

EFFECT OF SURFACE-ACTIVE AGENTS ON INDICATORS†

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INTRODUCTION

It is known that surface-active substances influence the determination of pH when carried out by the indicator method. Smith and Jones¹ found that the presence of commercial wetting agents (Gardinol CA and Gardinol WA) often caused an error of more than one unit in pH when the common indicators are employed in the measurement. Hartley² made an extensive qualitative study of the phenomenon employing paraffin chain salts and found that the order of magnitude of the influence could be correlated with the valence change in indicators accompanying the colour change. In a recent paper, Hartley and Roe³ have attempted to correlate the observed displacement of pH with the cataphoretic mobility of the micelles of the paraffin chain salts. The object of the present work is to study the effect quantitatively with a view to elucidate the phenomenon.

EXPERIMENTAL

The surface active substances used in the present work are Nekal BX (sodium di-alkyl naphthalene sulphonate) and Igepon T (sodium salt of oleyl-N-methyltaurine). Nekal BX was purified by the method described previously.⁴ Igepon T was purified by a similar method using ethyl alcohol as the solvent. The product was dried in vacuum at 80° C. to 90° C. as it melted when dried at 100° C.

The indicators employed were thymol blue and bromphenol blue supplied by the Hellige Company along with their comparator. 0.04 per cent. solutions were prepared by dissolving the solid indicators in the requisite quantity of alkali and making up with water.⁵

The Hellige comparator was found to be unsuitable for the present work. Apart from the method being approximate (correct only to 0.2 unit) it was found impossible to match the colour of the test solution against any of the

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discs, when the wetting agent was present. For, the wetting agent is found to influence the light absorption characteristics of the indicators. The Hellige colorimeter was therefore employed for determining the ratio of the concentration of basic form to that of the acid form present in the test solution. The apparent pH was calculated therefrom by means of the equation $\text{pH} = \text{pK} + \log \frac{(\text{basic form})}{(\text{acid form})}$. The standards used for such comparison always contained the wetting agent in the same concentration as in the test solution thus compensating for the change in the absorption characteristics. By taking this precaution excellent matching could always be obtained. With bromphenol blue colour matching was not so good. The standards used were of the following composition:—

Standards for thymol blue—

Acid standard.—The solution was made up from:

- (a) 0.5 c.c. of the stock solution of the indicator.
- (b) 1.0 c.c. of 2 N hydrochloric acid solution.
- (c) Wetting agent in quantities to give the same concentration as in test solution. And
- (d) Water to make up to 10 c.c.

Basic standard :—

- (a) 0.5 c.c. of the stock solution of the indicator.
- (b) Acetate buffer of pH 4.7 having sodium acetate concentration 0.2 N.
- (c) Sufficient amount of wetting agent to give the same concentration as in test solution. And
- (d) Water to make up to 10 c.c.

Standards for bromphenol blue—

Acid standard:—

- (a) 0.5 c.c. of the stock solution of the indicator.
- (b) 1 c.c. of 2 N hydrochloric acid solution.
- (c) Wetting agent in quantities to give the same concentration as in the test solution. And
- (d) Water to make up to 10 c.c.

Basic standard :—

- (a) 0.5 c.c. of the stock solution of the indicator.
- (b) 5 c.c. of N sodium acetate.
- (c) Wetting agent in quantities to give the same concentration as in the test solution. And
- (d) Water to make up to 10 c.c.

Test solutions were prepared as follows:—

- (a) 0.5 c.c. of the stock solution of the indicator.
- (b) Sodium acetate and hydrochloric acid in quantities to give a pH in the working range of the indicator and ionic strength of either 0.1 or 0.01 as required.
- (c) Wetting agent in quantities to get a required concentration.

And (d) Water to make up to 10 c.c.

The Sorenson values of the test solutions were determined by the quinhydrone method. The results obtained are given in Tables I to VIII.

