oil of the oil-in-water type. Five grams of the compound were necessary to disperse 10 cc. of oil thru 10 cc. of water, yielding an emulsion which was very viscid yet upon standing for a period of an hour began to separate.

The calcium salt of gluconic acid was treated in the following manner: One gram of the salt was rubbed with 5 cc. of oil, and water was gradually added with brisk trituration. (5 cc. of water in all). An emulsion of the water-in-oil type was obtained. A microscopic examination of the emulsion showed the particles of water to be rather large, yet the emulsion was viscous and stable over a period of several weeks.

Reversing the procedure of mixing and employing the same emulsifying agent, an emulsion was obtained of the oil-in-water type. The particles of oil emulsified were like the particles of the water in the previous experiment, somewhat larger than those found in most emulsions. Upon standing the oil and water separated, but not completely and evidence of an emulsion nucleus remaining permanent was shown by the fact that upon simple agitation, the emulsion was restored to its normal condition. It is of special interest to note the value of viscosity in determining the phases of emulsions of this type; those in which the viscous mineral oil was the external phase were quite viscous, whereas those in which the oil formed the inner phase had a low viscosity.

2. i-Galactonic Acid. The sodium salt of i-galactonic acid, like the sodium salt of gluconic acid, produced dispersions of the oil-in-water type, whereas the cadmium salt of this compound, like the calcium salt of gluconic exhibited the capacity of dispersing oil in water or water in oil. Efforts were made to prepare the aluminum and ferric compounds of gluconic and i-galactonic acids, but neither of these acids would combine with aluminum or trivalent iron.

3. Dioxystearic Acid. Having observed the capacity of each of these acids to form oil-in-water and water-in-oil emulsions, the next compound prepared and studied was dihydroxystearic acid, which has but two hydroxyl groups in a molecule containinf a chain of seventeen carbon atoms. The sodium salt of dihydroxystearic acid produced very stable emulsion of the oil-in-water type, whereas the magnesium salt of this acid produced emulsions of the water-in-oil type. Under no

circumstances was it found possible to prepare emulsions with magnesium dioxystearate of the oil-in-water type. Thus the dihydroxyl acid combined with a divalent metal behaved like a normal stearic acid salt, whereas the polyhydroxyl compounds i-galactonic and gluconic acid showed the unusual property of emulsifying water in oil and also oil in water. .

4. Salicylic Acid. Having observed the influence of hydroxyl groups in the straight chain acids, the next step was to study the influence of the introduction of hydroxyl groups into acids containing cyclic groups. Accordingly sodium salicylate was found to produce emulsions which were unstable, but always of the oil-in-water type. Calcium salicylate on the other hand produced rather stable emulsions of water in oil, although the water particles were quite large. Employing the procedures described under the gluconic acid salts, attempts were made to prepare emulsions of the oil-in-water type and although the particles of oil were exceedingly large and rapidly separated, there is undoubtedly some tendency on the part of calcium salicylate to form emulsions of the oil-in-water type.

5. Gallic Acid. The sodium salt of gallic acid, although a poor emulsifying agent, was shown to invariably produce dispersions of the oil-in-water type. The calcium salt of gallic acid produced rather stable emulsions of the water-in-oil type and also served, to a greater degree than did calcium salicylate, to produce emulsions of the oil-in-water type. From the observations made with gluconic and i-galac-

tonic acids in the form of their divalent salts, this is the behavior that might have been anticipated.

Table I.

Summary of Results.

Emulsifying Agent	Type of Emulsion		
	Oil-in-Water	Amphoteric properties	Water-in-Oil
sodium oleate	x		
magnesium oleate			x
calcium oleate			X
cobaltous oleate			x
nickelous oleate			x
manganese oleate			x
aluminum oleate			x
arabic acid	x		
sodium arabate	x		
magnesium arabate	x		
ferric arabate	x		
ammonium valerate	x		
sodium valerate	x		
magnesium valerate			x
zinc valerate			x
sodium gluconate	x		
calcium gluconate		x	
sodium i-galactonate	x		
cadmium i-galactonate		x	
sodium dihydroxystearate	x		
magnesium dihydroxystearate			x
sodium salicylate	x		
calcium salicylate		x	
sodium gallate	x		
calcium gallate		x	
lead arabate	did not serve as an emulsifying agent.		

Table I indicates that the simple hydrocarbon chain acids when attached to a univalent metal produce emulsions of the oil-in-water type and inverted emulsions when the metallic ion is divalent or trivalent. When, however, polar hydroxyl groups are introduced into the molecule, this condition does not hold as indicated by the character of emulsions prepared with magnesium and ferric arabates and other related compounds.

Throughout this investigation water was employed of definite hydrogen ion concentration P_H 5.8 to 6.4. Having established the character of emulsions produced when the salts of compounds of the nature of arabic acid are employed as emulsifying agents, the next series of investigations was directed to determine the influence of changes of hydrogen ion concentration upon the oil-in-water emulsions when acacia and tragacanth were employed as emulsifying agents.

Method of Study of the Influence of Hydrogen ion Concentration upon Oil-in-Water Emulsions.

Acacia and tragacanth were the two emulsifying agents studied with emulsions of cottonseed and mineral oils (Nujol). Solution of various hydrogen ion concentrations were prepared by mixing standard sodium hydroxide solution and standard hydrochloric acid respectively, with water in various dilutions. The P_H of these solutions was determined by the electrometric method. These solutions served as the diluents in the preparation of 25 per cent emulsions of the oil - the total volume of the emulsion in each case was 40 cc.

In the emulsions made with tragacanth 0.5 Gm. of the tragacanth was employed, whereas 2.5 Gm. of acacia was used in the emulsions prepared with this substance. The emulsions were prepared by trituration in a mortar - mixing the emulsifying agent with the oil and adding the aqueous solutions - as far as possible uniform conditions of temperature, pressure and time of trituration and rapidity of dilution were kept constant.

The finished emulsions were stored at room temperature in small graduated cylinders and their permanence studied. Complete separation of the emulsified portion from the aqueous layer is termed separation, creaming or partial separation, which is easily re-incorporated by simple agitation is not regarded as separation.

Observations upon the Changes of P_H in Oil-in-Water Emulsions.

Table II. Cottonseed Oil Emulsified with Acacia.

No.	pH.	Degree of Separation in cc. in different Time Periods. 1.5 Hours	7 Days	14 Days	22 Days	30 Days	37 Days	50 Days
1	0.4		14	C.S.	C.S.	C.S.	C.S.	C.S.
2	0.9		5	10	10	10	10	10
3	1.4		2	5	5	5	5	5
4	2.0							
5	2.94							
6	3.85							
7	4.45							
8	5.1							
9	6.3							
10	6.9							
11	7.85							
12	8.7							1
13	10.5							3
14	11.8		C.S.	C.S.	C.S.	C.S.	C.S.	C.S.
15	12.5		C.S.	C.S.	C.S.	C.S.	C.S.	C.S.
16	13.2	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.

C.S. = Complete Separation.

After this period there was no change noticed for weeks and the emulsions when discarded months later retained the relationship to permanence as indicated by the table. The creaming effect reached a maximum of 27 cc. in about 22 days. However, as mentioned before this phenomenon was not considered as separation.

Another series of cottonseed oil emulsions with acacia was prepared over approximately the same P_H range, but solutions of slightly different values were employed.

Table III.

Cottonseed Oil Emulsified with Acacia.

Degree of Separation in cc. in Different Time Periods.

No.	pH	1.5 Hr.	12 Hr.	D A Y S									
				2	3	6	9	14	21	29	37	45	63
1	0.6		1	1.5	2	3	3	3	5	6	C.S.	C.S.	C.S.
2	1.05		0.5	1	1	1	1	1	2	4	4	4	4
3	1.6			0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
4	2.65												
5	3.4												
6	4.2												
7	5.2												
8	6.25												
9	7.8												
10	8.5												
11	9.45												
12	10.35												
13	11.8			1	1	2	2	2	5	6	6	7	7
14	12.4		3 cc. yellow	deep yellow	deep yellow 3	deep yellow 3	5	5	7	15	C.S.	C.S.	C.S.
15	13.35	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.

Likewise in this series the creaming effect reached a maximum of 27 cc. in about 22 days.

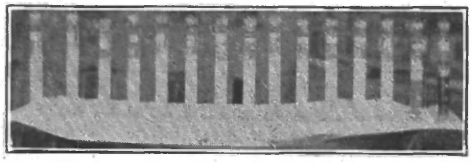


Fig. II.

Cottonseed Oil Emulsions with Acacia from Table IIIafter 37 days. From left to right 1-15.

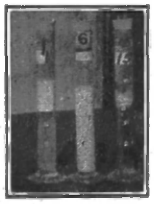


Fig. III.

Cottonseed Oil Emulsions with Acacia from Table IIIshowing #1, #6 and #15 after 37 days.

TABLE IV.

Cottonseed Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods

No.	pH	12 Hrs.	DAYS						
			7	14	22	30	37	50	74
1	0.4		3	5	5	5	5	5	C.S.
2	0.9		0.5	1	2	2	2	2	C.S.
3	1.4		0.5	1	1	1	1	1	1
4	2.0		3	6	9	10	13	13	C.S.
5	2.94		9	17	19	26	27	C.S.	C.S.
6	3.85		1	2	2	2	2	5	C.S.
7	4.45		9	18	26	28	29	C.S.	C.S.
8	5.1		2	3	4	6	8	C.S.	C.S.
9	6.3								1
10	6.9				25	28	29	C.S.	C.S.
11	7.85		6	10	22	24	26	26	C.S.
12	8.7		3	5	9	11	14	C.S.	C.S.
13	10.5		2	4	6	8	10	C.S.	C.S.
14	11.8		yellow	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.
15	12.5	yellow	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.
16	13.2	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.

TABLE V - Cottonseed Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods.

No.	pH	12 Hrs.	DAYS									
			2	5	10	17	25	33	41	58	100	130
1	0.6						2	3	4	5	8	10
2	1.05							1	1.5	2	6	10
3	1.6									1	8	20
4	2.65									5	16	25
5	3.4							2	5	11	17	C.S.
6	4.2					2	3	6	8	11	12	C.S.
7	5.2						2	5	10	15	23	C.S.
8	6.25						1	5	8	11	17	C.S.
9	7.8				1	5	22	30	30	35	35	C.S.
10	8.5					2	4	10	11	16	22	C.S.
11	9.45						3	8	10	16	21	C.S.
12	10.35					7	21	25	26	26	26	C.S.
13	11.8				25	25	25	25	27	27	27	C.S.
14	12.4	light yellow	deeper yellow	deeper yellow	3	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.
15	13.35	deep yellow	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.

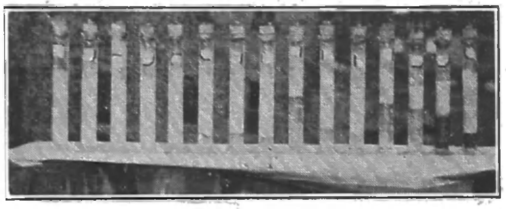


Fig. IV.

Cottonseed Oil Emulsions with Tragacanth
after 41 days from Table V.
From left to right 1-15

Fig. V.

Cottonseed Oil Emulsions with Tragacanth
#2 and #14 after 41 days.

Table VI - Mineral Oil Emulsified with Acacia

Degree of Separation in cc. in Different Time Periods.

No.	pH	3 Hrs.	DAYS										
			1	2	4	7	12	19	27	35	43	60	100
1	0.6			1	2	2	2	3	20	26	27	27	27
2	1.05				1	1	1	2	3	3	3	3	3
3	1.6												
4	2.65												
5	3.4												
6	4.2												
7	5.2												
8	6.25												
9	7.8												
10	8.5												
11	9.45												
12	10.35												
13	11.8									yellow	deeper yellow	deep yellow	deep yellow
14	12.4		1	1	2	25	25	25	26	26	26	26	26
15	13.35	yellow 1.5	deeper yellow 2	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.

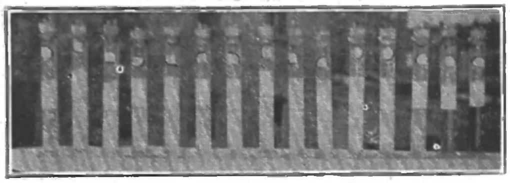


Fig. VI

Mineral Oil Emulsions with Acacia from
table VIafter 35 days.
From left to right No. 1 to 15.

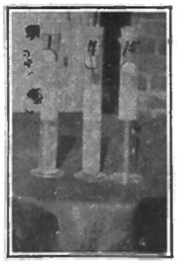


Fig. VII

Mineral Oil Emulsions with Acacia from
table VI- #1, #7 and #15 after
35 days.

Table VII - Mineral Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods.

