

THE BUFFER CAPACITIES OF ACACIA AND TRAGACANTH.*

BY JOHN C. KRANTZ, JR.

INTRODUCTION.

In a previous communication to THIS JOURNAL, Krantz and Gordon¹ reported their studies on the influence of changes of hydrogen-ion concentration upon the stability of certain oil-in-water emulsions. In this series of experiments cottonseed oil and mineral oil were emulsified in an aqueous dispersion phase, using acacia and tragacanth, respectively, as emulsifying agents. The changes in hydrogen-ion concentration were produced by adding the necessary quantities of sodium hydroxide and hydrochloric acid, respectively, to the external phase prior to the preparation of the emulsion. Following this procedure, it was observed that the most stable range of hydrogen-ion concentration for the external phase with acacia emulsions was between p_H 2 and 10.5, and with tragacanth the most stable range was between p_H 1.9 and 2.3.

It occurred to the author that it would be interesting to observe to what extent the respective gums influenced or buffered the external phase of the emulsion and that, possibly by virtue of this, the degree of stability was determined.

EXPERIMENTAL.

Accordingly, a series of cottonseed oil emulsions was prepared containing ten per cent by volume of the oil. For emulsification 2.5 Gm. of acacia were employed for 10 cc. of oil and 0.5 Gm. of tragacanth for the same volume of oil. The p_H of the external phase, prior to the preparation of the emulsion was measured electrometrically in each case.

Two days after the preparation of these emulsions, their hydrogen-ion concentrations were determined electrometrically. Table I records the results of these experiments.

TABLE I.

CHANGES IN HYDROGEN-ION CONCENTRATION IN THE EXTERNAL PHASE AFTER EMULSIFICATION OF COTTONSEED OIL.

No.	p_H of external phase.	Emulsifying agent.	p_H of emulsion.	Emulsifying agent.	p_H of emulsion.
1	0.1	Acacia	0.27	Tragacanth	0.27
2	1.07	Acacia	1.56	Tragacanth	1.37
3	2.00	Acacia	3.57	Tragacanth	2.80
4	2.9	Acacia	4.11	Tragacanth	4.22
5	3.89	Acacia	4.22	Tragacanth	4.64
6	4.64	Acacia	4.21	Tragacanth	4.50
7	5.52	Acacia	4.11	Tragacanth	4.21
8	6.97	Acacia	4.12	Tragacanth	4.49
9	8.98	Acacia	4.26	Tragacanth	4.37
10	9.86	Acacia	4.25	Tragacanth	4.80
11	10.85	Acacia	4.28	Tragacanth	9.82
12	11.74	Acacia	9.92	Tragacanth	10.93
13	12.65	Acacia	12.10	Tragacanth	12.13
14	13.53	Acacia	13.35	Tragacanth	Too gelatinous to measure

* Scientific Section, A. P. H. A., Portland meeting, 1928.

¹ JOUR. A. P. H. A., 15 (1926), 83.

The tragacanth emulsions were diluted with an equal volume of boiled distilled water in order to sufficiently reduce the viscosity to enable the measurement of hydrogen-ion concentration to be made.

A sample of grade "A" U. S. P. acacia was obtained and solutions of the gum prepared in aqueous solutions adjusted to a definite hydrogen-ion concentration. These solvents were prepared in the same manner as the external phase of the foregoing series of emulsions. The concentration of acacia in the solvent was the same in each solution, namely, 2.5 Gm. in 40 cc., *i. e.*, the same concentration per total

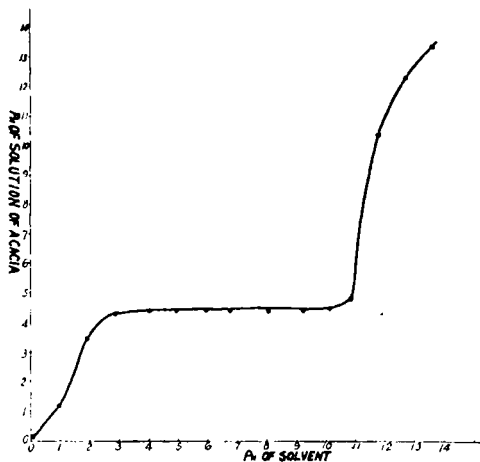


Fig. 1.—Buffer capacity of acacia solutions.

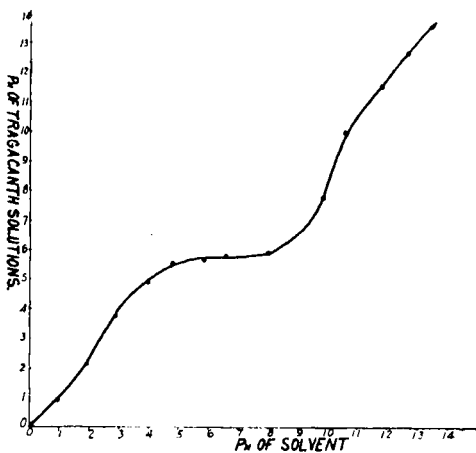


Fig. 2.—Buffer capacity of tragacanth solutions.

volume as was present in the acacia emulsions. Table II records the hydrogen-ion concentration of the solvent and of the acacia solutions.