In measuring the apparent pH values the adjustments with the colorimeter could be made correct to about 0.03 unit in the sensitive range. *The quinhydrone and the indicator methods gave slightly different values for buffered solutions and so an appropriate correction was applied in arriving at the $-\Delta\text{pH}$ values given in the tables.*

TABLE I

Wetting agent : Igepon T. Indicator : Thymol Blue. Ionic strength of buffer = 0.01.

g. of wetting agent in 100 c.c. of the solution	Sorenson value (pH by quinhydrone electrode)	Apparant pH as shown by the indicator	Apparent shift in pH ($-\Delta\text{pH}$)	$K_1 = 2.8; K_2 = 968$ ($-\Delta\text{pH}$ theoretical)
1.000	3.24	1.10	2.13	2.41
0.500	3.07	0.97	2.09	2.31
0.200	2.94	0.83	2.10	2.10
0.100	2.88	0.96	1.91	1.88
0.050	2.86	1.10	1.75	1.64
0.020	2.83	1.30	1.52	1.26
0.010	2.83	1.80	1.02	1.02
0.005	2.83	2.17	0.65	0.76
0.000	2.83	2.82	0.00	0.00

TABLE II

Wetting agent : Igepon T. Indicator : Thymol Blue. Ionic strength of buffer = 0.1.

g. of wetting agent in 100 c.c. of the solution	Sorenson value (pH by quinhydrone electrode)	Apparent pH as shown by the indicator	Apparent shift in pH ($-\Delta\text{pH}$)	$K_1 = 19.1; K_2 = 706$ ($-\Delta\text{pH}$ theoretical)
1.000	2.97	1.37	1.53	1.55
0.500	2.90	1.33	1.50	1.52
0.350	2.84	1.33	1.44	1.51
0.200	2.84	1.30	1.47	1.47
0.150	2.84	1.35	1.42	1.44
0.100	2.84	1.40	1.37	1.39
0.050	2.84	1.46	1.31	1.27
0.020	2.84	1.68	1.09	1.04
0.010	2.84	1.94	0.83	0.83
0.005	2.84	2.09	0.68	0.62
0.000	2.83	2.76	0.00	0.00

TABLE III

Wetting agent : Igepon T. Indicator : Bromphenol Blue. Ionic strength of buffer = 0.01

				$K_2 = 6.6$
2.00	4.54	3.21	1.41	1.52
1.00	4.41	3.61	0.88	0.88
0.50	4.41	3.82	0.67	0.63
0.35	4.41	3.86	0.63	0.52
0.20	4.39	4.04	0.43	0.37
0.10	4.39	4.22	0.25	0.22
0.05	4.37	4.28	0.17	0.12
0.00	4.36	4.44	0.00	0.00

TABLE IV

Wetting agent : Igepon T. Indicator : Bromphenol Blue. Ionic strength of buffer = 0.1.

g. of wetting agent in 100 c. c. of the solution	Sorenson value (pH by quinhydrone electrode)	Apparent pH as shown by the indicator	Apparent shift in pH ($-\Delta$ pH)	$K_2 = 21$ ($=\Delta$ pH theoretical)
2.00	4.70	3.35	1.51	1.63
1.00	4.70	3.52	1.34	1.34
0.50	4.70	3.80	1.06	1.06
0.20	4.71	4.13	0.74	0.72
0.10	4.71	4.30	0.57	0.49
0.05	4.73	4.43	0.46	0.32
0.00	4.73	4.89	0.00	0.00

TABLE V

Wetting agent : Nkal BX. Indicator : Thymol Blue. Ionic strength of buffer = 0.01.

2.50	3.17	1.52	1.58
1.00	3.00	1.42	1.51
0.50	2.92	1.64	1.21
0.35	2.86	1.90	0.89
0.20	2.86	2.27	0.52
0.16	2.84	2.34	0.43
0.10	2.84	2.40	0.37
0.08	2.84	2.42	0.35
0.04	2.84	2.54	0.23
0.02	2.83	2.61	0.15
0.00	2.83	2.76	0.00

TABLE VI

Wetting agent : Nekal BX. Indicator : Thymol Blue. Ionic strength of buffer = 0.1.