No.	pH	12 Hrs.	DAYS									
			1	3	6	11	17	25	33	41	60	100
1	0.6				2	4	8	12	18	21	22	22
2	1.05			0.5	5	10	17	21	22	23	24	27
3	1.6								2	2	9	22
4	2.65					1	3	5	8	12	19	25
5	3.4				2	7	12	17	21	22	26	28
6	4.2					2	3	6	10	10	20	26
7	5.2				4	8	11	15	16	17	21	26
8	6.25				1	5	10	18	23	26	28	29
9	7.8				3	6	10	16	21	23	25	28
10	8.5				2	8	11	18	20	21	23	24
11	9.45					10	24	28	30	30	31	38
12	10.35					7	10	16	20	22	25	38
13	11.8				25	25	30	30	30	30	30	30
14	12.4	yellow	deeper yellow 1	deeper yellow 2	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.
15	13.35	deep yellow 2	10	20	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.

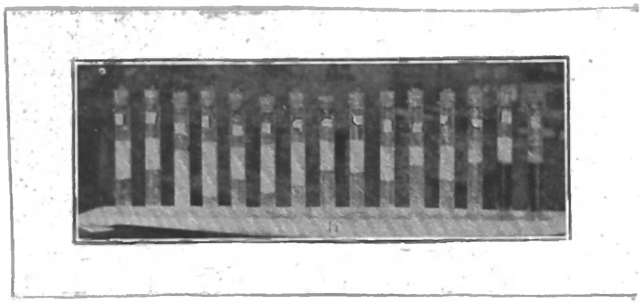


Fig. VIII

Mineral Oil Emulsions with Tragacanth
from Table VIIafter 33 days.
Left to right 1-15.

FIG. IX

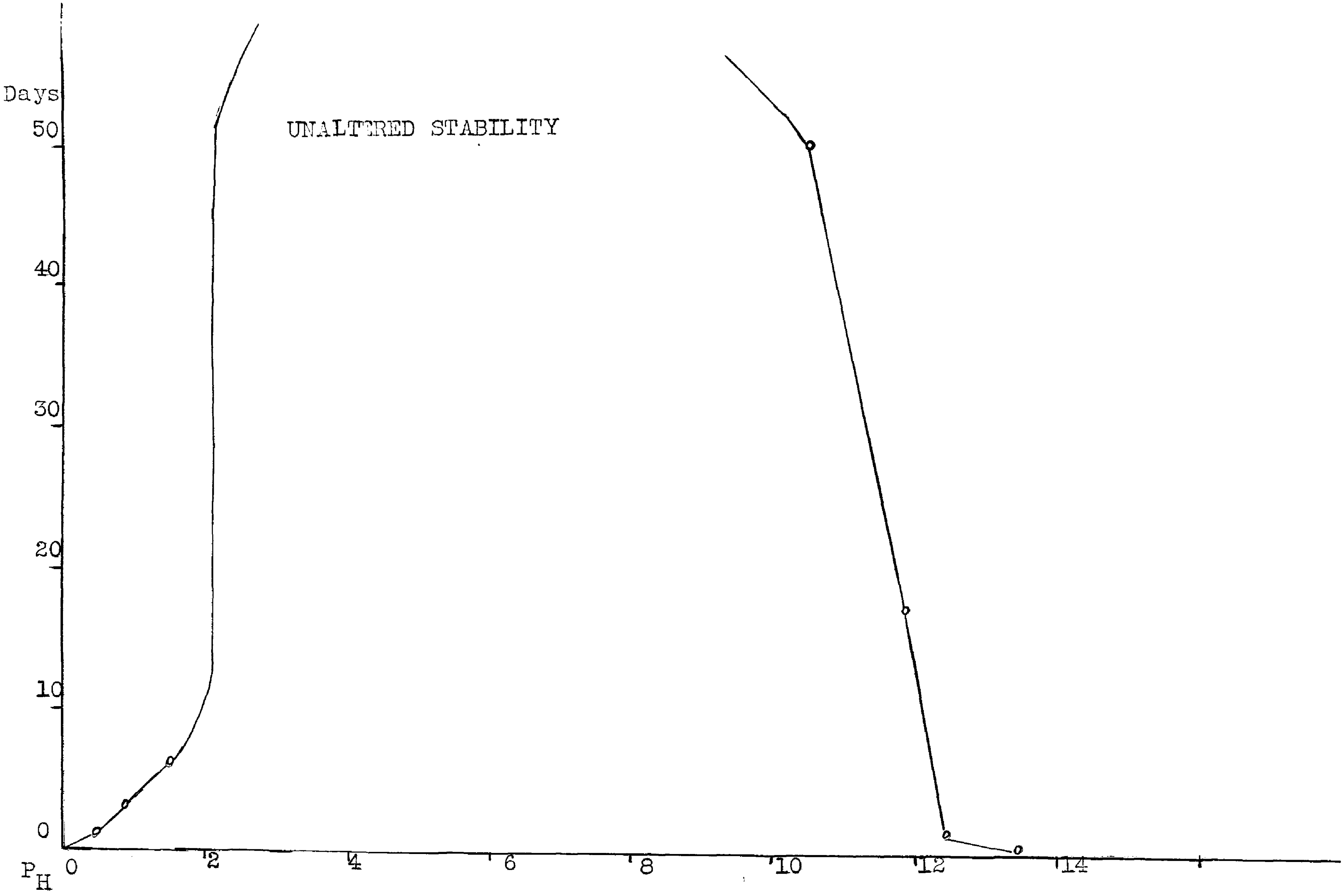
Mineral Oil Emulsions with Tragacanth
from Table VII#3 and #15.

Tables II to VII inclusive indicate that there is a long range of hydrogen ion concentration over which the emulsions made with acacia are stable and further that these results are the same with a vegetable or a mineral oil. With tragacanth the most stable point of hydrogen ion concentration is from P_H 1.8 to 2.3. The average stability of the experiments recorded in tables II to VII can be easily observed from Graphs I and II.

The ordinates of graph II represent the amount of separation per day over a period of 60 days and multiplied by ten to eliminate decimals.

Graph II indicates that over a large range of P_H the stable point is approximately P_H 1.90. With this in mind other series of emulsions were prepared covering the acid range of P_H with smaller variations in order to determine the exact stable point. These results with tragacanth are recorded in Tables VIIIto XIIand the average stability over a period of 20 days is plotted in graph III.

GRAPH NO. 1 - STABILITY OF EMULSIONS WITH ACACIA AND THEIR HYDROGEN ION CONCENTRATIONS



GRAPH NO. 2 - STABILITY OF EMULSIONS WITH TRAGACANTH AND THEIR HYDROGEN ION CONCENTRATIONS

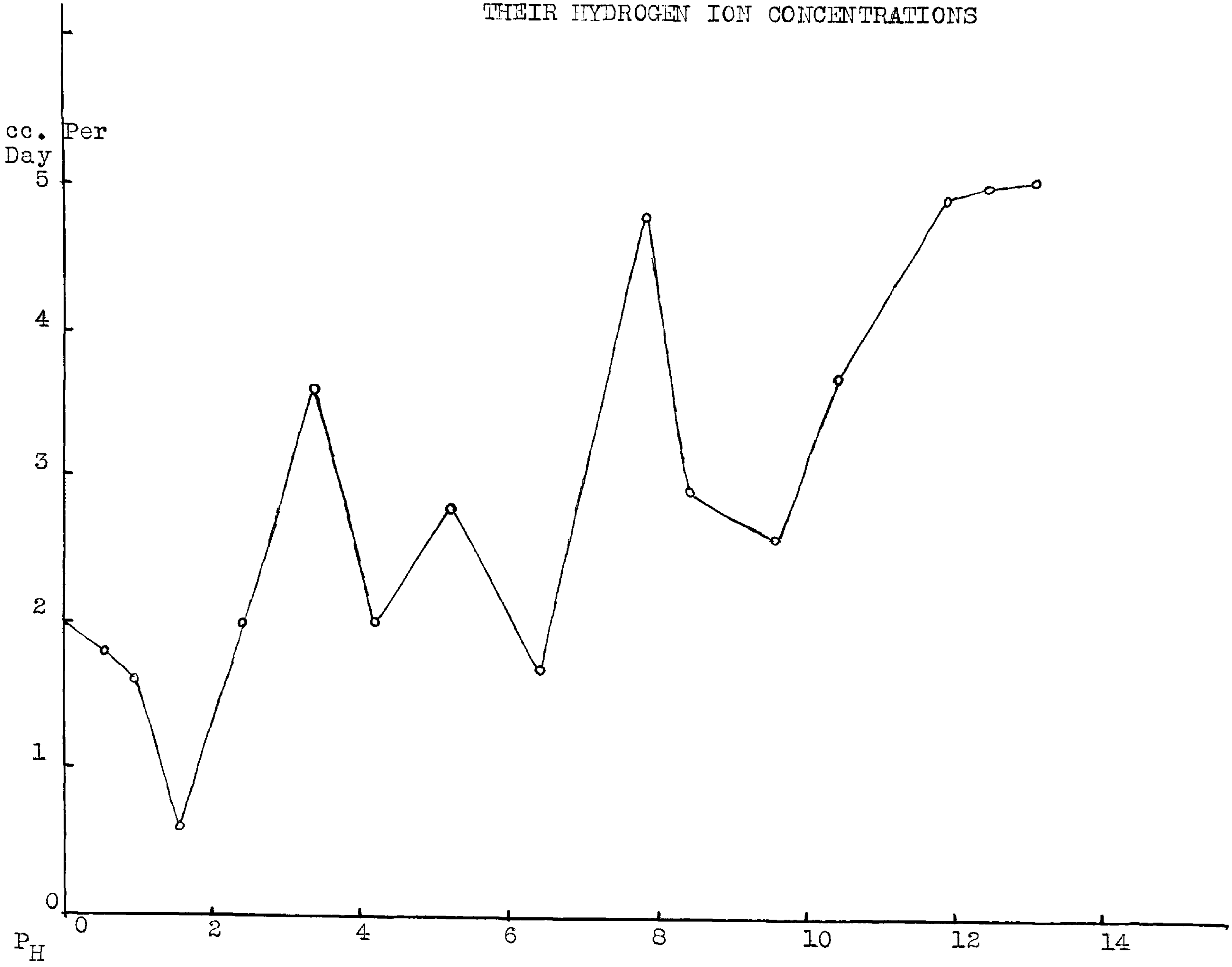


Table VIII

Cottonseed Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods.

No.	P_H	DAYS										
		4	6	8	10	12	14	17	21	25	32	38
1	1	1.5	1.5	1.5	2	2	2	3	4	5	6.5	8
2	1.92						1	2	3.5	5	8	11
3	2.08								0.5	1	2.5	4
4	2.22								1	3	8	13
5	2.4								0.5	1	2	3
6	2.65							1	2	5	11	14
7	2.94			1	1	2	2.5	4	4	5	9	12
8	3.02				0.5	0.5	1	1	2	3	3	5
9	3.15		1.5	3	4	6	7	9	11	13	16	18
10	3.3				1	1.5	2	3	4	6	8	10
11	3.6		2	4	7	9	11	13	17	19	22	23
12	3.7		2.5	4	7	9	11	13	17	19	22	24
13	3.82		3	5	9	12	15	17	20	21	22	23
14	4		3	7	13	17	19	22	23	24	24	25
15	4.1	2	5	9	13	17	19	22	25	26	26	27
16	4.4	1	5	10	15	17	19	21	23	24	25	26
17	4.5	2	8	21	27	28	28	28	29	29	29	29

Table IX

Cottonseed Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods.

No.	P_H	D A Y S										
		4	6	8	10	12	14	17	21	25	32	38
1	1	1	1	2	3	3	3	4	5	6	9	11
2	1.92			0.5	0.5	0.5	1	1.5	3	5	9	13
3	2.08									0.5	1.5	2
4	2.22								1	2	4	6
5	2.4							1	3	6	13	18
6	2.65					0.5	1	2	5	8	13	16
7	2.94		0.5	2	4	5	7	10	15	18	23	24
8	3.02			0.5	1	1	1	2	3	4	6	7
9	3.15					1	1	2	3	4	6	7
10	3.3			1	2	2.5	3	4	6	8	11	14
11	3.6		2	5	9	10	12	15	16	20	23	24
12	3.7		1	3	5	8	10	14	19	22	23	24
13	3.82		2	4	7	9	10	13	17	19	22	23
14	4.0	1.5	5	8	10	12	13	15	18	20	22	23
15	4.1	1	3	5	6	8	10	11	14	17	19	21
16	4.4	2	5	9	11	13	15	17	19	23	25	25
17	4.5	2	5	8	12	15	17	21	24	25	25	26

Table X.

Mineral Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods.

No.	P_H	D A Y S										
		3	5	7	9	11	13	16	20	24	31	37
1	1	1	2	5	9	12	14	14	19	20	22	23
2	1.92						1	1	3	7	14	19
3	2.08				1.5	3	5	10	20	20	27	27
4	2.22					0.5	0.5	1	6	15	24	26
5	2.4					1.5	4	9	17	22	26	27
6	2.65				1	2.5	4	6	11	16	C.S.	C.S.
7	2.94			5	14	19	22	25	25	25	C.S.	C.S.
8	3.02			2	14	19	22	25	28	28	C.S.	C.S.
9	3.15			1	2	3	4	6	9	12	17	19
10	3.3		2	6	14	19	23	23	27	27	C.S.	C.S.
11	3.6		3	11	22	25	26	27	27	27	C.S.	C.S.
12	3.7	1	8	18	22	24	25	25	26	27	C.S.	C.S.
13	3.82		9	13	23	25	26	27	28	28	C.S.	C.S.
14	4.0	2	17	21	24	24	26	27	27	27	C.S.	C.S.
15	4.1		13	23	25	26	26	27	28	28	C.S.	C.S.
16	4.4		4	12	22	26	27	29	29	29	C.S.	C.S.
17	4.5		10	21	25	26	27	28	28	28	C.S.	C.S.

