BUFFER ACTION OF SAPONINS

Part I.—Analytical Studies

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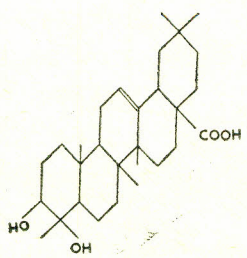
The buffer action of saponins has been described. They are found to be useful buffers in the range of 2.5 to 4.75 pH units and have a β-value of 0.074 at a concentration of 1.0% for dilute acid-base reactions. The buffer capacity has been compared with known buffers and it has been noted that a mixture of saponin and sodium acetate has a value of 0.1 for 2.5 to 5.6 pH units which is a considerable improvement in the activity and range of the individual buffer systems.

Introduction

The fruits and barks of various trees have been used extensively for a long time as surface active agents. Their extracts are now known to contain saponins. The chemistry of these compounds is fairly worked-out as reported in an excellent review by Barton.[1] The saponins have been shown to have the β-amyrin nucleus with a carboxyl group and a hydroxyl.



These functional groups give rise to an important property, namely their buffer action which seems to have received very little attention. It was therefore considered desirable to study this property of the saponins in detail.

Experimental

The saponins under investigation were either isolated from soap-nut, *Sapindus Mukarossi Gaerten*, or the commercially available products were used after purification. In the case of the nuts, they were dried in the sun, and the seeds were separated from the pericarp, which contains the saponin. Following the procedure outlined by Sarin and Beri.[4]

The isolated saponin was completely dried over phosphorus pentoxide. The aqueous solutions of varying percentages were made covering the range from 10.0 percent to 0.1 percent The solutions show variation of colour from distinct amber to pale-yellow and finally colourless with the decrease in concentration. The two sets of solution under investigation were:-

A. 10.0% 7.5% 5.0% 2.5% 1.0%

and

B. 1.0% 0.75% 0.5% 0.25% 0.1%

10 percent and 1 percent solutions were made by weight/volume, while other percentages were made by diluting to their respective concentrations.

Titrations were performed electrolytically with pH meter using glass electrode for 0 to 10 pH and to 50°C. against the standard calomel electrode, a saturated solution of KCl being used as the salt bridge. Measurements were made after the addition of 2.0 ml. of acid or alkali. The readings were recorded at room temperature maintaining it at 20° ± 1°C.

Set A of the solutions was first taken for the experimentation and titration made with decinormal solution of acid and alkali. Glass electrode of the pH meter was immersed in distilled water for 24 hours before the start of the experiment. The electrodes were washed and dried with a filter paper and then the assembly was completed.

The pH meter was first set at pH-5 and then at pH-3, with the aid of the standard buffers prepared by the usual methods. The saponin solution (50 ml.) was taken in a 200 ml. beaker. The pH of the solution was noted with each addition of 2 ml. of 0.1N hydrochloric acid, and shaking the mixture vigorously to ensure complete mixing. The change in the pH was recorded till it had decreased by 2-pH units. To start with a new

sample of saponin, or to proceed towards the alkaline range after neutralising, the pH meter was set at pH 5 to 7 respectively. Sodium hydroxide (0.1N) was added, 2 ml. at a time, until the pH started rising rapidly. The electrodes were washed with distilled water and soaked with filter paper before proceeding for the next sample. The procedure was repeated for the other solutions of saponin and also for Set B. The concentrations of the titrant in the latter case was centinormal. The results are shown graphically in Figs. 1 and 2.

As the saponins contain the β-amyrin nucleus and sugar residues, it was not possible to prepare solutions in terms of molar concentrations. In order to evaluate the buffer capacities the, data has been presented as concentration percentages for the different buffer systems. The 0.2M solutions of the acetic acid and sodium acetate, when mixed in the proportion of 30:70, respectively, correspond to 2.255 percent of the buffer mixture. The titration curve for this system is shown in Fig. 3. A similar curve is obtained for saponin and sodium acetate corresponding to 1.65 percent of this mixture.