<i>g.</i> of wetting agent in 100 c. c. of the solution	Sorenson value (pH by quinhydrone electrode)	Apparent pH as shown by the indicator	Apparent shift in pH ($-\Delta$ pH)
1.70	2.80	1.22	1.60
0.83	2.63	1.29	1.36
0.45	2.54	1.33	1.23
0.35	2.41	1.42	1.01
0.20	2.41	1.69	0.74
0.18	2.41	1.70	0.73
0.12	2.41	1.96	0.47
0.08	2.41	2.25	0.18
0.04	2.41	2.42	0.01
0.02	2.41	2.42	0.01
0.00	2.40	2.42	0.00

TABLE VII

Wetting agent : Nekal BX. Indicator : Bromphenol Blue. Ionic strength of buffer = 0.01.

2.0	4.42	3.96	0.50
1.0	4.40	4.14	0.30
0.5	4.37	4.34	0.07
0.3	4.37	4.39	0.02
0.1	4.37	4.40	0.01
0.0	4.36	4.40	0.00

TABLE VIII

Wetting agent : Nekal BX. Indicator : Bromphenol Blue. Ionic strength of buffer 0.1.

2.00	4.68	4.20	0.61
1.00	4.70	4.34	0.49
0.50	4.71	4.65	0.19
0.30	4.71	4.77	0.07
0.20	4.71	4.80	0.04
0.10	4.71	4.84	0.00
0.05	4.71	4.85	0.00
0.00	4.71	4.84	0.00

DISCUSSION

1. *The mechanism of displacement of pH.*—After making an extensive qualitative study of the effect of a few paraffin chain salts on a number of indicators, Hartley has suggested that the observed displacement of pH is due to the preferential adsorption of one of the forms of the dye on paraffin chain salt micelles. Indication of pH by a dye is dependent on the equilibrium between the two forms of the dye differing in valence. The equilibrium ratio of the two forms is determined by the pH of the solution. The acid form

of the dye is produced by the union between the basic form and the hydrogen ion. The valence of the acid form is therefore higher algebraically than the valence of the basic form. The various possible types of valence for the two forms are:—

- I. Both forms positively charged,
- II. Acid form positively charged; basic form uncharged;
- III. Acid form uncharged; basic form negatively charged; And
- IV. Both forms negatively charged.

The surface active substances can also be divided into the different classes according to the charge possessed by their micelles in solution. When an indicator is added to a solution containing a surface-active agent, there is a possibility that the micelles of the latter may preferentially adsorb one of the forms of the indicator. Normally cationic micelle, however, would not take up any of the indicator of type I and anionic micelle would not adsorb any of the indicator of type IV owing to electrical repulsion; in these cases therefore, the surface-active substance would not affect the determination of pH. This forms the basis of the sign rule of Hartley.² In the other cases, there would be a preferential adsorption of one of the forms of the indicator. Owing to the influence of the electric forces, the acid form which has a higher positive charge (or a lower negative charge) would be preferentially taken up by an anionic micelle. The equilibrium between two forms would be consequently displaced, there being a shift towards the acid side. This results in the indication of lower pH. A cationic micelle would behave in the opposite way causing an apparent increase in pH.

In a later paper, Hartley has put forth another mechanism for explaining the displacement of pH brought about by paraffin chain salts when diphenylazo-*o*-nitrophenol is used as indicator. In this case both the forms are almost completely adsorbed by the paraffin chain micelles. The micelle being negatively charged has in its immediate neighbourhood a high concentration of H^+ ions. The indicator therefore finds itself in a region of low pH. The pH indicated therefore is low and gives an idea of H^+ ion concentration near the surface of the micelles. Hartley has shown that there is an approximate correlation between the zeta potential of the micelle got from mobility measurements and that calculated from indicator experiments.

A complete picture of the phenomenon however can only be got by combining both the ideas put forth by Hartley and the following detailed mechanism is therefore proposed in the present paper. The usual indicators are amphipathic substances having both a hydrophobic and hydrophilic portion in the molecule. The surface-active agents are also amphipathic

by nature. When both these types of molecules are present in solution there is a tendency for complex formation. The complex formation is brought about by the union of hydrophobic portion of the indicator with the hydrophobic portion of the molecules or micelles of the surface-active substances. The proportion of the acid and the basic forms of the indicator present in the complex would be controlled by (a) the local H^+ ion concentration near the indicator ion and (b) the relative life of the two types of the complexes. Due to the difference in the electrical charge associated with the two forms of the indicator, one of the forms may produce a much stabler complex than the other. It is to be pointed out that both the factors act in the same direction in any particular system. A careful study of these factors reveals that a quantitative formulation including these two factors is best done by applying the law of mass action on the basis of activities. Since, however, the activity coefficients are not available for the complicated molecules or micelles dealt with in the present work it is simpler to formulate, employing the concentration terms, and discuss qualitatively the effect of the activity coefficients.