Table XI

Mineral Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods.

No.	P_H	DAYS									
		3	5	7	10	12	14	17	21	25	37.
1	1	1	3	9	15	18	18	21	23	23	C.S.
2	1.92				0.5	1	2	4	13	18	C.S.
3	2.08		0.5	2	4	6	9	12	17	23	C.S.
4	2.22		0.5	2	5	7	10	16	24	25	C.S.
5	2.4			0.5	3	5	8	14	21	25	C.S.
6	2.65			1	4	7	16	22	28	30	C.S.
7	2.94		0.5	2	4	7	11	16	22	25	C.S.
8	3.02		0.5	1.5	3	5	6	8	14	16	C.S.
9	3.15		1	3	4	6	8	10	15	17	C.S.
10	3.3		3	8	21	25	27	28	28	28	C.S.
11	3.6	3	9	15	21	23	25	26	27	27	C.S.
12	3.7	4	10	14	21	21	22	22	23	24	C.S.
13	3.82	4	12	12	21	22	22	24	25	25	C.S.
14	4	5	12	17	21	23	24	24	25	25	C.S.
15	4.1	3	15	22	28	28	29	29	29	29	C.S.
16	4.4	7	14	18	23	25	26	27	28	30	C.S.
17	4.5	5	14	20	25	26	26	27	28	28	C.S.

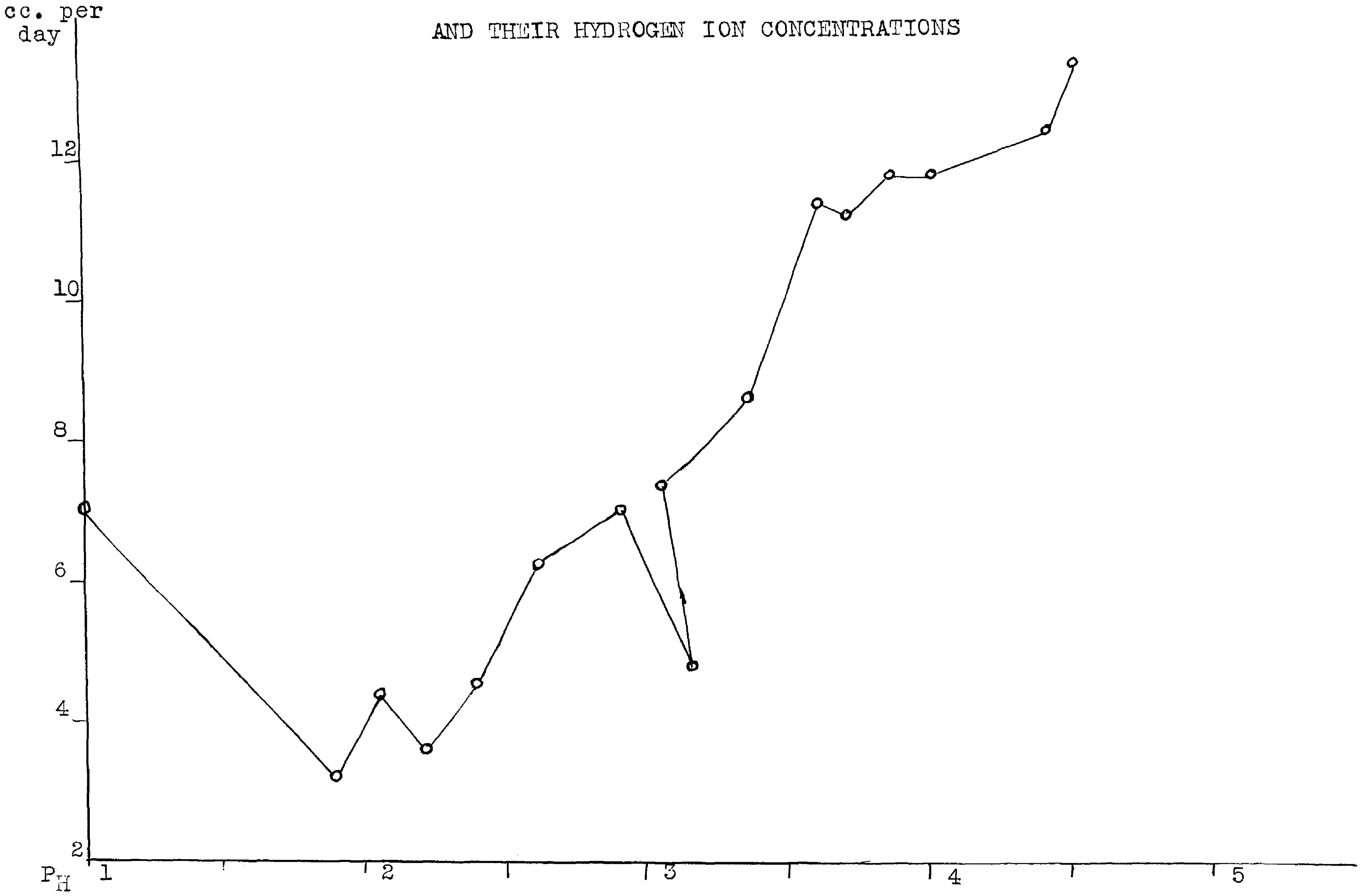
TABLE XII

Mineral Oil Emulsified with Tragacanth

Degree of Separation in cc. in Different Time Periods.

No.	P_H	DAYS								
		5	8	10	12	14	20	24	30	37
1	1	3.5	8	11	13	16	19	20	22	23
2	1.92	1	2	4.5	7	9	9	17	20	22
3	2.08			0.5	1	2	5	12	20	23
4	2.22					2	6	10	16	17
5	2.4					1	2	5	9	12
6	2.65			1	4	8	15	20	25	27
7	2.94					1	2	3	6	8
8	3.02			1	2	3	6	8	12	15
9	3.15		3	3	4	5	9	9	19	23
10	3.3	5	9	9	16	19	22	25	26	C.S.
11	3.6	14	20	23	25	25	27	27	27	C.S.
12	3.7	15	20	24	26	27	27	C.S.	C.S.	C.S.
13	3.82	7	15	22	28	28	28	28	28	C.S.
14	4	9	15	18	22	24	25	25	25	C.S.
15	4.1	9	15	20	24	24	25	25	25	C.S.
16	4.4	9	15	18	20	22	23	24	25	C.S.
17	4.5	10	17	19	21	22	23	24	25	C.S.

GRAPH NO. 3 - STABILITY OF EMULSIONS WITH TRAGACANTH AND THEIR HYDROGEN ION CONCENTRATIONS



The cc. of separation per day was multiplied by ten to construct the ordinates of this graph.

Three series of acacia emulsions were prepared over the same range of hydrogen ion concentration, but little or no variation in their stability was observed. Those prepared with a P_H 1 seemed to separate a creamy layer more readily and ultimately (after about 20 days) separate to the extent of 5 to 10 cc.

The effect of sodium chloride solution in various concentrations upon these emulsions was studied in order to determine the influence of the sodium ion. When studied in concentrations from 1 N. to 10^{-6}N; it was found that none of these concentrations of sodium chloride solution affected the stability of the emulsion. Within 4 or 5 days all emulsions prepared with acacia separated a creamy layer of 25-27 cc. and remained in that condition for more than 150 days, the effect of all concentrations of sodium chloride used showing the same results, as shown by figure X.

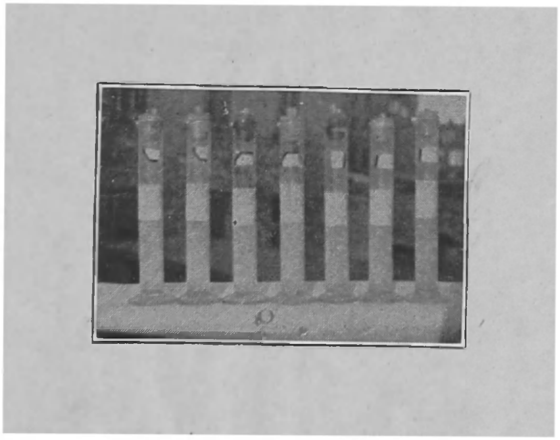


Fig. X

Mineral Oil Emulsions with Acacia and Sodium Chloride Conc. of NaCl left to right 1N. to 10^{-6}N.

The influence of sodium chloride solutions upon tragacanth emulsions of Mineral Oil is shown by the following table:

Table XIII

Mineral Oil Emulsified with Tragacanth in Various Concentrations of Sodium Chloride Solution.

Degree of Separation in cc. in Different Time Periods.

No.	Normality	DAYS						
		5	11	19	27	25	53	100
1	1			3	5	8	10	15
2	0.1			1	2	5	8	10
3	10^{-2}			1	1	2	4	8
4	10^{-3}		1	5	9	15	20	27
5	10^{-4}		1	3	5	8	15	27
6	10^{-5}		10	10	15	17	23	27
7	10^{-6}	10	15	21	23	25	27	27

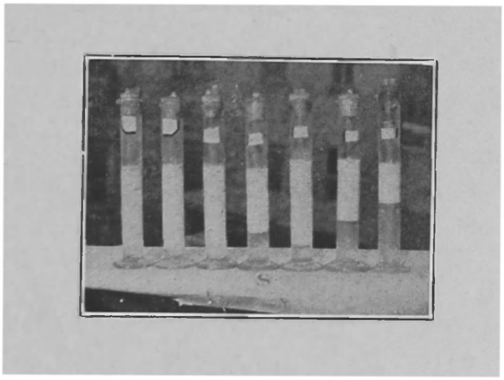


Fig. XI

Mineral Oil Emulsions with Tragacanth from Table XIII after 27 days.

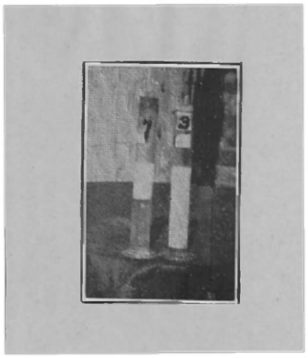


Fig. XII

Mineral Oil Emulsions with Tragacanth and Sodium Chloride, #7 and #3 after 27 days.

In order to study the influence of the hydrogen ion produced from another source, solutions of sulphuric acid were prepared and the same type of emulsions were made from these. With acacia little change was noticed except in the emulsion of a P_H 1.2 where partial separation occurred. The results obtained with tragacanth may be observed from tables 14 and 15 and Graph IV.

Table XIV

Mineral Oil Emulsified with Tragacanth in the Presence of Sulphuric Acid.

Degree of Separation in cc. in Different Time Periods.