TABLE II.

ACACIA SOLUTIONS AND THEIR HYDROGEN-ION CONCENTRATIONS.

No.	p_H of solvent.	p_H of solution.	No.	p_H of solvent.	p_H of solution.
1	0.04	0.15	9	8.07	4.51
2	0.95	1.19	10	9.20	4.50
3	1.92	3.51	11	10.13	4.52
4	2.88	4.33	12	10.82	4.89
5	4.02	4.40	13	11.85	10.46
6	4.95	4.34	14	12.74	12.47
7	6.0	4.50	15	13.56	13.51
8	6.75	4.47			

When these data are plotted with the p_H of the solvent as abscissae and the p_H of the solution as ordinates a typical neutralization curve is obtained as shown in Fig. 1.

With the gels that tragacanth forms with water, difficulty was experienced in measuring the hydrogen-ion concentration in concentrations of 0.5 Gm. in 40 cc. (the amount employed in the emulsions) on account of the great viscosity of the gels. Consequently gels were prepared containing 0.5 Gm. of tragacanth in 100 cc. of aqueous solution. These gels were sufficiently limpid to measure their hydrogen-

ion concentrations electrometrically. Table III records the hydrogen-ion concentration of the solvents and of the tragacanth gels.

TABLE III.
TRAGACANTH GELS AND THEIR HYDROGEN-ION CONCENTRATIONS.

No.	p_H of solvent.	p_H of gel.	No.	p_H of solvent.	p_H of gel.
1	0.04	0.04	8	6.48	5.88
2	0.95	0.96	9	7.86	5.82
3	1.92	2.10	10	9.75	7.70
4	2.88	3.81	11	10.47	9.99
5	3.93	4.93	12	11.85	11.50
6	4.78	5.54	13	12.74	12.68
7	5.80	5.56	14	13.56	13.55

Figure 2 represents these data; the p_H of the solvent are the abscissae and the p_H of the tragacanth gels are the ordinates.

In order to study the change of p_H caused by dilution of acacia solutions or, in other words, the buffer capacity of acacia solutions upon the addition of water, a sample of acacia was dissolved in boiled, distilled water p_H 6.05. Certain diffusion experiments¹ have indicated the molecular weight of acacia to be 1750. Using this value as the molecular weight a tenth-molar solution was prepared. The p_H of this solution and those solutions obtained by dilution of this with water p_H 6.05 are given in Table IV.

TABLE IV.
EFFECT OF DILUTION UPON THE p_H OF ACACIA SOLUTIONS.

Conc.	p_H .	Conc.	p_H .
$\frac{M}{10}$	4.03	$\frac{M}{70}$	4.56
$\frac{M}{20}$	4.16	$\frac{M}{100}$	4.69
$\frac{M}{30}$	4.35	$\frac{M}{500}$	5.07
$\frac{M}{50}$	4.44	$\frac{M}{1000}$	5.27

These data are plotted in Fig. 3. The abscissae when multiplied by ten give the mole fraction dilution of the acacia solution.

Van Slyke² has established a standard for the measurement of the buffer capacities of various solutions. The unit adopted by Van Slyke is the differential ratio

$$\frac{dB}{dp_H}$$

This expresses the relationship between the increment in Gm. equivalents of strong base added to the buffer solution and the resultant increment in p_H . If an acid is added the values dB and dp_H are negative, so that the ratio designated by Van

¹ E. F. Burton, "The Physical Properties of Colloidal Solutions" (1916), 122.

² D. D. Van Slyke, *J. Biol. Chem.*, 53 (1922), 528.

Slyke as " β " has always a positive value. A solution has a buffer capacity of unity when a liter will take up one Gm. equivalent of strong acid or strong base per unit change in p_H .

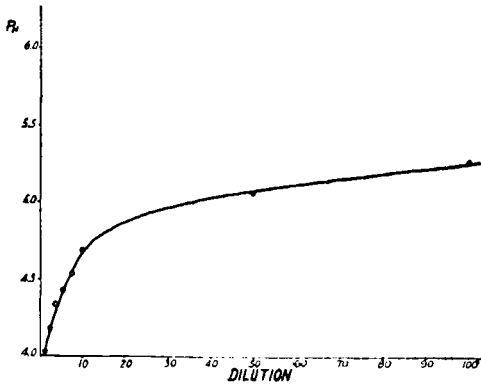


Fig. 3.—Effect of dilution upon p_H of acacia solution.

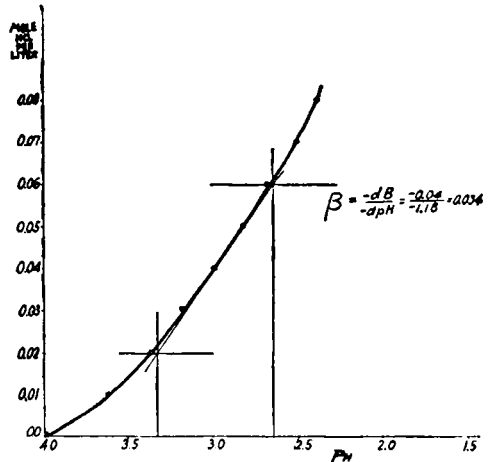


Fig. 4.—Buffer capacity of acacia.