The quantitative aspect of the problem may now be considered. In a solution containing the indicator and the surface-active agent, we have (1) the acid form of the indicator, $H\text{In}$. (2) the basic form of the indicator In^- (3) the complex between the acid form of the indicator and the surface active ion $H\text{In} \dots W^-$. And (4) the complex between the basic form of the indicator and the surface-active substance $\text{In}^- \dots W^-$. These are in equilibrium. If activity coefficients are not taken into account and if the influence of micelle formation is assumed to be negligible, the following relationship can be formulated. The theory would be applicable to the region wherein micelle formation does not set in or in cases where micelle formation would not effect the general behaviour of the system. Let the total concentration of the indicator be c_i . Let a fraction α be in the free basic form and a fraction β in the free acid form. Applying the law of mass action to complex formation, we get

$$[\text{In} \dots W^-] = k_1 c_i \alpha \{c_w - [\text{In}^- \dots W^-]\}$$

where k_1 is a constant.

$$\therefore [\text{In}^- \dots W^-] = \frac{k_1 c_i \alpha c_w}{1 + k_1 c_i \alpha}$$

Similarly,

$$[H\text{In} \dots W^-] = \frac{k_2 c_i \beta c_w}{1 + k_2 c_i \beta}$$

where k_2 is a constant. If x and y are the true and apparent pH values respectively, we get,

$$10^{x-y} = \frac{c_i \alpha}{c_i \beta}$$

and
$$10^{y-pk} = \frac{c_i \alpha + \frac{k_1 c_i \alpha c_w}{1 + k_1 c_i \alpha}}{c_i \beta + \frac{k_2 c_i \beta c_w}{1 + k_2 c_i \beta}}$$

$$\therefore -\Delta \text{pH} = x - y = \log \frac{1 + \frac{k_2 c_w}{1 + k_2 c_i \beta}}{1 + \frac{k_1 c_w}{1 + k_1 c_i \alpha}} \quad (1)$$

Now,

$$k_1 c_i \alpha = \frac{[\text{Wetting agent—basic form complex}]}{[\text{Free wetting agent}]}$$

and
$$k_2 c_i \beta = \frac{[\text{Wetting agent—acid form complex}]}{[\text{Free wetting agent}]}$$

These quantities are small as compared with unity since only a small fraction of wetting agent forms the complex. Thus, equation (1) gets reduced to,

$$-\Delta \text{pH} = \log_{10} \frac{1 + k_2 c_w}{1 + k_1 c_w} \quad (2)$$

2. *Thymol Blue-Igepon T system*.—(i) The data obtained with the Igepon T-thymol blue system, are found to be in very good agreement with the above theory, as can be seen from Tables I and II. Equation (2) has been used for calculating the theoretical values. The values of k_1 and k_2 have been determined by making use of two of the experimental values of the pH shift.

Apart from the fact that the experimental values can be fitted into the equation, it is to be pointed out that there are other interesting features in the experimental data to show that the theory adequately accounts for the experimental results:—

Igepon T being a sulphonate gives a surface-active ion which is negatively charged. The indicator thymol blue in the acid range has the basic form negatively charged and the acid form uncharged. The acid form consequently gives rise to a stabler complex. Moreover, owing to the Debye effect the negative surface-active ion induces a high local concentration of H^+ ions in the neighbourhood of the complex. Thus the proportion of acid form in the complex would be very high. In equation 3 therefore k_1 would be much smaller than k_2 . This is found to be the case.

$$(0.01 \text{ N buffer } k_1 = 2.8; k_2 = 968,$$

$$0.1 \text{ N buffer } k_1 = 19; k_2 > = 706)$$

(ii) At sufficiently high concentrations of the wetting agent, complex formation may be more or less complete; and consequently the pH shift would be practically independent of concentration. This has been found to be the case.