No.	P_H	DAYS					
		4	7	11	15	20	26
1	1.2	2	8	15	16	19	20
2	2.05					1	3
3	2.83			2	3	5	7
4	4.1	3	10	16	19	22	24
5	4.45	5	14	22	23	24	25
6	4.94	3	19	25	26	26	27

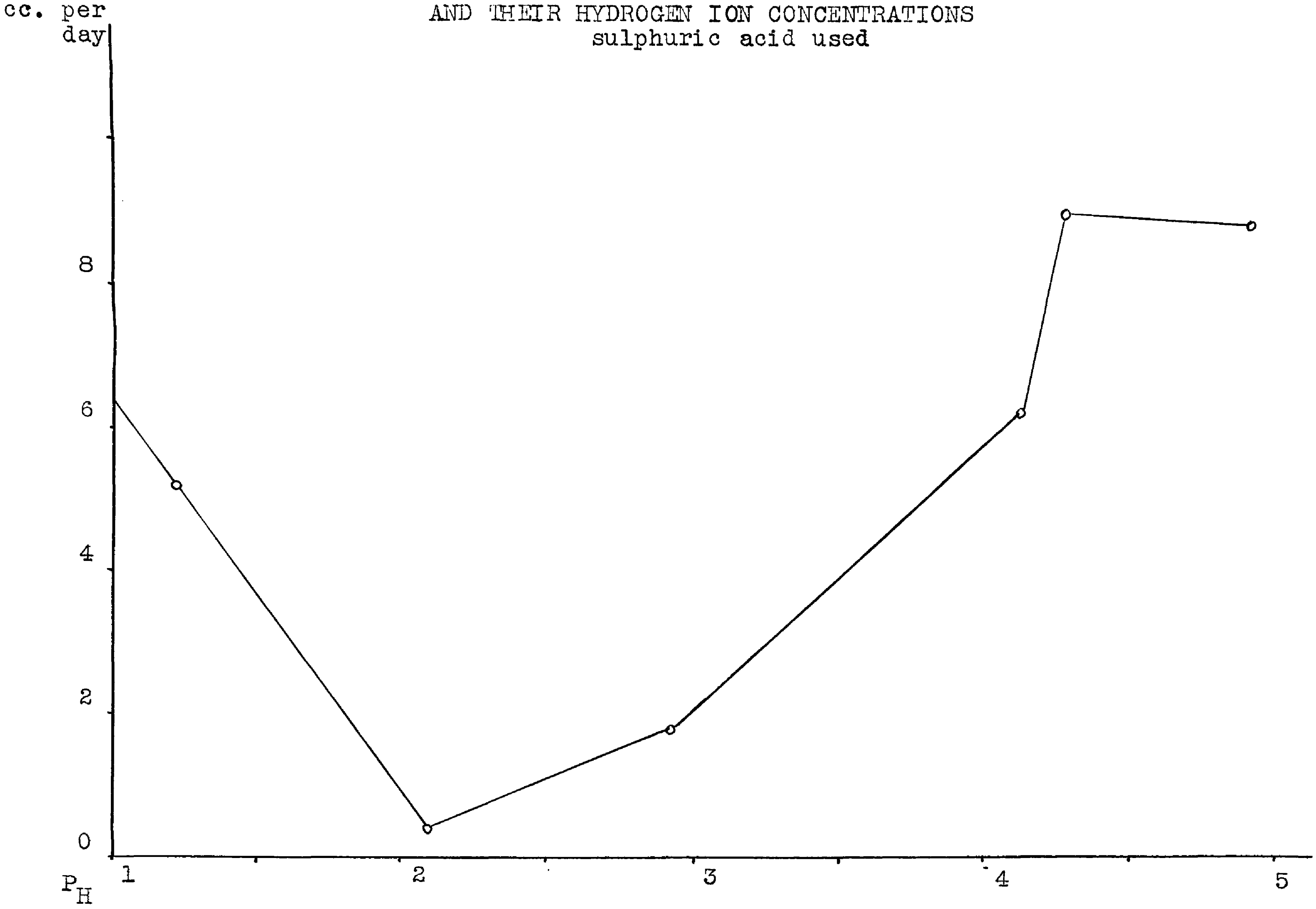
Table XV

Cottonseed Oil Emulsified with Tragacanth in the Presence of Sulphuric Acid.

Degree of Separation in cc. in Different Time Periods.

No.	P_H	DAYS				
		6	10	14	19	27
1	1.2		1	2	2	4
2	2.05					
3	2.83			1	2	6
4	4.1			2	3	6
5	4.45	1	6	10	12	12
6	4.94		3	5	9	10

GRAPH NO. 4 - STABILITY OF EMULSIONS WITH TRAGACANTH AND THEIR HYDROGEN ION CONCENTRATIONS
sulphuric acid used



Study of the Physical Properties of the Emulsions.

Surface Tension.

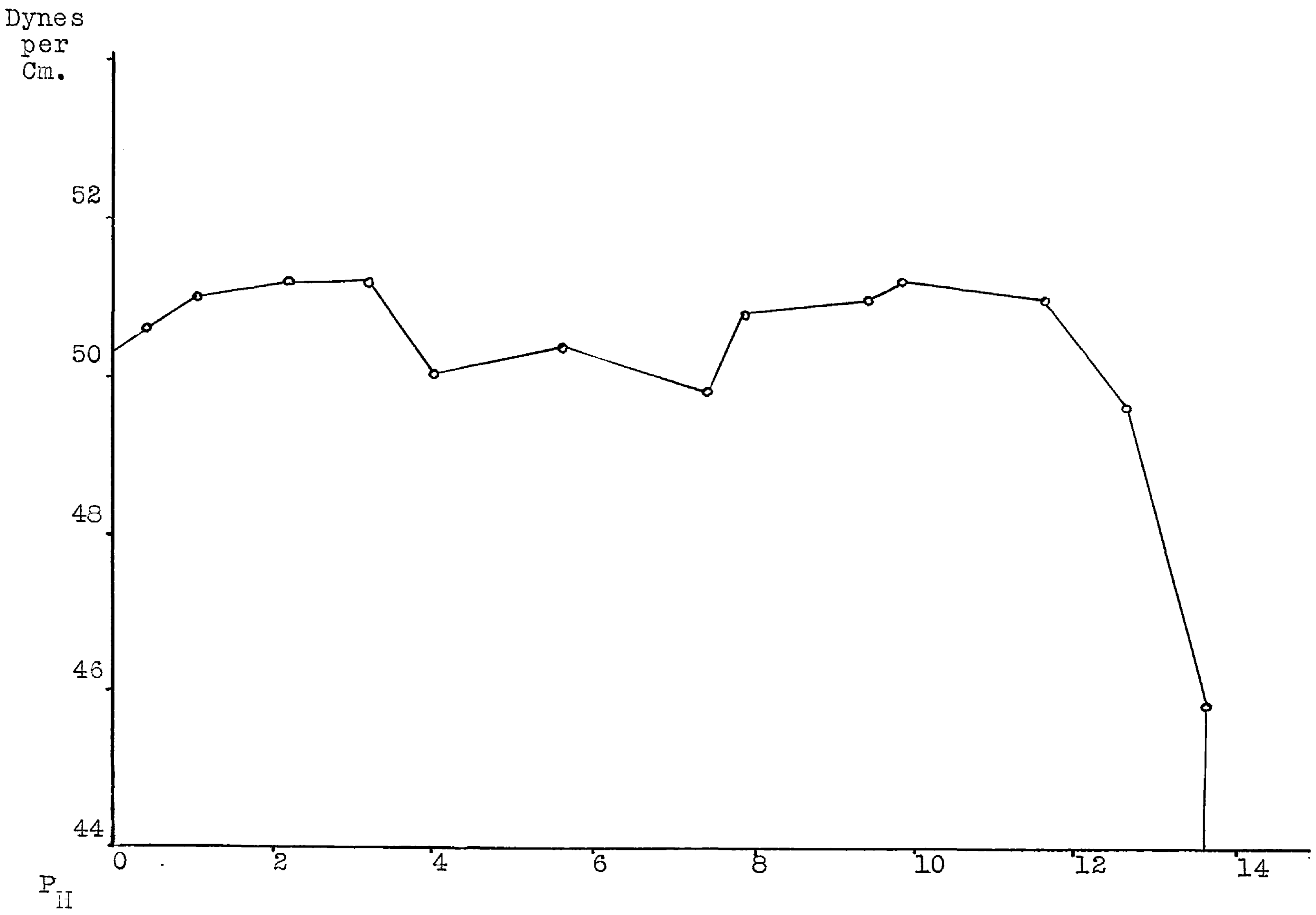
This property was determined at 35° C. with a standardized Du Noüy tensiometer. The results with tragacanth can be seen in Graph V and with acacia in Table 16.

Table XVI

Surface Tension of Emulsions with Acacia at 35° C.

No.	P_H	Dynes per Cm.
1	0.4	54.8
2	1	57.3
3	2.08	62.2
4	3.02	63
5	4	64.8
6	5.6	66.1
7	7.3	66.6
8	7.75	66.2
9	9.2	65.9
10	9.95	64.1
11	11.75	62.3
12	12.25	68.1
13	13.25	59.4

GRAPH NO. 5 - SURFACE TENSION OF EMULSIONS WITH TRAGACANTH and THEIR HYDROGEN ION CONCENTRATIONS.



Interfacial tension.

The interfacial tension was measured at 27° C. by a pipette similar to the one used by Donnan (17) and his students (see figure XIII). The interfacial tension of water was taken as 10 and the following

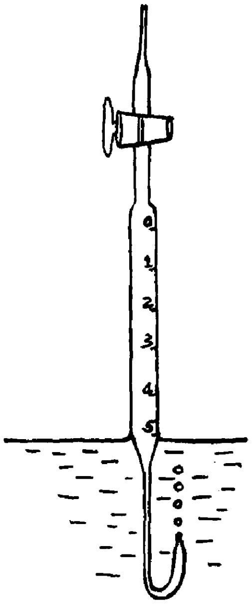


Fig. XIII

formula employed, where T is the interfacial tension, V the volume of oil and N the number of drops.

$$T \propto \frac{V}{N}$$

$$T = K\frac{V}{N}$$

for pure water $10 = \frac{3K}{24}$

and $K = 80$

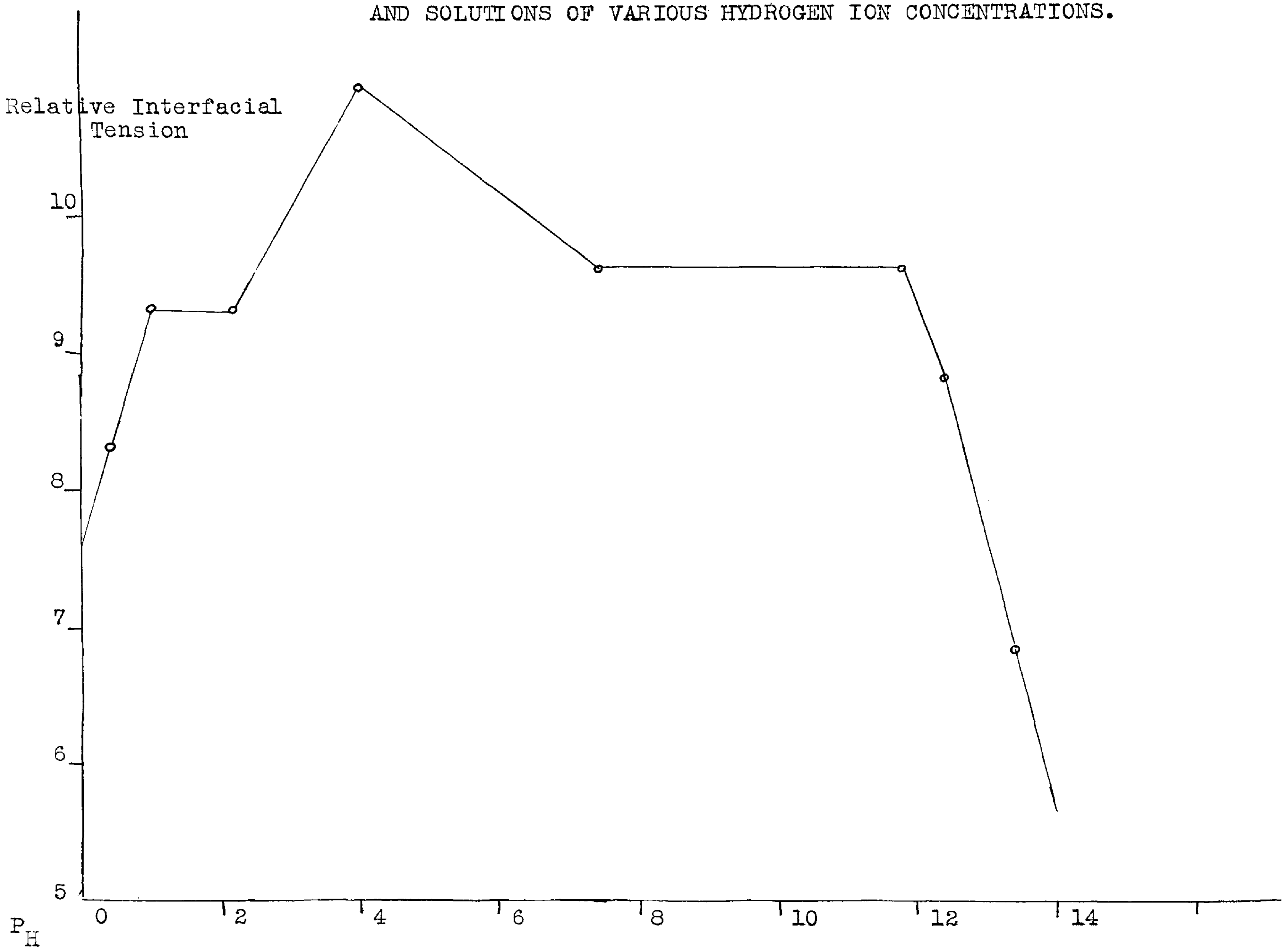
then $T = 80\frac{V}{N}$

The results of these measurements are plotted in Graph VI.

