

THE EFFECT OF CHANGES OF HYDROGEN-ION CONCENTRATION  
UPON EMULSIONS OF THE WATER-IN-OIL TYPE.\*

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In a previous communication to THIS JOURNAL, Krantz and Gordon<sup>1</sup> studied the effect of hydrogen-ion concentration upon the stability of oil-in-water emulsions when acacia and tragacanth were employed as emulsifying agents. The results of these investigations were sufficiently interesting to warrant the study of the effect of changes of hydrogen-ion concentration upon the emulsions of the inverted type. It is well known, from the work of Harkins,<sup>2</sup> that sodium oleate, and similar compounds, produce emulsions of the oil-in-water type; whereas, when two hydrocarbon radicals are attached to one metallic atom, as in the case of calcium and magnesium oleates, these substances serve to produce water-in-oil emulsions. Hence, for this investigation magnesium oleate was selected as the emulsifying agent, and olive oil and mineral oil as the dispersion phases.

## EXPERIMENTAL.

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 granular 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 by adding 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  $p_H$  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 viscosity 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.

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\* Scientific Section, A. PH. A., Portland meeting, 1929.

<sup>1</sup> Krantz and Gordon, JOUR. A. PH. A., 15 (1926), 83.

<sup>2</sup> Harkins, *et al.*, J. Am. Chem. Soc., 39 (1917), 353.

The separation of an 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. With certain emulsions of this type, employing freshly precipitated magnesium oleate, the authors have 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 EFFECT OF CHANGES OF  $p_H$  IN WATER-IN-OIL EMULSIONS.

TABLE I.—EMULSIONS OF SOLUTIONS OF VARIOUS HYDROGEN-ION CONCENTRATIONS IN MINERAL OIL.

No.	$p_H$	Degree of Separation in Cc. in Different Time Periods.																
		$\frac{1}{2}$ hr.	1 hr.	4 hrs.	1.	3.	4.	7.	11.	15.	20.	28.	Days.					
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
3	1.87			5	6	7	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	3.97					2	3	4	4	4	4	4	5	5	5	5	5	5
6	4.85						1	2	2	2	2	3	4	4	4	4	4	5
7	5.55							1	2	3	3	3	3	3	3	3	3	3
8	7.55							1	2	2	2	3	3	3	3	3	3	4
9	8.02					2	2	3	4	4	4	4	5	5	5	5	5	5
10	9.25					2	2	3	3	4	4	5	5	5	5	5	5	5
11	10.97					3	3	4	5	5	5	5	5	5	5	5	5	5
12	11.75								1	1	1	1	2	2	2	2	2	3
13	12.38																	
14	13.0	Yellow	Granular															

C. S. = Complete separation.

TABLE II.—EMULSIONS OF SOLUTIONS OF VARIOUS HYDROGEN-ION CONCENTRATIONS IN MINERAL OIL.

No.	$p_H$	Degree of Separation in Cc. in Different Time Periods.																
		$\frac{1}{2}$ hr.	1 hr.	4 hrs.	1.	3.	4.	7.	11.	15.	20.	28.	Days.					
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	7
4	3.05					1	1	2	3	3	3	5	5	5	5	5	5	5
5	3.97					4	4	5	5	5	5	5	5	5	5	6	6	6
6	4.85						1	3	3	4	4	4	4	5	5	5	5	5
7	5.55						1	1	2	2	3	3	3	3	4	4	4	4
8	7.55						1	1	1	2	2	3	3	4	4	4	4	4
9	8.02					2	2	2	3	3	4	4	4	5	5	5	5	5
10	9.25					1	1	2	2	3	3	3	3	4	4	5	5	6
11	10.97					2	2	3	3	4	4	4	4	4	4	5	5	5
12	11.75								2	2	2	2	2	3	3	3	3	3
13	12.38																	
14	13.0	Yellow	Granular															

C. S. = Complete separation.

Tables I and II indicate that the staple point of these emulsions is near  $p_H$  12.38. The magnesium oleate employed in preparing these emulsions had been

prepared about 14 days prior to its use. Graph No. I shows the average stability of these two series of emulsions over a period of 94 days.

TABLE III.—EMULSIONS OF SOLUTIONS OF VARIOUS HYDROGEN-ION CONCENTRATIONS IN MINERAL OIL. (FRESHLY PRECIPITATED MAGNESIUM OLEATE.)

No.	$p_H$ .	Degree of Separation in Cc. in Different Time Periods.												
		1 hr.	3.	7.	12.	20.	30.	37.	Days.					
								44.	51.	58.	65.	72.	79.	86.
1	0.9	8	8	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
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

TABLE IV.—EMULSIONS OF SOLUTIONS OF VARIOUS HYDROGEN-ION CONCENTRATIONS IN OLIVE OIL.

