SCIENTIFIC SECTION

THE EFFECT OF HYDROGEN-ION CONCENTRATION UPON EMULSIONS.*

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INTRODUCTION.

Since the recent publication of Clayton's Monograph (1) on Emulsions, the attention of the pharmacist and physical chemist has been brought very definitely to this comparatively virgin field of investigation.

Although pharmacists for years have considered the presence of acids detrimental to the stability of emulsions, whereas alkalis 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 hydrogen-ion concentration upon emulsions. 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.

Aside from the before-mentioned practical applications of this problem, it is extremely interesting from a purely scientific point of view to determine the influence of hydrogen-ion concentration upon emulsification and emulsions, as this factor has played an important role in other chemical and physical problems. These facts were the salient points which prompted the investigation of this problem.

METHOD OF STUDY.

Acacia and tragacanth were the two emulsifying agents studied with emulsions of cottonseed and heavy liquid petrolatum (Nujol). Solutions of various hydrogen-ion concentrations were prepared by mixing normal sodium hydroxide solution and normal 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% 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.

* Read before Scientific Section, A. PH. A., Des Moines meeting, 1925.

[1] A portion of the thesis submitted by the first author to the graduate faculty of the University of Maryland in partial fulfilment of the requirements for the degree of doctor of philosophy.

RESULTS.

TABLE I.—COTTONSEED OIL EMULSIFIED WITH ACACIA.

Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	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 range of p_H but solutions of slightly different values were employed.

TABLE II.—COTTONSEED OIL EMULSIFIED WITH ACACIA.

Degree of Separation in Cc. in Different Time Periods.

				Days.									
No.	p_H.	1.5 Hr.	12 Hr.	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
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 3	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.

TABLE III.—COTTONSEED OIL EMULSIFIED WITH TRAGACANTH.

Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	12 Hrs.	7 Days.	14 Days.	22 Days.	30 Days.	37 Days.	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.

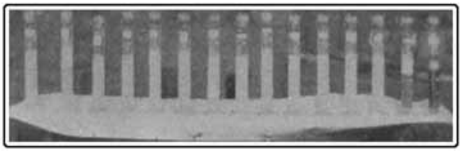


Fig. 1.—Cottonseed Oil Emulsions with Acacia from Table II after 37 days. From left to right 1–15.

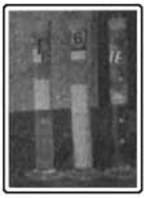


Fig. 2.—Cottonseed Oil Emulsions with Acacia from Table II showing #1, #6 and #15, after 37 days.

TABLE IV.—COTTONSEED OIL EMULSIFIED WITH TRAGACANTH.

Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	12 Hrs.	2 days.	5.	10.	17.	25.	Days. 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 cc.	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 cc.	21	25	26	26	26	C. S.
13	11.8	..	..	..	25 cc.	25 cc.	25	25	27	27	27	C. S.
14	12.4	light yellow	deeper yellow	deeper yellow	3 cc.	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.

TABLE V.—NUJOL EMULSIFIED WITH ACACIA.

Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	3 Hrs.	1.	2.	4.	7.	12.	Days. 19.	27.	35.	43.	60.	100.
1	0.6	..	..	1	2	2	2	3	20	26	27	27	27
2	1.05	..	..	..	1	1	2	2	3	3	3	3	3
3	1.6	..	..	..	..	..	..	..	..	..	..	..	..

TABLE V.—(*Continued*).

No.	p_H.	3 Hrs.	Days. 1.	2.	4.	7.	12.	19.	27.	35.	43.	60.	100.
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	..	yellow 1 2 cc.	1 cc.	2 cc.	25 cc.	25	25	26	26	26	26	26
15	13.35	yellow 1.5	deeper yellow	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.

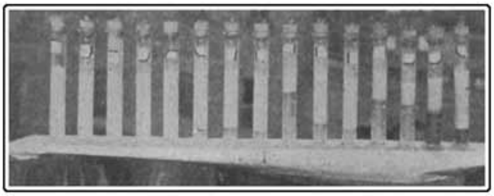


Fig. 3.—Cottonseed Oil Emulsion with Tragacanth after 41 days from Table XIV. From left to right 1–15.

Fig. 4.—Cottonseed Oil Emulsions with Tragacanth #2 and #14 after 41 days.

