EFFECT OF SALTS ON THE DETERMINATION OF pH BY THE INDICATOR METHOD IN PRESENCE OF IGEPON T*

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While investigating the effect of Igepon T on the colorimetric method of determination of pH, it was noticed that the pH changed considerably when sodium chloride was added to the solution. A similar effect was also noticed when sodium sulphate and calcium chloride were employed, in place of sodium chloride. A systematic study of this interesting effect was undertaken.

EXPERIMENTAL

To remove the salt impurities in Igepon T, the solid was shaken up with ethyl alcohol and the clear solution was distilled off. The solid thus obtained had an ash content of 5·0%,. 0·02% solutions of thymol blue and bromophenol blue were employed. In the following investigations, the concentrations of the indicator, the wetting agent and the buffer solutions were kept constant, while the concentration of the salt was changed.

Effect of sodium chloride on Igepon T-Thymol blue systems.—To 5 ml. of the acetate buffer (0·02 M) electrolyte concentration) 1 ml. of the thymol blue solution and 1 ml. of 0·5% of Igepon T solution were added and the total volume made up to 10 ml. The pH of this solution as determined by the glass electrode was 3·09. The pH was also determined colorimetrically employing Gillespie's method, using a Hellige Colorimeter. The acidic and basic standards of the indicator, employed for comparison, consisted of hydrochloric acid (0·2 N) and acetate buffer (4·7 pH) respectively, having the same concentrations of the indicator, the salt and the wetting agent as in the test solutions. The pH by the colorimetric method (apparent pH) was calculated by the equation

$$\mathrm{pH} = \mathrm{pK} + \log \frac{\text{basic form}}{\text{acidic form}},$$

where K is the dissociation constant of the indicator.

To another sample of the buffer-indicator-wetting agent mixture prepared as above, a known amount of sodium chloride was added and its

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apparent and true pH values were determined. The experiment was repeated for various concentrations of sodium chloride.

The effect of sodium sulphate and calcium chloride on the pH shift was also investigated.

Using bromophenol blue as the indicator, the pH shift was determined for varying concentrations of sodium and calcium chlorides. The following tables give the results obtained.

The shift in pH is expressed as:

(— Δ pH) = pH by the glass electrode — pH by the indicator method.

TABLE I

Igepon T-Thymol blue-Sodium chloride systems

pH of buffer = 3·09

Electrolyte concn. of buffer = 0·01 M

Molar concentration of sodium chloride	– ΔpH
0·00	1·73
0·02	1·62
0·04	1·57
0·05	1·54
0·06	1·47
0·08	1·41
0·10	1·32
0·30	1·18
0·50	1·07
0·80	1·00
1·10	1·00

TABLE II

Igepon T-Thymol blue-Sodium sulphate system

pH of buffer = 3·09

Electrolyte concn. of buffer = 0·01 M

Molar concentration of sodium sulphate	– ΔpH
0·00	1·73
0·01	1·68
0·02	1·59
0·03	1·51
0·04	1·47
0·05	1·42
0·40	1·05

TABLE III

Igepon T-Thymol blue-Calcium chloride system

pH of buffer = 3·09

Electrolyte concn. of buffer = 0·01 M

Molar concentration of calcium chloride	−ΔpH
0·000	1·73
0·00016	1·63
0·00049	1·54
0·0008	1·44
0·0011	1·36
0·0015	1·26
0·0016	1·20
0·0033	1·15
0·0049	1·12
0·0065	1·11
0·0200	0·90
0·0330	0·80
0·0800	0·75

TABLE IV

Igepon T-Bromophenol blue-Sodium chloride system

pH of buffer = 4·27

Electrolyte concn. of buffer = 0·005 M

Molar concentration of sodium chloride	−ΔpH
0·00	0·08
0·02	0·15
0·10	0·26
0·30	0·42
0·50	0·49
0·80	0·53

TABLE V

Igepon T-Bromophenol blue-Calcium chloride system

pH of buffer = 4·27

Electrolyte concn. of buffer = 0·005 M

Molar concentration of calcium chloride	−ΔpH
0·0000	0·08
0·00017	0·11
0·00041	0·15
0·0017	0·23
0·0041	0·27
0·016	0·39
0·033	0·42
0·050	0·45

TABLE VI

Igepon T-Thymol blue-Calcium chloride system

pH of buffer = 3·08

Electrolyte concn. of buffer = 0·01 M

Concn. of Igepon T = 0·10%

Molar concentration of calcium chloride	– ΔpH
0·0000	1·89
0·0016	1·40
0·0024	1·36
0·0049	1·25
0·0055	1·21
0·0065	1·10
0·0330	0·90
0·0800	0·80