No.	$p_H$ .	Degree of Separation in Cc. in Different Time Periods.														
		1/2 hr.	1 hr.	1.	4.	12.	17.	25.	35.	Days.						
									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
4	3.05								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

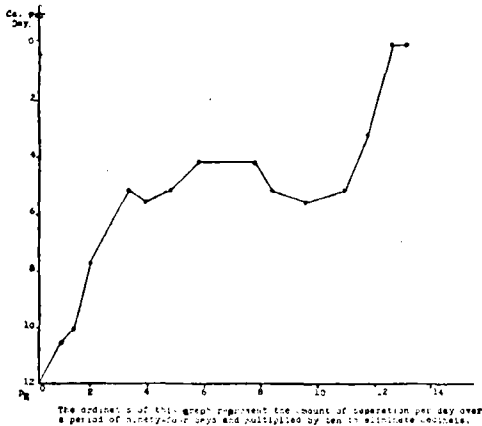
Figure 1 shows the emulsions from Tables I and II after thirty days. Reading from left to right these emulsions are numbered as given in Table I.

With magnesium oleate which was freshly precipitated, as was previously mentioned, 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 was stable as shown by Table III. 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 III shows the stability of these emulsions over a period of eighty-six days.

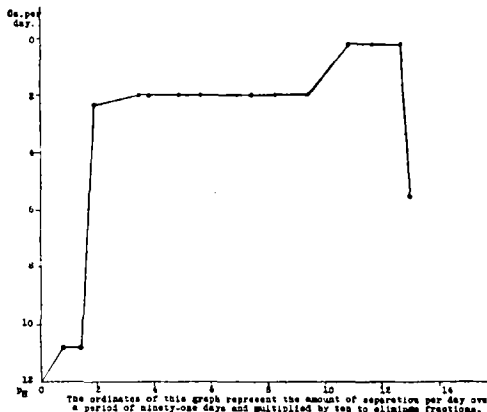


chloride in concentrations 1 N to 10<sup>-6</sup> N it was observed that this substance had practically no influence upon the emulsions dispersed in mineral oil.

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.



Graph No. I.—Stability of emulsions in mineral oil and their hydrogen-ion concentrations.



Graph No. II.—Stability of emulsions in olive oil and their hydrogen-ion concentrations.

The degrees of separation with each of these series of emulsions is shown in Tables VI and VII. Figure 3 shows the emulsions in mineral oil after thirty days. Reading from left to right, the emulsions are numbered as given in Table VI.

TABLE VI.—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 <sup>-1</sup>														
3	10 <sup>-2</sup>													No separation	
4	10 <sup>-3</sup>													No separation	
5	10 <sup>-4</sup>													No separation	
6	10 <sup>-5</sup>													No separation	
7	10 <sup>-6</sup>													No separation	
8	10 <sup>-7</sup>													No separation	

TABLE VII.—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	3
2	10 <sup>-1</sup>	1	2	2	2	2	2	2	2	2	2	2	2
3	10 <sup>-2</sup>	1	1	1	1	1	1	1	1	1	1	1	1
4	10 <sup>-3</sup>	1	1	1	1	1	1	1	1	1	1	1	1

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<sub>H</sub> 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 VIII and IX record these results.



TABLE XI.—EMULSIONS OF SOLUTIONS OF VARIOUS HYDROGEN-ION CONCENTRATIONS IN MINERAL OIL.

No.	$p_H$ .	Degree of Separation in Cc. in Different Time Periods.												
		$\frac{1}{2}$ hr.	4.	9.	17.	27.	34.	Days. 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													

STUDY OF THE PHYSICAL PROPERTIES OF THE EMULSIONS.

*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 XII.

*Viscosity.*—Using the external phase, mineral oil, as a standard at 20° C., the relative viscosities of a series of emulsions were determined by measuring the rate of flow of the emulsion from a capillary tube. 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 XIII, and plotted in Graph No. IV.

*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 XIV.

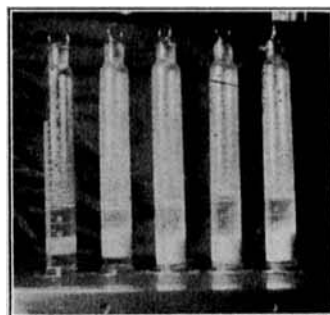
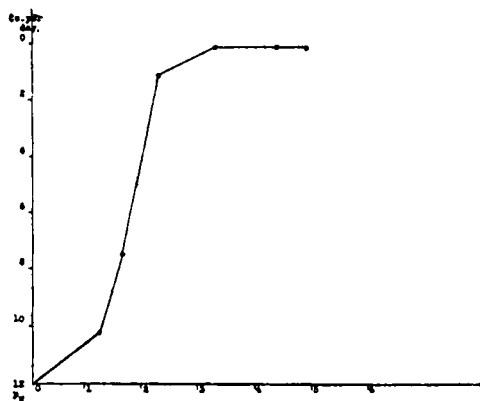
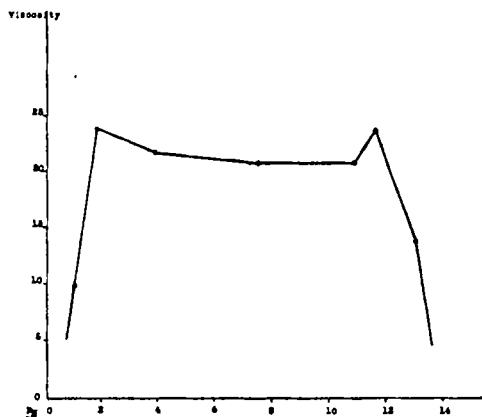


Fig. 4.—Emulsions of solutions of various hydrogen-ion concentrations in mineral oil.