Results

The pH change for the different solutions of Set A, are shown graphically in Fig. 1 and of Set B, in Fig. 2. The mean average fall of pH in the range 4.7 to 3.0 units on the addition of every

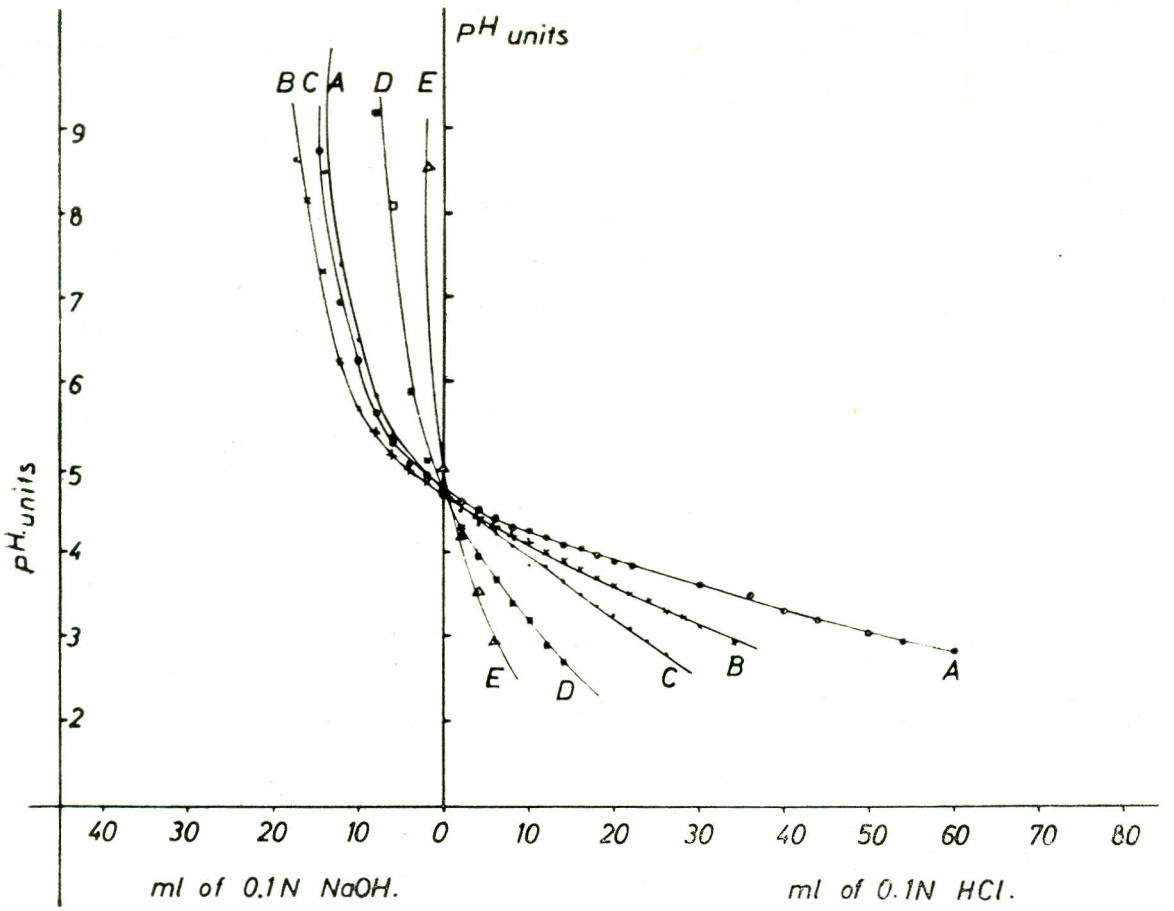


Fig. 1.—Showing pH change for solutions of set A.