DISCUSSION

1. *Effect of Sodium chloride on Thymol blue-Igepon T systems.*—Table I shows that the rate of fall of – Δ pH is rapid in the beginning but with an increase in concentration of the salt, –Δ pH attains a limiting value. This can be explained in the following manner. Thymol blue is uncharged[2] in the acid form and has a single negative charge, in the basic form. At a given pH of the buffer, there will be an equilibrium between the acid and the basic forms, governed by the equation

$$\mathrm{pH} = \mathrm{pK} + \log \text{basic form} \;/\; \text{acidic form} \;.$$

When the wetting agent is added, a complex is formed between the wetting agent and the indicator. The stability of this complex however, depends upon the nature of the ions produced by the wetting agent and the indicator. In the case of thymol blue system, the extent of complex formation between the negatively charged basic form of the indicator and the anion of the wetting agent, will be comparatively small, owing to the like charges. On the other hand, a complex of higher stability is formed between the acid form of the indicator, which is uncharged, and the anion of the wetting agent. Formation of this complex shifts the equilibrium between the acidic and the basic forms of the indicator. As the complex has the same colour effect as the free acid form of the indicator, there is an apparent enhancement of the acid form and the pH of the solution appears as having shifted to the acid side. A salt added to the system scarcely affects the formation of the complex between the uncharged acid form of the indicator and the anion of the wetting agent.[1] But, as the salt lowers the zeta potential, it reduces the repulsion between the anions of the wetting agent and of the basic form of the indicator and enhances the tendency to form a complex between the two (*viz.*, wetting agent and the basic form of the indicator). The shift in pH thus becomes less. It is known that the zeta potential is reduced to a limiting value with the progressive addition of a salt.[3] The formation of the complex between the wetting agent and the basic form of the indicator and consequently the value of $-\Delta$ pH can therefore be expected to reach a limiting value.

2. *Effect of Sodium sulphate on Thymol blue-Igepon T systems.*—The results obtained with sodium sulphate are similar to those got with sodium chloride. This is to be expected, as we are dealing with the same cation, in the two salts.

3. *Effect of Calcium chloride on Thymol blue-Igepon T systems.*—In general, calcium chloride affects the system in the same way. But the effect of concentration of salt is far more marked than in the case of sodium chloride. This is due to the divalency of the cation of the salt. The ratio of the concentrations of sodium and calcium ions required to induce the same pH shift, is about 40, as in the case of the " Hardy-Schulze Law ".

The effect of aluminium chloride could not be tried as the wetting agent was precipitated by this salt. The results in Tables III and VI indicate that the general nature of the pH shift remains practically unaltered when the concentration of the wetting agent is changed from 0·05% to 0·1%.

4. *Effect of Sodium chloride on Bromophenol blue-Igepon systems.*—In this system, the shift in pH, *viz.*, $-\Delta$ pH increases with an increase in the concentration of the salt. This effect is the opposite of what has been noticed in the case of Thymol blue-Igepon T systems but can be explained on the same basis, *viz.*, the influence of the electrical charge on complex formation. Unlike thymol blue, the indicator bromophenol blue has one negative charge in the acid form and two negative charges in the basic form. The repulsion between the acid form of the indicator and the wetting agent ion is therefore much lower than that between its basic form and the wetting agent. Complex formation between the acid form of the indicator and the wetting agent will be greater than that between the basic form and the wetting agent. The apparent pH will therefore be always lower than the pH got by E.M.F. method. When a salt is added, the zeta potential will be lowered in both forms of the indicator. But the effect of the negative charge on the basic form would be roughly twice as great as on the acid form of the indicator. Complex formation with the basic form will therefore be less. Owing to the relatively larger formation of the complex of the acid form

the value of $-\Delta$ pH increases with an increase in the concentration of the salt.

The results obtained with calcium chloride are similar in nature to those got with sodium chloride. As pointed out already, the effect of concentration on the change of $-\Delta$ pH is very pronounced. The reasons for such a behaviour have already been discussed.

SUMMARY

1. In presence of Igepon T, the pH of solutions, as measured colorimetrically with thymol blue and bromophenol blue as indicators, is found to be lower in value than that obtained with the glass electrode. The value of $-\Delta$ pH (pH by the glass electrode $-$pH by the colorimetric method) is found to be influenced by the presence of salts like sodium chloride, sodium sulphate and calcium chloride.

2. With thymol blue, an increase in salt concentration diminishes the value of $-\Delta$ pH, while with bromophenol blue the opposite effect is observed.

3. With calcium chloride, the effect of salt concentration on $-\Delta$ pH is far more pronounced than with sodium chloride.

4. The results are explained on the basis of the effect of the salts on zeta potential, in relation to the formation of complexes by the acidic and the basic forms of the indicator, with the wetting agent.

REFERENCES

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