Graph No. III.—Stability of emulsions of solutions of various hydrogen-ion concentrations in mineral oil ( $H_2SO_4$ ).



Graph No. IV.—Relative viscosity of solutions of various hydrogen-ion concentrations in mineral oil.

TABLE XII.—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

TABLE XIII.—RELATIVE VISCOSITIES OF EMULSIONS 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

TABLE XIV.

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.

A study of the graphs showing the stability of these emulsions in mineral oil and olive oil, 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  $p_H$  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. It is especially interesting to note the increased stability of these emulsions when magnesium oleate, freshly prepared, is used as an emulsifying agent. Similar observations were made with mineral oil and olive oil. If the hydrogen-ions were produced, either by sulphuric or hydrochloric acid the same results were obtained, which seems to indicate that the instability is due to the presence of a high hydrogen-ion concentration. When solutions of sodium chloride in various concentrations were emulsified, there was no influence in stability as far as emulsions in mineral oil were concerned; but when olive oil was used as the external phase, the instability of the emulsions increased with the increase of concentration of sodium chloride in the dispersed phase. A summary of the physical properties of the emulsions shows that there is no significant difference in the surface tension of any of the emulsions. The viscosity determinations show that the emulsions of liquids of various hydrogen-ion concentrations in mineral oil are far less viscid than the external phase alone. On the extreme acid and alkaline side of the  $p_H$  scale ( $p_H$  0.9 and  $p_H$  13), there was a marked drop in viscosity. It was of special interest to note that these emulsions of extreme low viscosity were those which were the 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 of any other of the 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. These experiments indicate 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. According to Harkins, 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 influence of changes in hydrogen-ion concentrations on the emulsions prepared with magnesium oleate has been studied.
2. Certain physical constants of these emulsions have been determined.
3. The range of greatest stability of these emulsions is when the internal phase is well on the alkaline side of the  $p_H$  scale, namely,  $p_H$  11 to 12.5.

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#### CALCIUM METABOLISM.

*Calcium Metabolism Studies on the Nature and Rôle of the Activators: Researches on Fundamentals for the Prevention of Dental Caries.* W. A. PRICE. *J. Am. Dent. Assoc.*, 16 (1929), 265.—Through *Squibb Abstract Bulletin*, Feb. 13, 1929.

In an attempt to interpret previously reported data and recent additions on the subject, the author indicates the importance of proper calcium utilization and its effect on resistance and susceptibility to infection as well as for tooth and bone formation. Calcium in milk, blood and many biologic fluids, which exists partly as diffusible and partly as non-diffusible, can readily be treated so as to change the percentages of diffusible and nondiffusible, by several means, including irradiation or shaking with raw cod-liver oil and with activated cod-liver oil; raw cod-liver oil usually decreases diffusibility, while activated cod-liver oil and irradiation increase it. Normally, there seems to be about 5% more diffusible than nondiffusible calcium, *i. e.*, with total serum Ca of 10 mg., a little more than 5 should be diffusible and a little less than 5 nondiffusible; a variation of 2-3 mg., in either direction seems usually to express itself with distinct physical disturbances. Exposure to radiant energy to 2800 A tend to raise the diffusible calcium; some of the bands beyond 2900 have distinctly harmful effects. A study of the effects of the irradiation of fluids compared both with effects of a demonstration of the irradiation of fluids compared also with effects of administration of the sterol ergosterol, separately and in association, gives evidence of its being similar in effect to, if not directly associated with, the diffusibility phenomena presented. Disturbed calcium metabolism was treated in both ex-

perimental animals and in practice by the use of activators, more than 1500 blood chemical studies being made on the latter. The treatment consisted of about 0.5 cc. of activated or raw cod-liver oil in accordance with the balance between diffusible and nondiffusible calcium, and 5-grain tablet of calcium lactate. Evidence of wastage of calcium was shown by the urine calcium and roentgenogram study of the texture of bone with regard to tendency to general calcification or decalcification. "The relation of these phenomena to some of life's problems seems to indicate that herein is an important step forward both in the understanding of bone and tooth formation and disease and the means for the forming of better hard tissues and the prevention of subsequent disease in these tissues."—J. P.

#### DIRECT SELLING COMPANIES.

Recently the Federal Trade Commission announced that "representatives of between seven and eight million people engaged in 'direct selling' of all kinds of merchandise will meet in a trade practice conference at Dayton, Ohio, next October under auspices of the Commission. Members of the industry will endeavor to adopt standards for correction of unfair advertising. Commissioner William E. Humphrey will supervise the conference." Application for the conference was made by the National Association of Direct Selling Companies, Inc., of Winona, Minn. They are said to do a business of \$300,000,000 a year and to employ close to one-half million people. E. C. Brokmeyer (*General Bulletin* No. K-27) comments that retailers should watch this and all other activities designed to eliminate the middleman, wholesaler or retailer.