The value of the Van Slyke " β " for a tenth-molar solution of acacia was determined by preparing 1000 cc. of acacia solution of this concentration and adding definite equivalents of tenth-normal hydrochloric acid and determining the p_H after each addition. Table V records these results.

TABLE V.

No.	Cc. 0.1 HCl added.	Mole HCl per L.	p_H .	No.	Cc. 0.1 HCl added.	Mole HCl per L.	p_H .
1	00	00	4.03	6	500	0.05	2.82
2	100	0.01	3.63	7	600	0.06	2.70
3	200	0.02	3.36	8	700	0.07	2.50
4	300	0.03	3.18	9	800	0.08	2.36
5	400	0.04	2.99				

Plotting these values as shown in Fig. 4 we may obtain the ratio $\frac{-\Delta B}{-\Delta p_H}$, where each of these values is a measurable increment. Thus, to change the p_H from 4 to 3, 0.039 mole of hydrochloric acid was added. Then

$$\frac{-\Delta B}{-\Delta p_H} = \frac{-0.039}{-1.00} = 0.039$$

To obtain the exact value of β , however, a tangent is drawn to the curve at say 0.04, the base line intercepts of this tangent at 0.06 and 0.02 are determined to be 3.32 and 2.14, respectively, then

$$\frac{-dB}{-dp_H} = \frac{-0.04}{-1.18} = 0.034 \text{ or } \beta$$

$$-dB = 0.06 - 0.02 = 0.04 \text{ and } -dp_H = 3.32 - 2.14 = 1.18$$

Thus the buffer capacity of acacia at p_H 3 is 0.034.

DISCUSSION OF RESULTS.

The correlation of the data included in this investigation with the before-mentioned work of Krantz and Gordon¹ indicates that with emulsions prepared with acacia, the buffering action of acacia upon acid or alkali added to the emulsion influences the stability of the emulsion. Acacia being the potassium, calcium and magnesium salts of a weak acid, namely, arabic acid, one might expect its buffer capacity to be more effective in the neutralization of acids than the neutralization of alkalis. An examination of Fig. 1 shows this to be the case, on account of the abruptness of the curve on the alkaline side p_H 10.5 and the gradient curvature on the acid side of the p_H scale. This information agrees with the findings of Gordon and the author in the stability of emulsions prepared with acacia, *i. e.*, the instability begins on the alkaline side at a lesser concentration of alkali than it does on the acid side with a corresponding concentration of acid. The alkaline concentration, where instability begins, lies between $\frac{N}{10^3}$ and $\frac{N}{10^4}$ sodium hydroxide solution, whereas with hydrochloric acid a concentration of $\frac{N}{10^2}$ is required to produce relative instability.

Dilution with water was shown to have little influence upon the p_H of acacia solutions. The buffering effect of tragacanth does seem to play as important a rôle in the determination of emulsion-stability as it does with acacia. Gordon and the author found tragacanth emulsions prepared with an external phase of about p_H 2 to be most stable, yet tragacanth exerts a considerable buffer capacity between p_H 3.0 and 10.00. In the case of the emulsions prepared with tragacanth, the stability of the gel which the gum forms with water seems to be the main criterion of emulsion-stability. The acid gels p_H 1.5 to 2.5 were found to be most stable, as recorded in the previous investigation of Gordon and the author.

CONCLUSIONS.

1. The buffer capacities of acacia and tragacanth have been studied.
2. The effect of dilution on the p_H of acacia solutions has been determined. The Van Slyke " β " for acacia in 0.1 *M* solution at p_H 3 has been found to be 0.034.
3. An explanation correlating the buffer capacity of acacia and the stability of emulsions prepared with this substance has been proposed.

PHARMACEUTICAL RESEARCH LABORATORY,
SHARP AND DOHME,
BALTIMORE, MARYLAND.

ESTIMATION OF NITROGLYCERIN SOLUTION D. A. B. VI.

The conventional method of "D. A. B. VI," based on the saponification of the nitroglycerin, gives as a rule too high values. The addition of H_2O_2 does not seem advantageous, and the process is unsuitable in practice. For ordinary checking it is sufficient to estimate the dry residue of 10-Gm. solution, using a Soxhlet flask, and drying over $CaCl_2$. One

can also fall back on the test of "Pharm. Netherl. V.;" 10 cc. of nitroglycerin solution are mixed with 15 cc. H_2O and warmed to just over $35^\circ C.$, when a clear solution results. When carefully cooled the mixture becomes turbid between 29° and $34^\circ C.$ —C. Brumming (*Apoth. Ztg.*, 43, 81, 1235; through *Pharm. J.* for March 16, 1929.