(iii) At low values for $k_1 c_w$, equation 3 becomes,

$$-\Delta \text{pH} = \log_{10} (1 + k_2 c_w) \quad (3)$$

It can be deduced from equation 3 that if a pH shift of 0.3 is produced by a certain concentration c_1 of the wetting agent (a) a shift of 1.0 unit would be produced by a concentration 9 c_1 and (b) a shift of 2.0 units would be brought about by a concentration 99 c_1 . These conclusions hold within the limits of the experimental error in the experiments with 0.01 N buffer solutions. With 0.1 N buffer solutions also the relation (a) is satisfied. The relation (b) is not obeyed since $k_1 c_w$ becomes comparable with unity when c_w is equal to 99 c_1 .

3. *The bromphenol blue-Igepon T system.*—It is known that the acid form of bromphenol blue has a single negative charge while the basic form has a double negative charge. According to Hartley, there should be no shift in pH with this indicator, when a surface-active substance of the type of Igepon T (which has a surface-active anion) is added.² Hartley based his conclusions on the idea that complexes between like charged molecules was improbable. But, the experiments recorded in this paper show that there is a considerable displacement of pH in the present case. This shows that in spite of the electrical repulsion between like charged molecules, complex formation between them does occur owing to the strong attractive forces between the hydrophobic portion of the wetting agent ion and that of the indicator ion. It may, however, be expected that complex formation would be relatively low; this would be especially true of the basic form which bears two negative charges. One may therefore apply equation 3 which corresponds to the existence of the complex only with the acid form. The calculated values of $-\Delta \text{pH}$ on the basis of this equation and the corresponding experimental values are given in Tables III and IV. An examination of the tables shows that the experimental data support the theory. The other interesting features which support the theory are:—

(a) The values of k_2 for bromphenol blue are much lower than the corresponding values for thymol blue showing that complex formation is much less in the former case. This is but to be expected since the acid form of the former indicator which forms the complex is negatively charged, whereas that of the latter indicator is uncharged.

(b) For the reason indicated above, the complex formation with bromphenol blue may be expected to be incomplete even at very high concentration of the wetting agent. This is in agreement with the experimental data.

(c) The conclusions drawn from equation 3 for thymol blue, also hold for bromphenol blue. The concentration of wetting agent required to effect a shift of unity in pH is about 9 times the concentration required to cause a shift of 0.3 unit.

(d) The shift in pH is found to be practically independent of indicator concentration

4. *Effect of ionic strength on the pH shift.*—A comparison of tables I and II shows that an increase in ionic strength diminishes the pH shift in the case of thymol blue. At lower concentrations of wetting agent, the effect of salts is small whereas it becomes considerable at high concentrations. The effect can be quantitatively treated on lines similar to the treatment of neutral salt effect in reaction kinetics.⁶ The exact magnitude of the effect however cannot be calculated since the value of β in the equation, of Bronsted⁶ is not known for the different molecules. Due to the “ α terms”, however (which correspond to the zeta potential effect of Hartley) k_1 would increase whereas k_2 would be unaffected. Experimentally this is found to be approximately the case. This explains, in fact, why at low concentrations of the wetting agent (where k_1 does not enter the equation), the effect of ionic strength is small. It is of interest to note that k_2 does decrease to some extent with increase of ionic strength. This decrease of the value of k_2 shows that the life of the complex from the acid form of the indicator is appreciably decreased by increase in the ionic strength. This is somewhat surprising since the acid form of thymol blue is known to be uncharged (from the simple theory of the neutral salt effect) and should not be affected by ionic strength. It is to be noted however that the acid form of the indicator has a “Zwitterion” constitution and the observed effect only shows that the wetting agent ion is nearer to the positive charge of the “Zwitterion” than to the negative charge; this is but to be expected in view of the flexible nature of the hydrocarbon chain in Igepon T, which would help the orientation of its charged end to a position of minimum potential energy.

At high concentrations of Igepon T where the complex formation is more or less complete, a change of ionic strength from 0.034 (in 1 per cent. solution of Igepon T in 0.01 N buffer) to 0.12 (in 1 per cent. solution of Igepon T in 0.1 N buffer), decreases the pH shift by about 0.6 unit. It is of interest to note that this corresponds very nearly to the effect of ionic

strength (c.a. 0.55 unit) observed by Hartley in the system investigated by him (indicator: diphenylazo-*o*-nitrophenol; surface-active substance: triethanol-ammonium cetane sulphonate). This shows that the changes in potential in the neighbourhood of the complex brought about by salts are almost the same in the two systems.