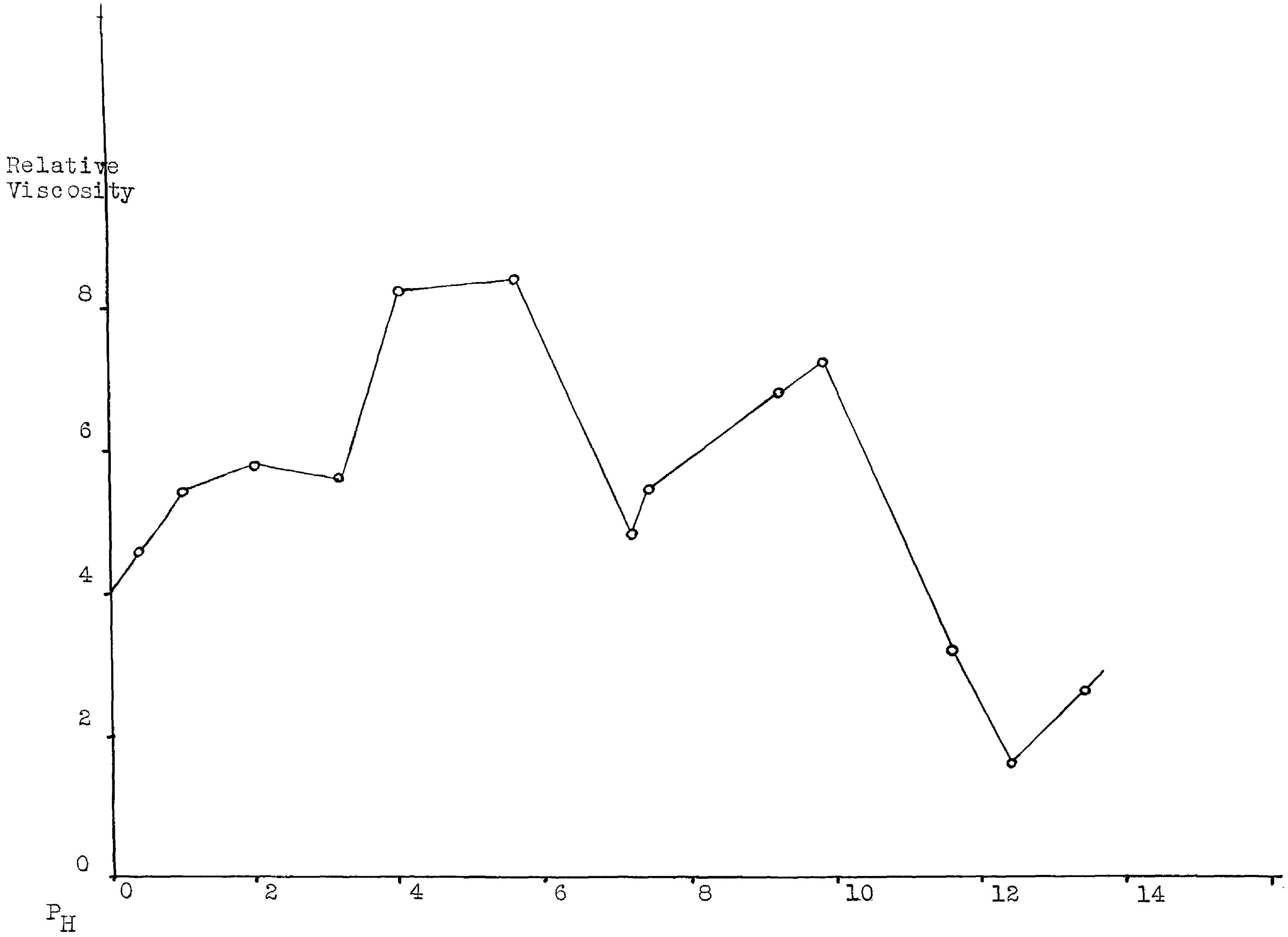
Viscosity.

Using distilled water as a standard at 30° C. the relative viscosities of a series of emulsions were determined by measuring the time in seconds required for a definite volume of the emulsion to run from a pipette with a capillary tip compared with the time required for the flow of the same volume of water. Through the entire range of hydrogen ion concentration the relative viscosity of the acacia emulsions was 1.25. The viscosities of the tragacanth emulsions may be seen in Graph VII.

GRAPH NO. 6 - INTERFACIAL TENSION OF MINERAL OIL AND SOLUTIONS OF VARIOUS HYDROGEN ION CONCENTRATIONS.



GRAPH NO. 7 - EMULSIONS WITH TRAGACANTH, THEIR RELATIVE VISCOSITIES AND THEIR HYDROGEN ION CONCENTRATIONS.



Size of Particle.

Emulsions of Mineral Oil were prepared after coloring the oil with alkanet root and the size of the particles measured microscopically. The results are tabulated in Tables XVII and XVIII.

Table XVII

Mineral Oil Emulsified with Acacia.

No.	P_H	Average Diameter of Particles in Microns					
1	0.4	3	8	10	12	15	18
2	7.3	3	6	9	13	13	13
3	7.75	4	5	10	12	12	12
4	13.25	4	7	13	15	15	15

Table XVIII

No.	P_H	Average Diameter of Particles in Microns			
1	0.4	17	20	25	30
2	1	17	20	25	25
3	5.6	10	17	20	20
4	13.25	40	50	100	110

Gels of tragacanth in water of different hydrogen ion concentrations were prepared and after standing for 3 days figure XIV shows the separation of water at the surface. The gels were prepared by rubbing 0.5 Gm. of tragacanth with 25 cc. of water until gelatinization occurred.

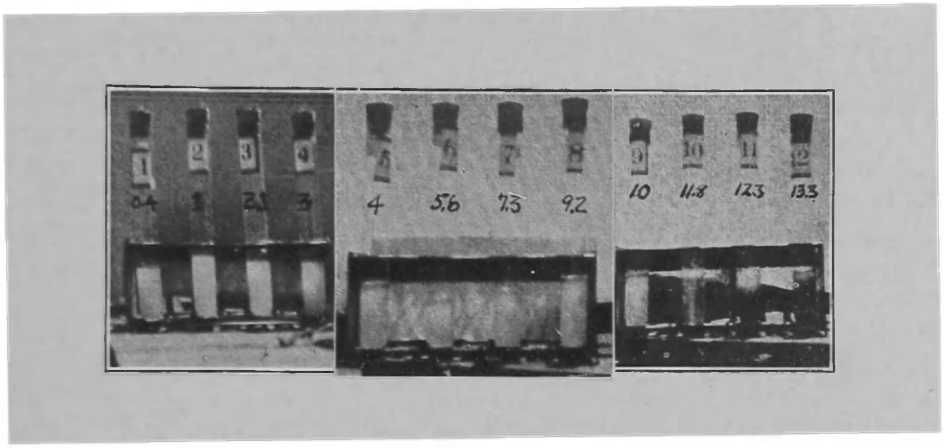


Figure XIV.

Tragacanth Gels.

Lower figures indicate P_H of Gel.

Method of Study of the Influence of Changes of Hydrogen Ion Concentration upon Emulsions of the Water-in-Oil Type.

The emulsions were prepared in quantities of 40 cc. each, emulsifying in each case 10 cc. of the aqueous material, producing a 25 per cent by volume water-in-oil emulsion. Preliminary experimentation with magnesium oleate as an emulsifying agent showed that one gram of the compound was sufficient to emulsify the designated quantity of water. It was further observed that the age of the magnesium oleate influenced its emulsifying capacity. Upon keeping, even in tightly stoppered containers the compound tends to harden and become brittle, in this condition it does not mix readily with the oil and the emulsions formed by using this substance are grandular and unstable. The relative degrees of stability of the emulsions made with freshly precipitated magnesium oleate, and those made with the product which had been kept for six or eight weeks can be observed by studying the following tables of stability.

The aqueous solutions of various hydrogen ion concentrations were prepared as in the foregoing experiments by the additions of various quantities of hydrochloric acid and sodium hydroxide to distilled water. The P_H of these solutions was determined electrometrically. As these unbuffered mixtures, near the neutral point, change in hydrogen ion concentration quite quickly, the emulsions of the mixtures near P_H 7 were prepared as soon as possible after the hydrogen ion concentration measurement.

The emulsification was accomplished by triturating the emulsifying agent with 18 cc. of oil at 25° C. and adding, in one portion the 10 cc. of aqueous fluid. After brisk trituration the formation of the emulsion nucleus could be easily ascertained by the sudden increase in viscousness and the occurrence of a crackling sound when the pestle was pulled through the emulsion. With continued trituration the emulsion nucleus was diluted to the proper volume and stored in dry, well-stoppered graduated containers.

The separation of inverted emulsion must not be mistaken for the gradual settling of the heavier emulsified water to the bottom of the container, for this might easily be incorporated by agitation. When actual separation occurs there appears a clear aqueous fluid at the bottom of the emulsion which cannot be reincorporated by agitation. With certain emulsions of this type, employing freshly precipitated magnesium oleate, the author has observed no separation in a period of eight or ten months. When, however, emulsions are prepared with older samples of the emulsifying agent, the separation begins in a much shorter period of time.

Observations upon the Changes of P_H in Water-in-Oil Emulsions.

TABLE XIX

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil.

Degree of Separation in Different Time Periods.

No.	P_H	1/2 hr.	1 hr.	4 hrs.	DAYS																
					1	3	4	7	11	15	20	28	38	45	52	59	66	73	80	87	94
1	0.9	10	C.S																		
2	1.36	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
3	1.87			5	6	7	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
4	3.05					2	2	3	5	5	5	5	5	5	5	5	5	5	5	5	5
5	3.97					2	3	4	4	4	4	4	5	5	5	5	5	5	5	5	5
6	4.85						1	2	2	2	2	3	4	4	4	4	4	4	5	5	5
7	5.55							1	2	3	3	3	3	3	3	3	3	3	3	3	4
8	7.55							1	2	2	2	3	3	3	3	3	3	3	4	4	4
9	8.02					2	2	3	4	4	4	4	5	5	5	5	5	5	5	5	5
10	9.25					2	2	3	3	4	4	5	5	5	5	5	5	5	5	5	5
11	10.97					3	3	4	5	5	5	5	5	5	5	5	5	5	5	5	5
12	11.75								1	1	1	1	2	2	2	2	2	2	3	3	3
13	12.38																				
14	13.0	yellow	Granular																		

C. S. = Complete Separation

Table XX.

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil.

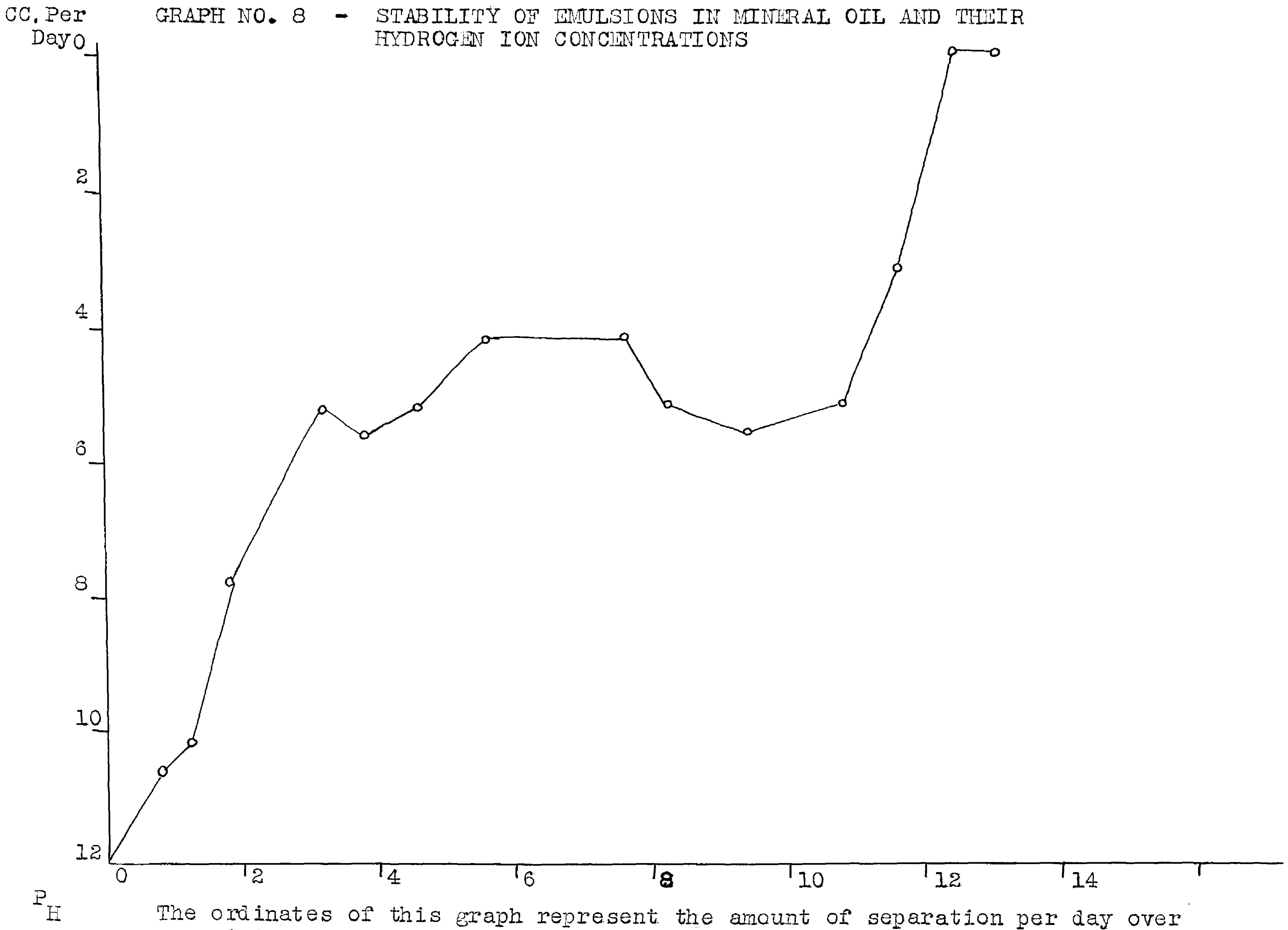
Degree of Separation in cc. in different time periods.