Curves shown by (—O—O—) A-10.0%,
(—X—X—) B-7.5%, (—●—●—) C-5.0%
(—□—□—) D-2.5%, (—△—△—) E-1.0%

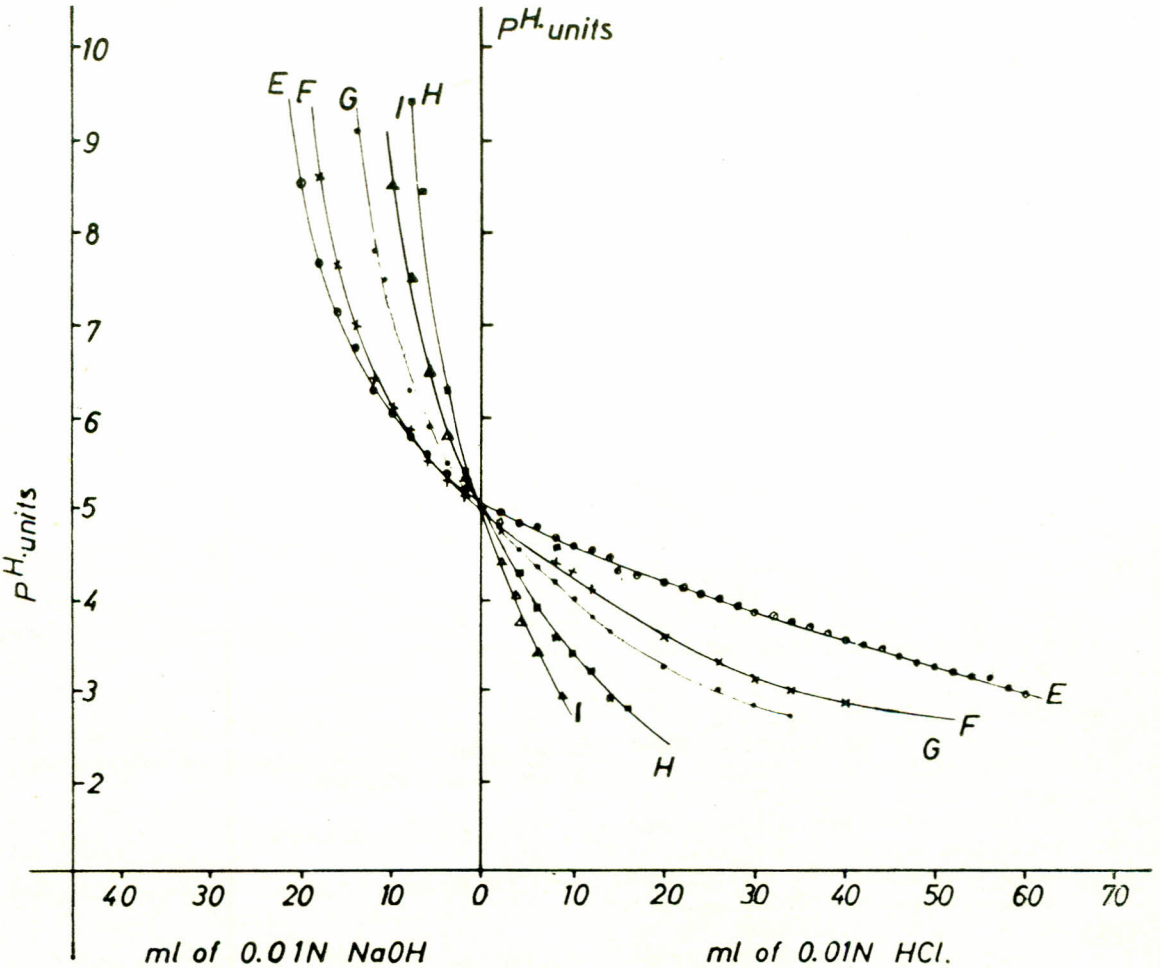


Fig. 2.—Showing pH changef or solutions of set B.

Curves shown by (——O——O——)E-1.0%, (——X——X——)F-0.75%, (——●——●——)G-0.50% (——□——□——)H-0.25%, (——△——△——)I-0.10%

2.00 ml. of acid and the initial pH of the solutions are shown in the following.