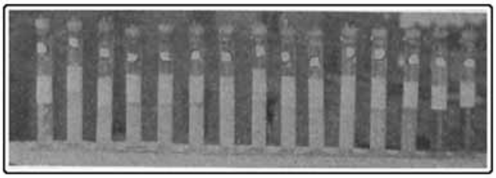


Fig. 5.—Nujol Emulsions with Acacia from Table V after 35 days. From left to right 1–15.

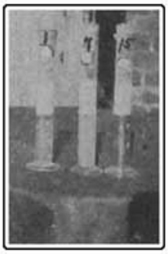


Fig. 6.—Nujol Emulsions with Acacia from Table V—#1, #7, and #15 after 35 days.

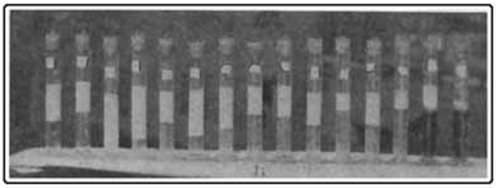


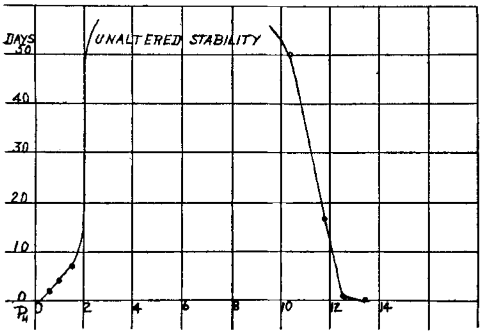
Fig. 7.—Nujol Emulsions with Tragacanth from Table VI after 33 days. Left to right 1–15.

Fig. 8.—Nujol Emulsions with Tragacanth from Table VI #3 and #15.

Tables I to VI 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 I to VI can be easily observed from Graphs Nos. 1 and 2. The ordinates of Graph No. 2 represent the amount of separation per day over a period of 60 days and multiplied by ten to eliminate decimals.

Graph No. 2 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

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

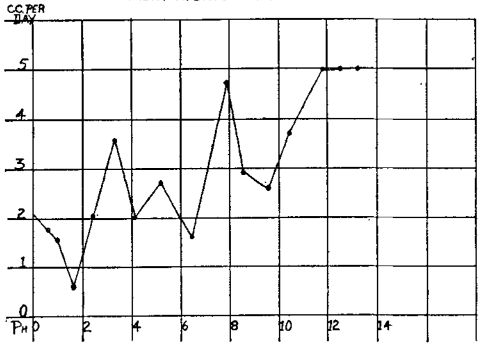


TABLE VI.—NUJOL EMULSIFIED WITH TRAGACANTH.
Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	12 Hrs.	1.	3.	6.	11.	Days. 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 color	deeper yellow 1 cc.	deeper 2 cc.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.
15	13.35	deep yellow 2 cc.	10	20	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.	C. S.

TABLE VII.—COTTONSEED OIL EMULSIFIED WITH TRAGACANTH.
Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	4.	6.	8.	10.	12.	Days. 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

TABLE VII.—(*Continued*).

No.	p_H.	4.	6.	8.	10.	12.	Days. 14.	17.	21.	25.	32.	38.
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 VIII.—COTTONSEED OIL EMULSIFIED WITH TRAGACANTH.

Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	4.	6.	8.	10.	12.	Days. 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 IX.—NUJOL EMULSIFIED WITH TRAGACANTH.

Degree of Separation in Cc. in Different Time Periods.

No.	p_H.	3.	5.	7.	9.	11.	Days. 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 X.—NUJOL 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.	
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 XI.—NUJOL 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.

stable point. These results with Tragacanth are recorded in Tables VII to XI and the average stability over a period of 20 days is plotted in Graph No. 3. 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) separated 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 chlorine 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 separated a creamy layer of 25–27 cc. and remained in that condition for more than 150 days, the effect all concentrations of sodium chloride used showing the same results, as shown by Fig. 9.

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

TABLE XII.—NUJOL 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.	35.	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^{-6}	..	10	10	15	17	23	27
7	10^{-6}	10	15	21	23	25	27	27

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 at p_H 1.2 where partial separation occurred. The results obtained with tragacanth may be obtained from Tables XIII and XIV and Graph No. 4.

TABLE XIII.—NUJOL 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 XIV.—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

STUDY OF THE PHYSICAL PROPERTIES OF THE EMULSIONS.