No.	P_H	1/2 hr.	1 hr.	4 hrs.	DAYS																
					1	3	4	7	11	15	20	28	38	45	52	59	66	73	80	87	94
1	0.9	10	C.S																		
2	1.36		8	10	10	C S															
3	1.87			3	5	5	5	6	6	6	6	6	6	6	6	6	6	6	6	7	7
4	3.05					1	1	2	3	3	3	5	5	5	5	5	5	5	5	5	5
5	3.97					4	4	5	5	5	5	5	5	5	5	5	6	6	6	6	6
6	4.85						1	3	3	4	4	4	4	5	5	5	5	5	5	5	5
7	5.55					1	1	2	2	3	3	3	3	4	4	4	4	4	4	4	4
8	7.55					1	1	1	2	2	3	3	4	4	4	4	4	4	4	4	4
9	8.02					2	2	2	3	3	4	4	4	5	5	5	5	5	5	5	5
10	9.25					1	1	2	2	3	3	3	3	4	4	5	5	5	6	6	6
11	10.97					2	2	3	3	4	4	4	4	4	4	4	5	5	5	5	5
12	11.75								2	2	2	2	2	3	3	3	3	3	3	3	3
13	12.38																				
14	13.0	yellow	Granular																		

C.S. = Complete Separation

Tables number XIX and XX indicate that the stable point of these emulsions is near the point P_H 12.38. The magnesium oleate employed in these emulsions had been prepared about fourteen days prior to its use. Graph number VIII shows the average separation of these two series of emulsions over a period of ninety-four days.

GRAPH NO. 8 - STABILITY OF EMULSIONS IN MINERAL OIL AND THEIR HYDROGEN ION CONCENTRATIONS



The ordinates of this graph represent the amount of separation per day over a period of ninety-four days and multiplied by ten to eliminate decimals.

Figure number XV shows the emulsions from table number XIX after thirty days. Reading from left to right these emulsions are numbered as given in table number XIX.

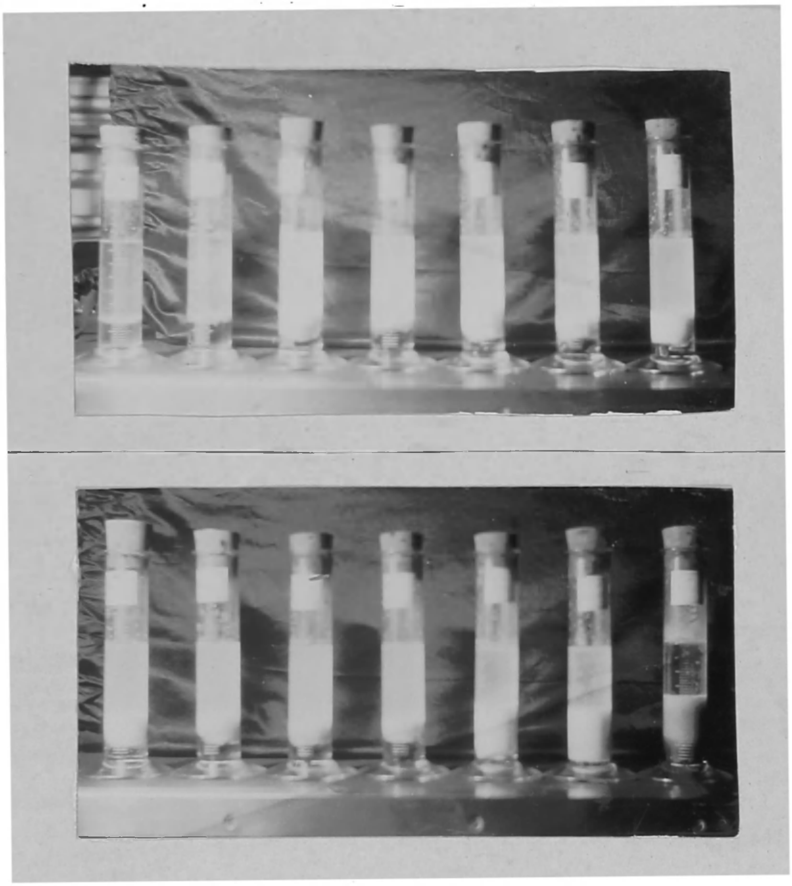


Figure XV.

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil.

With magnesium oleate which was freshly precipitated, as observed with the foregoing experiments, the range of hydrogen ion concentration at which the emulsions are unstable is on the acid side. With the freshly precipitated emulsifying agent practically the entire range of the P_H scale from P_H 1.87 to P_H 12.38 were stable as shown by table number XXI. Yet on the alkaline side of the P_H scale

P_H 10.97, 11.75 and 12.38, the degree of creaming was less than when the internal phase was closer to the neutral point. Table XXI shows the stability of these emulsions over a period of eighty-six days.

Table No. XXI

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil. (Freshly Precipitated Magnesium Oleate)

Degree of Separation in cc. in different time periods.

No.	P_H	1 hr.	DAYS												
			3	7	12	20	30	37	44	51	58	65	72	79	86
1	0.9	8	8	9	9	9	9	9	9	9	9	9	9	9	9
2	1.56		1	1	1	1	1	1	1	1	1	1	1	1	1
3	1.87														
4	3.05														
5	3.97														
6	4.85														
7	5.55														
8	7.5														
9	8.02														
10	9.25														
11	10.97														
12	11.75														
13	12.38														
14	13.0		coarse solid mass												

When olive oil was employed as the external phase, employing the same magnesium oleate that was used in the first series of emulsions, the emulsions as a whole were more permanent. The degrees of separation of this series of emulsions are given in tables XXIIand XXIII and the summary of these results is plotted in Graph IX.

Table XXII

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Olive Oil.

Degree of Separation in cc. in different time periods.

No.	P_H	1/2 hr.	1 hr.	DAYS													
				1	4	12	17	25	35	42	49	56	63	70	77	84	91
1	0.9	10	C.S														
2	1.36		8	10	C.S												
3	1.87			1	2	2	2	2	2	2	2	2	2	2	2	2	2
4	3.05								1	1	1	1	1	1	1	1	1
5	3.97									1	1	1	1	1	1	1	1
6	4.85									1	1	1	1	1	1	1	1
7	5.55									1	1	1	1	1	1	1	1
8	7.55									1	1	1	1	1	1	1	1
9	8.02									1	1	1	1	1	1	1	1
10	9.25									1	1	1	1	1	1	1	1
11	10.97																
12	11.75																
13	12.38																
14	13.0	yellow	yellow					1	6	6	6	6	6	6	6	6	6

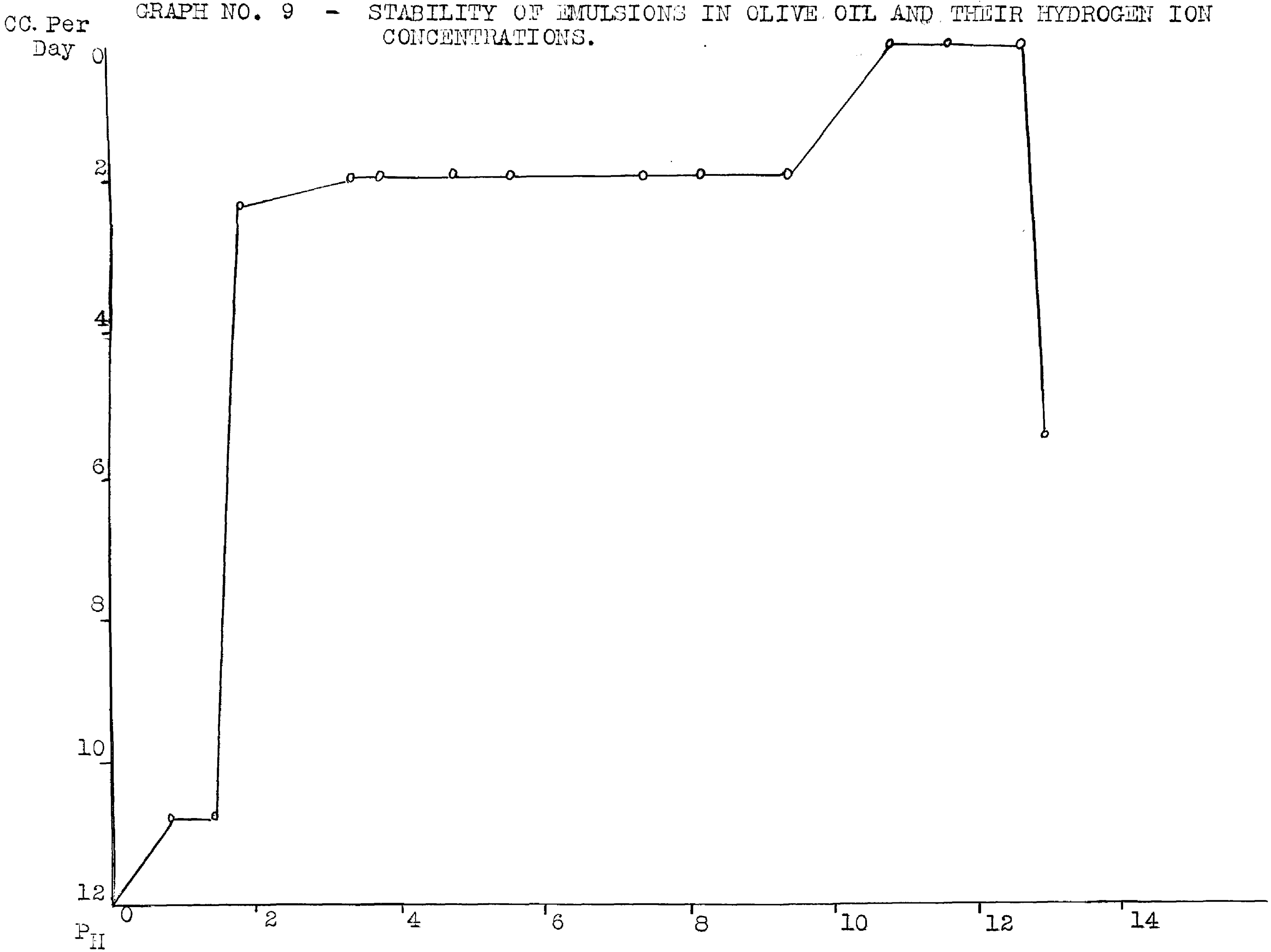
Table No. XXIII

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Olive Oil.

Degree of Separation in cc. in different time periods.

No	P_H	1/2 hr.	1 hr.	DAYS														
				1	4	8	12	17	25	35	42	49	56	63	70	77	84	91
1	0.9	10	C.S															
2	1.36		8	10	C.S													
3	1.87				1	1	1	2	2	2	2	2	2	2	2	2	2	2
4	3.05									1	1	1	1	1	1	1	1	1
5	3.97										1	1	1	1	1	1	1	1
6	4.85										1	1	1	1	1	1	1	1
7	5.55										1	1	1	1	1	1	1	1
8	7.55										1	1	1	1	1	1	1	1
9	8.02										1	1	1	1	1	1	1	1
10	9.25										1	1	1	1	1	1	1	1
11	10.97																	
12	11.75																	
13	12.38																	
14	13.0	yellow	yellow							6	6	6	7	7	7	7	7	7

GRAPH NO. 9 - STABILITY OF EMULSIONS IN OLIVE OIL AND THEIR HYDROGEN ION CONCENTRATIONS.



The ordinates of this graph represent the amount of separation per day over a period of ninety-one days and multiplied by ten to eliminate fractions.

Figure number XVI shows the emulsions made with olive oil after a period of thirty days. Reading from left to right the emulsions are numbered as given in table number XXII.