Set A	Solutions	Initial pH	Mean value
	A	4.70	0.032
	B	4.70	0.053
	C	4.70	0.079
	D	4.75	0.140
	E	5.00	0.590
Set B	E	5.00	0.033
	F	5.00	0.058
	G	5.00	0.070
	H	5.00	0.130
	I	5.100	0.160

Discussion

The experimental details bear out the buffering tendency of the saponin. The buffer capacity,[3] however, is concentration dependent and in the present case best results are obtained with a 1 percent solution for low concentration acid base reactions and in a similar manner a 10 percent solution is most effective for higher concentrations. The buffer capacity may be calculated either graphically by the D.D. Van. Slyke's[4] method or may be obtained by classical method. The former method consists in plotting $\Delta B/\Delta$ pH/against B, where ΔB is change in the amount of acid or base, ΔpH is

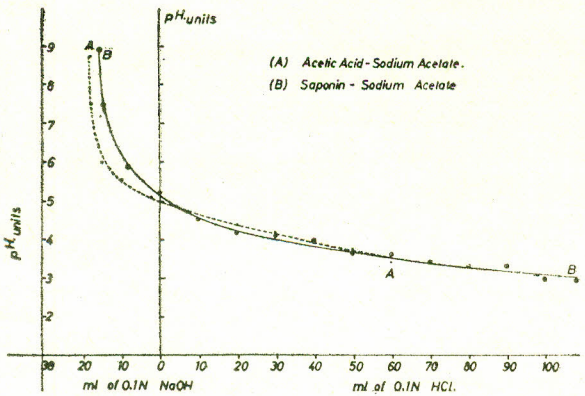


Fig. 3.—Showing pH change for acetic acid—sodium acetate and saponin sodium acetate buffer system.

the change in pH and B is number of g. equivalent of the buffer. This method gives β-value (buffering capacity) 0.074 for a 10 percent saponin solution for the pH range of 3.75 to 4.75. By the classical method the β-value of 0.08 is obtained. The effective range of the buffer may extend from 2.5 to 4.75 and maximum to 5 pH units. Thereafter it shows a sharp rise and loses the buffer activity.

The β-value for the saponin is then comparable with the known buffers, 3-5 eg. sodium acetate+acetic acid[6] which is effective in the range 3.7 to 5.6 having a β-value 0.074. It would be of interest to compare the values of such mixtures as saponin +sodium acetate and saponin+acetic acid. It has been found that the β-value for a 50:50 mixture of 0.2M sodium acetate and 2 percent saponin is 0.1 for a range of 2.5 to 5.6 pH units (Fig. 3) which is a considerable improvement on the values of both the components.[7] The mixture of saponin and acetic acid, however, has a β-value 0.08 and the presence of acetic acid does not seem to alter the buffer capacity of the saponin.

The mechanism of the buffer action of the saponin seems to be difficult to elucidate but it is probably due to the participation of the hydroxyl groups in the acid medium and the carboxyl group in the alkaline.

$$\text{Saponin} + H^{+} \rightleftharpoons \text{Saponin}^{+} + H_2O$$
$$\text{Saponin} + OH^{-} \rightleftharpoons \text{Saponin}^{-} + H_2O$$

This however needs an elaborate study and nothing definite can be said at this stage.

Another phenomenon which has been noted during this investigation is that after standing for some time in the alkaline range, the pH decreases again towards neutralisation. This and the observations noted above indicate the formation of a salt of saponin. It is probable that the hydrolysis of the sodium salt occurs slowly in the alkaline medium and finally results in the neutralisation of the solution. This may be written as:

$$\text{Saponin} + NaOH \rightleftharpoons Na^{+}\,\text{Saponin}^{-} + H_2O$$

The loss of buffer activity may also be attributed to the formation of the sodium salt.

Conclusions

Saponin may be used as a buffer in the range of 2.5 to 4.75 pH units. The buffer action may be enhanced by the addition of sodium acetate to increase the range to 5.6 pH units. Their solutions must, however be freshly prepared as they flocculate on standing.

The use of saponins and their mixture as buffer in industries is being taken up and will be described in a future publication.

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