(*a*) *Surface Tension*.—This property was determined at 35° C. with a standardized tensimeter. The results with tragacanth can be seen in Graph No. 5 and with acacia in Table XV.

TABLE XV.—SURFACE TENSION OF EMULSIONS WITH ACACIA AT 35° C.

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

(*b*) *Interfacial Tension.*—The interfacial tension was measured at 27° C. by a pipette similar to the one used by Donnan (2) and his students (see Fig. 12). The interfacial tension with water was taken as 10 and the following formula employed, where T is the interfacial tension, V the volume of oil and N the number of drops.

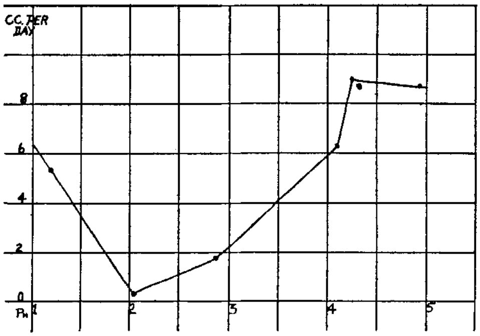
$$T \alpha \frac{V}{N} \qquad \text{for pure water } 10 = \frac{3K}{24}$$

$$T = K\frac{V}{N} \qquad \text{and } K = 80$$

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

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

GRAPH NO. 4
STABILITY OF EMULSIONS WITH TRAGACANTH AND THEIR HYDROGEN ION CONCENTRATIONS.



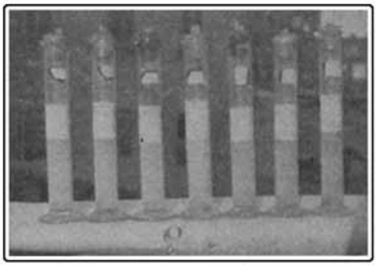


Fig. 9.—Nujol Emulsions with Acacia and Sodium Chloride Conc. of NaCl. Left to right 1 *N* to 10^{-6} *N*.

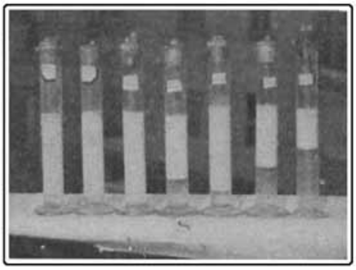


Fig. 10—Nujol Emulsions with Tragacanth from Table VII after 27 days.

Fig. 11.—Nujol Emulsions with Tragacanth #7 and #3 after 27 days.

(*c*) *Viscosity.*—Using distilled water as a standard at 30° C. the relative viscosities of a series of emulsions were determined by the pharmacopœia method. 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 No. 7.

(*d*) *Size of Particle.*—Emulsions of Nujol were prepared after coloring the oil

TABLE XVI.—NUJOL 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 XVII.—NUJOL EMULSIFIED WITH TRAGACANTH.

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

with alkanet root and the size of the particles measured microscopically. The results are tabulated in Tables XVI and XVII.

Gels of tragacanth in water of different hydrogen-ion concentrations were prepared and, after standing for 3 days, Fig. 13 shows the separation of water at the

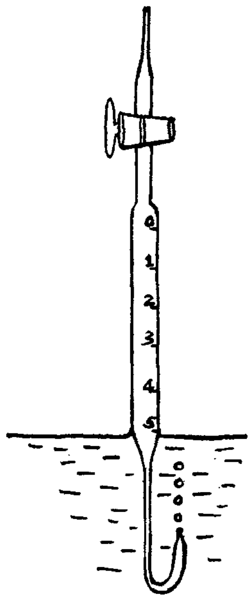
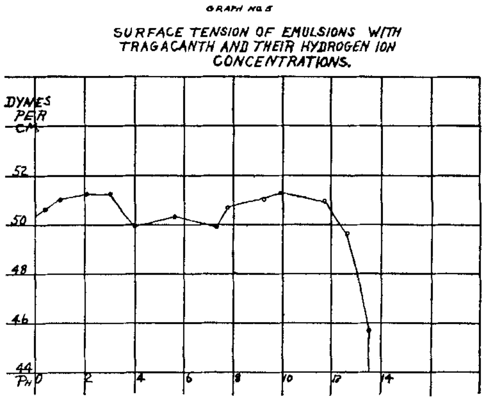
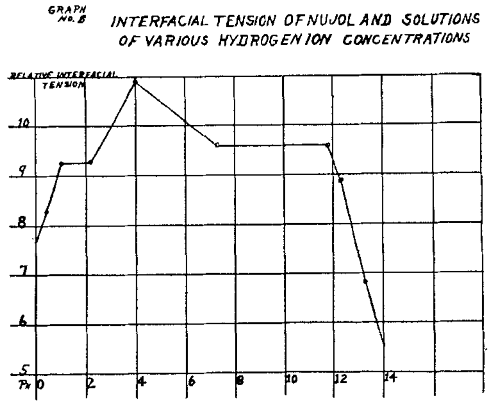