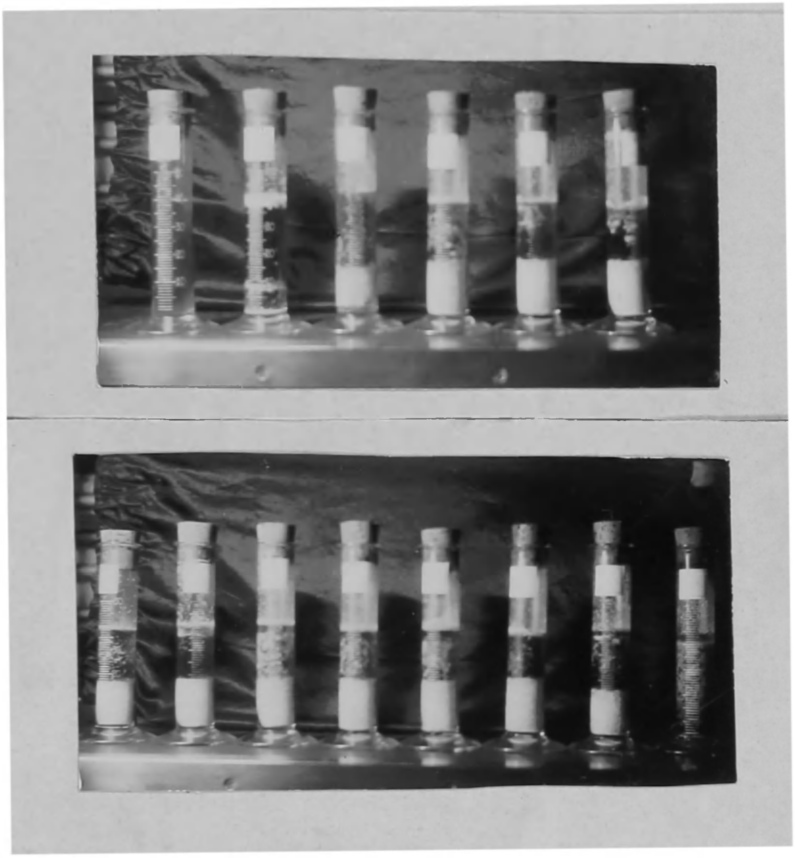


Figure XVI

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Olive Oil.

The effect of sodium chloride solution in various concentration was studied in order to determine the influence of the sodium ion. With solutions of sodium chloride in concentrations 1N. to 10^{-6} N. it was observed that this substance had practically no influence upon the emulsions dispersed in mineral oil.

When olive oil was employed, it was observed that the emulsions exhibited a degree of stability which was inverse to the concentrations of sodium chloride.

The degrees of separation with each of these series of emulsions is shown in tables XXIV and XXV. Figure XVII shows the emulsions in mineral oil after thirty days. Reading from left to right, the emulsions are numbered as given in table XXIV.

Table No. XXIV

Emulsions of Solution of Sodium Chloride in Mineral Oil

Degree of Separation in cc. in different time periods.

No.	Normality	DAYS													
		1	4	9	14	22	32	39	46	53	60	67	74	81	88
1	1					1	1	1	1	1	1	1	1	1	1
2	10^{-1}											no separation			
3	10^{-2}											"		"	
4	10^{-3}											"		"	
5	10^{-4}											"		"	
6	10^{-5}											"		"	
7	10^{-6}											"		"	
8	10^{-7}											"		"	

Table No. XXV.

Emulsions of Solution of Sodium Chloride in Olive Oil.

Degree of separation in cc. in different time periods.

No.	Normality	DAYS										
		1	4	9	14	22	32	39	46	53	60	67
1	1	1	3	3	3	3	3	3	3	3	3	3
2	10^{-1}	1	2	2	2	2	2	2	2	2	2	2
3	10^{-2}	1	1	1	1	1	1	1	1	1	1	1
4	10^{-3}	1	1	1	1	1	1	1	1	1	1	1

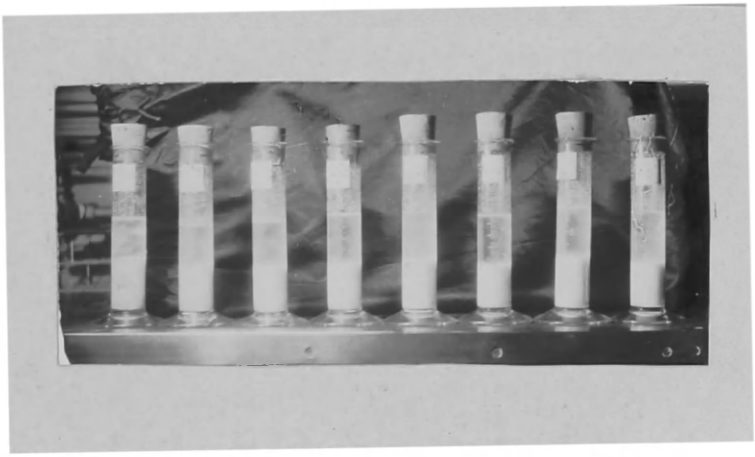


Figure XVII.

Emulsions of Solutions of Sodium Chloride in Mineral Oil.

In order to study the influence of hydrogen ions produced by a source other than hydrochloric acid, solutions of sulphuric acid were prepared, their P_H determined and these were emulsified in mineral oil and olive oil. With olive oil and mineral oil the results were similar to those observed when hydrochloric acid solutions were emulsified. Tables XXVI and XXVII record these results.

Graph number X shows the stability of the sulphuric acid solutions emulsified in mineral oil.

Table No. XXVI

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil.

Degree of Separation in cc. in different time periods.

No.	P_H	1 hr.	2 hrs.	DAYS													
				1	4	9	14	22	32	39	46	53	60	67	74	81	88
1	1.04	10	C.S														
2	1.51	4	6	6	6	6	6	6	6	6	6	7	7	7	7	7	7
3	2.17				1	1	1	1	1	1	1	1	1	1	1	1	1
4	3.06													no separation			
5	4.21													"		"	
6	4.86													"		"	

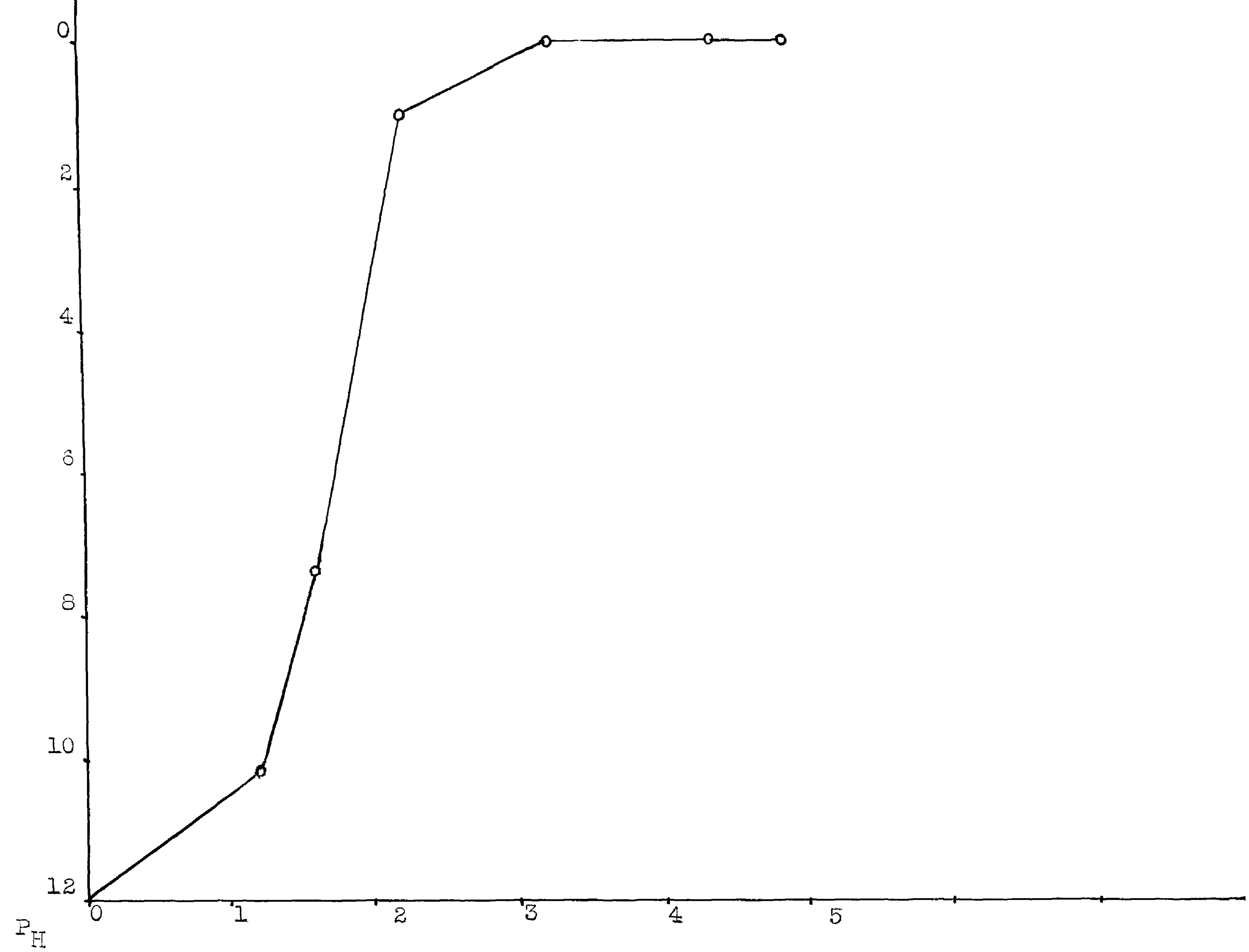
Table No. XXVII

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Olive Oil.

Degree of separation in cc. in different time periods.

No.	P_H	1/2 hr.	DAYS												
			1	4	9	17	27	34	41	48	55	67	69	76	83
1	1.04	8	8	8	8	9	9	10	C.S						
2	1.51	6	7	7	7	7	7	7	7	7	7	7	7	7	7
3	2.17		2	2	3	3	3	3	3	3	3	3	3	3	3
4	3.06		2	2	3	3	3	3	3	3	3	3	3	3	3
5	4.21		1	1	1	1	2	2	2	2	2	2	2	2	2
6	4.86		1	1	1	1	1	1	1	2	2	2	2	2	2

GRAPH NO. 10 – STABILITY OF EMULSIONS OF SOLUTIONS OF VARIOUS HYDROGEN ION CONCENTRATIONS IN MINERAL OIL (H_2SO_4)



In order to determine within a closer range the hydrogen ion concentration at which the range of instability on the acid side begins, the following series of emulsions were prepared using mineral oil as the external phase. Tables XXVIII and XXIX show the degree of separation of these emulsions over a period of eighty three days and figure XVIII shows the emulsions listed in table XXIX after thirty days. Reading from left to right the emulsions in figure XVIII are numbered as given in table XXIX.

Table No. XXVIII.

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil.

Degree of Separation in cc. in different time periods.

No.	P_H	1/2 hr.	DAYS											
			4	9	17	27	34	41	48	55	62	69	76	83
1	0.9	5	10	C.S										
2	1.36	2.5	3	3	3	3	3	3	3	3	3	3	3	3
3	1.87				1	1	1	1	1	1	1	1	1	1
4	2.17								1	1	1	1	1	1
5	3.05													

Table No. XXIX

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil.

Degree of Separation in cc. in different time periods.

No.	P_H	1/2 hr.	DAYS											
			4	9	17	27	34	41	48	55	62	69	76	83
1	0.9	5	9	9	9	9	9	9	9	9	9	9	9	9
2	1.36	1	1	1	1	1	1	1	1	1	1	1	1	1
3	1.87			1	2	2	2	2	2	2	2	2	2	2
4	2.17													
5	3.05													

Figure XVIII

Emulsions of Solutions of Various Hydrogen Ion Concentrations in Mineral Oil.

Study of the Physical Properties of Emulsions Water-in-Oil Type.

Surface Tension - The surface tensions of the various emulsions of solutions of different hydrogen ion concentrations in mineral oil were measured at 20° C. with a standardized DuNoüy tensiometer. The results of these measurements are tabulated in table XXX.

Table XXX.

Surface Tension of Emulsions in Mineral Oil at 20° C.