A few experiments were tried with a view to get the maximum possible pH shift. It was possible to get as high a shift as 2.4 units by having the wetting agents at a concentration of 0.2 per cent. in water and adjusting the pH to 4.2 (quinhydrone electrode) by adding acetic acid.

With bromphenol blue, increase in ionic strength *increases* the pH shift. This surprising feature is just the opposite of what has been observed in the present work with thymol blue and by Hartley and Roe with diphenylazo-*o*-nitrophenol. This effect can be explained as follows:—As is already pointed out, the basic forms of the indicator which bears two negative charges, does not form any complex at all due to strong electrical repulsion. Increase of ionic strength no doubt decreases electrical repulsion; but the repulsion is yet too strong (at ionic strength = 0.1) for any complex formation. Thus the basic form does not play any role in bringing about the observed effect. For the same reason the observed pH changes are entirely determined by k_2 and follow equation (4). Complex formation of the acid form of the indicator however, is enhanced by the increase in ionic strength due to diminution in the electrical repulsion and thus causes the observed effect.

5. *Nekal BX-Thymol Blue System*.—An examination of the data in Tables 5 and 6 shows that the theory worked out for Igepon T is not applicable to the present system. In the present case there is a certain concentration of the wetting agent at which the pH shift begins to increase considerably with concentration. This concentration value is 0.2 to 0.3 per cent. with 0.01 N buffer and 0.04 to 0.08 per cent. with 0.1 N buffer. There is a striking coincidence between these values and the micelle formation concentrations got from surface tension studies⁴ (*viz.*, 0.07 per cent. in 0.1 N buffer and 0.27 per cent. in 0.01 N buffer). In this system the micelles appear to be much more effective than the single molecules in bringing about the pH shift. The complex formation is not as strong as with Igepon T since Nekal BX is relatively a short molecule and the electrical repulsion between the two negatively charged portions in the complex is consequently strong.

6. *Nekal BX-Bromphenol Blue System*.—The displacement of pH in the above system is very small. This is to be expected for (a) Nekal BX is

a short molecule and hence electrical repulsive forces would be strong rendering the complex relatively unstable and (b) bromphenol blue having both the forms negatively charged would not be taken up by the wetting agent to any large extent. Since the shift is very small, no discussion of the quantitative aspect is possible. It may, however, be pointed out that the shift is marked, only at concentrations higher than at which micelle formation has occurred.

7. *Wetting power and pH shift.*—Since wetting action and the pH shift both involve the union of hydrophobic portions, it may be expected that there should be a general correlation between pH shift and wetting power. An extensive investigation is desirable from this point of view. The observations in the present work show that Igepon T is a much better wetting agent than Nekal BX, a conclusion which is also supported by surface tension studies⁴.

SUMMARY

1. There is an apparent shift towards the acid side in the pH of buffered solutions as measured by the use of the indicators, thymol blue and bromphenol blue when wetting agents like Igepon T and Nekal BX are present in the system.

2. Igepon T shows a very large shift with thymol blue. Under favourable conditions the shift may be as large as 2.4 units, an effect much bigger than what has been reported in literature so far for any system; Nekal BX shows less of the pH shift. Both the wetting agents affect bromphenol blue to a smaller extent.

3. A quantitative investigation of the phenomenon has been made. A theory has been put forth, based on the formation of a complex between the wetting agent and the indicator to account quantitatively for the effect of concentration of the wetting agent on the pH shift.

4. Igepon T shows a marked shift with bromphenol blue as well. This forms a clear exception to the sign rule of Hartley.

5. Increase in ionic strength decreases the pH shift with thymol blue as it is the case with the system worked by Hartley and Roe. When bromphenol blue is used neutral salts produce an opposite effect. An explanation is offered which account for these diverse results.

6. The variation of pH shift with concentration of Nekal BX with thymol blue indicates that micelle formation of the wetting agent occurs rather suddenly.

7. The possible relationship between the pH shift and wetting power is pointed out.

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