Fig. 12





surface. The gels were prepared by rubbing 0.5 Gm. of tragacanth with 25 cc. of water until gelatinization occurred.

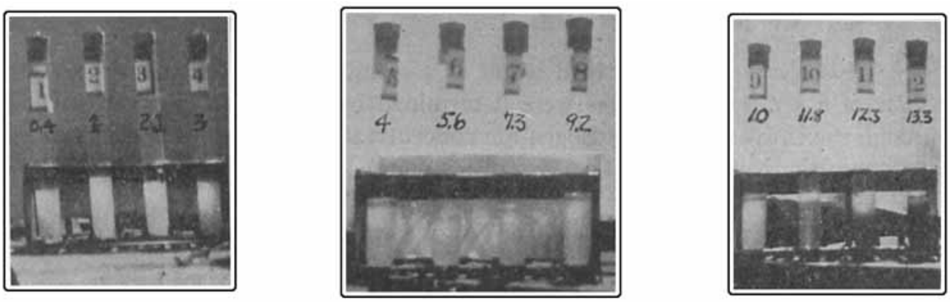


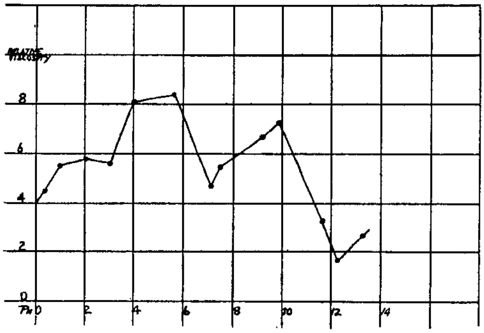
Fig. 13.—Tragacanth Gels. Lower figure indicates p_H of Gel.

DISCUSSION OF RESULTS AND THEORETICAL CONSIDERATIONS.

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 particle in the acacia emulsions is 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 No. 4 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 Fig. 10.

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



A study of Graph No. 7 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 authors feel that a maximum viscosity is not desirable as indicated by the Graph No. 8, but an optimum relative viscosity which we find to be 4 and 6; Holmes and Child (3) 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 No. 5 shows that those emulsions prepared with tragacanth decrease in surface tension toward the alkaline side of the p_H scale. We, however, do not consider the phenomenon of surface tension of paramount surface in view of the postulates of Langmuir (4) 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 Nujol and tragacanth gels of various hydrogen-ion concentrations. Invariably a steady stream was obtained instead of drops as was obtained by Donnan (5) with solutions of the sodium salts of certain high molecular weight fatty acids. The interfacial tension of Nujol of solutions of various hydrogen-ion concentrations as plotted in Graph No. 5 show that the alkaline solutions reduce the interfacial tension which should increase the power of emulsification, were the emulsifying agent not affected. We conclude 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 Fig. 13 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, however 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 (6) 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. We believe 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.

CONCLUSIONS.

1. The range of greatest stability for either vegetable or mineral oils prepared with acacia lies between p_H 2 to 10 and with tragacanth the range is p_H 1.9–2.3.
2. The size of the particles, surface tension, interfacial tension 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 side of the p_H scale.
3. Fischer's Hydrate Theory is substantiated in emulsions prepared with tragacanth.

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PLASTICITY MEASUREMENTS IN PHARMACY.*

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In the manufacture of various products, such as dental creams, cold creams, ointments, etc., it is important to maintain uniformity in what is generally referred to as "consistency." It is therefore highly desirable to have a method for measuring quantitatively this property of these substances.

The substances above mentioned belong to the class known as plastic materials, and should be sharply differentiated from viscous liquids. In general, a plastic substance is one which will undergo continuous deformation or flow under a shearing stress only after the latter exceeds a certain value which we call the "yield shearing stress" or "yield value." In a viscous liquid this yield shearing stress

* Read before Scientific Section, A. Ph. A., Des Moines meeting, 1925.