No.	P_H	Dynes per cm.
1	Mineral Oil	35.62
2	0.9	36.33
3	1.87	37.08
4	3.97	36.81
5	7.55	36.81
6	9.25	36.43
7	10.97	36.60
8	11.75	37.08
9	13.0	36.64

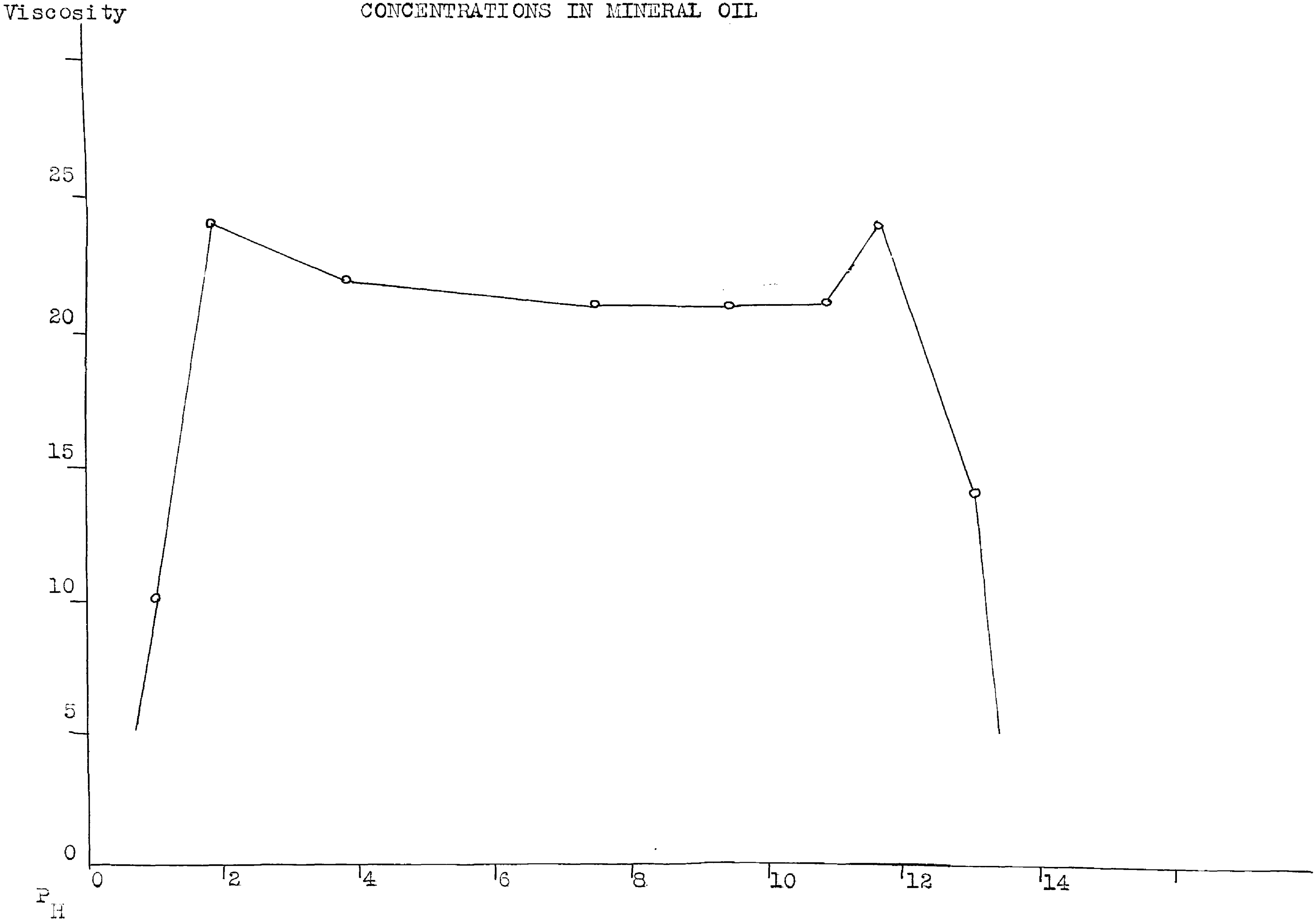
Viscosity - Using the external phase, mineral oil, as a standard at 20° C., the relative viscosities of a series of emulsions were determined by the method previously described. The relative viscosities of these emulsions showed little variation except on the extreme acid and alkaline side of the P_H range. The results of these measurements are tabulated in table XXI and plotted in graph XI.

Table XXXI

Relative Viscosities of Emulsions in Mineral Oil
at 20° C.

No.	P_H	Relative Viscosities
1	Mineral Oil	243 sec. unity
2	0.9	0.106
3	1.87	0.242
4	3.97	0.224
5	7.55	0.219
6	9.25	0.214
7	10.97	0.214
8	11.75	0.245
9	13.0	0.144

GRAPH NO. 11 - RELATIVE VISCOSITY OF SOLUTIONS OF VARIOUS HYDROGEN ION CONCENTRATIONS IN MINERAL OIL



Size of Particle - Emulsions of solutions of various hydrogen ion concentrations (colored with a water-soluble dye) were prepared using mineral oil as the external phase. The size of the particles was measured microscopically. The results of these measurements are given in table XXXII.

Table XXXII.

No.	P_H	Average diameter of particles in microns
1	0.9	38.9
2	1.87	21.2
3	3.97	20.6
4	7.55	17.7
5	9.25	22.4
6	10.97	17.7
7	11.75	30.0
8	13.0	30.0

Summary of Results and Theoretical Considerations.

Emulsifying Agents - With mineral oil, similar to Harkins' observation with benzene; magnesium, calcium, cobaltous, nickelous, manganous and aluminum oleates produce emulsions of the water-in-oil type. With valeric acid similar to Harkins' and Newman's observations with oleic acid, the univalent salts produce oil-in-water emulsions, whereas the salts of divalent metals produce water-in-oil emulsions. The salts of arabic acid produce oil-in-water emulsions irrespective of the valence of the metallic atom in combination. Having demonstrated the amphoteric emulsion characteristic of the divalent salts of acids, in which there are several hydroxyl groups, it is entirely possible that for this reason acacia always tends to produce an oil-in-water emulsion. According to the observations made with the divalent salts of l-galactonic and gluconic acids it is likely that the presence of hydroxyl groups in the molecule of arabic acid in addition to the fact that acacia contains some univalent salts of arabic acid, are responsible for its invariably producing emulsions of the oil-in-water type. As the gum tragacanth is essentially the calcium salt of bassoric acid and produces emulsions of the oil-in-water type, it is likely that this condition exists for reasons similar to those proposed for the salts of arabic acid.

According to the postulates of Harkins and his associates, when the cross-section of the hydrocarbon chain of an emulsifying agent and the metallic end are of the same magnitude, there is little or no tendency to curvature and hence no stable emulsion will result. With univalent salts of these acids containing hydroxyl groups the packing of the emulsifying agent molecules need not be altered because the polar metallic atoms and also the hydroxyl groups dip into the water. When, however, these compounds are attached to a divalent metal, the hydroxyl groups so increase the magnitude of the hydrocarbon chain that there is little tendency to curvature and the emulsions obtained are not very stable. It is possible that the presence of so many polar hydroxyl groups in the molecule makes the production of emulsions of either the oil-in-water type or the water-in-oil type possible.

It is interesting to note that Weston,(18) working with colloidal clays, observed that these substances would produce emulsions of the oil-in-water or water-in-oil type.

Influences of Changes in P_H upon Oil-in-Water Emulsions.

The data and graphs correlating the results obtained indicate that vegetable and mineral oil emulsions prepared with acacia are stable over a hydrogen ion concentration varying from P_H 2 to P_H 10. The presence of alkalies is especially detrimental to the stability of these emulsions. Emulsions with acacia at various hydrogen ion concentrations show little change in their surface tensions and their relative viscosities are identical. The size of the particles in the acacia emulsions are far more uniform and smaller than those of the tragacanth emulsions and on the acid and alkaline side of the P_H scale there is a slight increase in the size of the particle. This is exactly what one would expect as at these points also the smallest degree of stability was observed. Microscopically it was observed that this increase in the size of the particle is due to coalescence, preliminary to separation.

The emulsions prepared with tragacanth are especially stable at P_H 1.9 to P_H 2.3 and quickly separate on the alkaline side of the P_H scale. Examination of Graph number IV indicates that this range of hydrogen ion concentration does not change when the acidity is produced by sulphuric acid instead of hydrochloric acid. We cannot, however, consider this as a specific effect of the hydrogen ion alone for sodium chloride produces a similar stability when the sodium ion concentration is about 10^{-2}N. as observed in figure XI.

A study of Graph number VII indicates that there is a considerable drop in viscosity with an increase of hydroxyl ion concentration, which is characteristic of most mucilaginous material, namely, that the presence of alkali reduces the viscosity of the gel. There was no change in viscosity in the emulsions prepared with acacia.

The author feels that a maximum viscosity is not desirable as indicated by graph number VII, but an optimum relative viscosity which is found to be between 4 and 6; Holmes and Child (19) working with gelatin solutions support this view.

It seems that in tragacanth emulsions, as observed by other investigators in other fields, that viscosity aids emulsification solely by virtue of the hindrance offered to agglutination of the oil particles.

Graph V shows that those emulsions prepared with tragacanth decrease in surface tension toward the alkaline side of the P_H scale. The author, however, does not consider the phenomenon of surface tension of paramount importance in view of the postulates of Langmuir (20) who states that similar liquids may have the same surface tension against air, owing to the fact that in their surface layer similar groups or atoms may be similarly oriented.

The interfacial tension of the two liquids has been used by some as a measure of the emulsifying power of one liquid upon another. Accordingly this measurement was attempted between mineral oil and tragacanth gels of various hydrogen ion concentrations. Invariably a steady stream was obtained instead of drops as was obtained by Donnan (21) with solutions of the sodium salts of certain high molecular weight fatty acids. The interfacial tension of mineral oil and solutions of various hydrogen ion concentrations as plotted in graph VI show that the alkaline solutions reduce the interfacial tension which should increase the power of emulsification, were the emulsifying agent not affected. It is concluded therefore that the changes in hydrogen ion concentration influence the permanency of the gel and thus affect the stability of the emulsion.

A close examination of figure XIV will show that only those tragacanth gels between P_H 0.4 and 2.1 remain free from the separation of water at the surface, or in other words the liquids between P_H 1 and 2.1 prepare the most stable gels with tragacanth; it will be recalled that the stable range of P_H for emulsions made with tragacanth practically lies within this scale. This supports Fischer's (22) Hydrate theory of emulsification, which postulates that oil is most permanently emulsified in a hydrophile colloid when just a sufficient amount of water is present to form a hydrate. It is believed that with tragacanth this amount of water is a function of its hydrogen ion concentration; therefore at the range of the P_H scale where tragacanth shows itself to possess the highest degree of hydratability, this range is the stable point for emulsions prepared with this colloid.

Influences of Changes in P_H upon Water-in-Oil Emulsions.

A study of the graphs showing the stability of the emulsions in mineral oil and olive oil (graphs VIII and IX) indicate that the most stable range of hydrogen ion concentration for the internal phase of these emulsions lies well on the alkaline side of the P_H scale. The P_H range at which the emulsions were most stable was between 11 and 12.5. From P_H 11 to P_H 2.5 there is a range of moderate stability, whereas from P_H 2.5 to P_H 0.9 may be looked upon as the range of extreme instability. With freshly precipitated magnesium oleate there is little or no separation from P_H 2.5 to 11 but the field of instability is on the acid side of P_H 2.5 and the maximum point of stability lies between P_H 11 and 12.5.

With mineral oil and olive oil the similar observations were made if the hydrogen ion concentration was produced by the addition of sulphuric acid indicating that the instability was due to the presence of a high hydrogen ion concentration. When various concentrations of solutions of sodium chloride were emulsified, there was no influence in stability as far as emulsions in mineral oil were concerned, but with those dispersed in olive oil the instability of the emulsions increased with the increase of concentration of sodium chloride in the dispersed phase.

A study of the physical properties of the emulsions shows that as far as surface tension is concerned (table XXX) there is no significant difference in any of the emulsions. Viscosity measurements show (table XXXI) that the emulsions of liquids of various hydrogen ion concentrations in mineral oil are far less viscous than the external phase alone. On the extreme acid and alkaline sides of the P_H scale (P_H 0.9 and P_H 13) there was a marked drop in viscosity. It is of interest to note that these emulsions of extreme low viscosity were those which were least stable.

The size of the particles of the emulsions in mineral oil increased on the alkaline side of the P_H scale without any appreciable influence upon stability, the unstable emulsion of an internal phase of P_H 0.9 had particles which were larger than those in any of the other emulsions. A careful microscopic study of the size of the particles in relation to stability showed that in emulsions, when the average size of the particles was between 17 and 30 microns, there was no influence in stability, particles above 30 microns (average size) tend to coalesce and separate as a layer beneath.

It is likely that the most important factor in the determining of the stability of these emulsions is the influence of the hydrogen ion concentration of the dispersed phase upon the magnesium oleate. The magnesium atoms dip down into the aqueous particles and when the hydrogen ion concentration of the aqueous phase is high enough P_H 2.5, there is a gradual decomposition of the emulsifying agent which results ultimately in the disintegration of the emulsion.

Conclusions.

1. The character of emulsions produced by several oleates, certain univalent and divalent salts of arabic acid and some related compounds has been studied. An explanation for the invariable oil-in-water nature of emulsions prepared with acacia and tragacanth has been proposed.

2. The range of greatest stability for either vegetable or mineral oil emulsions prepared with acacia lies between P_H 2 to 10 and with tragacanth the range is P_H 1.9 to 2.3.

3. The size of the particles, surface tension, interfacial tensions and viscosity have been determined at various points on the P_H scale. Changes in particle size and viscosity is caused by changing the hydrogen ion concentration of emulsions prepared with tragacanth. The viscosities of acacia emulsions are not altered by changing the P_H, the size of the particle, however, increases on the alkaline size of the P_H scale.

4. Fischer's Hydrate theory is substantiated in emulsions prepared with tragacanth.

5. With water-in-oil emulsions prepared with magnesium oleate, olive oil is found to be a more stable dispersion phase than mineral oil. The most stable range of hydrogen ion concentration was found to be between P_H 11 and 12.5. With a hydrogen ion concentration more acidic than P_H 2.5, extreme instability was observed.

6. With emulsions of the water-in-oil type changes in P_H of

the inner phase did not affect the surface tension, the unstable emulsions had a lower viscosity than the stable ones and the size of the particles does not alter the stability up to 30 microns average size.

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