INFLUENCE OF SURFACE ACTIVE AGENTS ON SPECTROPHOTOMETRIC DETERMINATIONS OF pH

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Received September 11, 1958

(Communicated by Dr. K. S. G. Doss, f.a.sc.)

INTRODUCTION

pH of a solution containing an indicator and surface active agent when determined colorimetrically shows an apparent shift from the true Sorenson value. Smith and Jones,[1] Hartley[2] and Roe[3] have in the past studied this phenomenon qualitatively. They also tried to correlate the effect with valence change in indicators and the cataphoretic mobility of the micelles formed by paraffin chain salts used as wetting agents. Later Krishnappa *et al.*[4] tried to apply the law of mass action to the complexes formed by the wetting agents with the indicators. They thus postulated a quantitative approach according to which

$$- \Delta \text{pH} = \log \frac{1 + k_2 C_w}{1 + k_1 C_w}$$

where k_1 and k_2 are the stability constants for the complexes formed by the wetting agent with the indicator and C_w is the concentration of the wetting agent. Their experiments using Igepon-T agreed with the above relation whereas Nekal-BX showed large deviations. However, a literature survey indicated that during the last 10, 12 years not much further work has been done in this direction and that the above equation has not been applied to the large number of other wetting agents now known. It was, therefore, considered worthwhile to study the effect of a few more wetting agents on thymol blue itself in acid solutions and the results are reported in this paper.

EXPERIMENTAL

Manoxol-OT (a B.D.H. product, 100% Aerosol-OT), Teepol and Dodecyl benzene sodium sulfonate (active constituent of Stanvac detergent 4OE) have been used in this work.

The Stanvac detergent 4OE (containing 38% of dodecyl benzene sodium sulfonate and balance mostly sodium sulfate with small percentage of phosphate and sodium chloride) was extracted with methanol (GR), filtered and

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the filtrate evaporated to dryness over a steam-bath. The residue was obtained as an yellowish-white soapy solid. The methanol extraction was repeated to remove all the inorganic sulphate and chloride and the residue thus obtained was used in the work.

A 0·04% solution of thymol blue is prepared by dissolving the solid indicator (Mercks GR quality) in 0·5 c.c. of N NaOH and making up with water.

UNICAM SP 600 spectrophotometer was employed to determine the ratio of the concentrations of the basic to acidic form of the indicator present in the test solution. The apparent pH was calculated from the equation

$$\mathrm{pH} = pk - \log \frac{a_b - a_x}{a_x - a_a}$$

where a_b, a_x and a_a are the absorbancies of the basic standard, the test solution and the acid standard respectively. The standards used were the following ones:—

Acid standard.—2·5 c.c. of 0·04% solution of thymol blue + 36·65 c.c. of N HCl; made up to 50 c.c. (the Sorenson value of this solution was found to be about 0·494).

Basic standard.—2·5 c.c. of 0·04% solution of thymol blue + 10 c.c. of buffer of pH 4·95; made up to 50 c.c.

Test solution.—To 2·5 c.c. of 0·04% solution of thymol blue, appropriate amounts of sodium acetate and hydrochloric acid were added to get the required pH when made up to 50 c.c. But, before making up different volumes of a solution of wetting agent (WA) were added to give the required concentration when finally made up to 50 c.c. with water.

The Sorenson values of test solutions and standards were determined by the quinhydrone method using an OSAW potentiometer and a multiflex galvanometer with a sensitivity of $4·45 \times 10^{-9}$ A/mm.

RESULTS AND CALCULATIONS

A set of experiments, with varying amounts of 0·60% solution of the Manoxol-OT, was carried out with potassium chloride and hydrochloric acid buffer of pH 2·0. It was noted that some experimental solutions, particularly at higher concentrations of WA are not absolutely clear and hence only concentrations below 0·4% of WA were reported. The absorbancies of all the solutions were measured at a wavelength of light = 543 $m\mu$, corresponding to maximum absorption as found by studying the absorption spectrum of thymol blue in the acid standard.

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In order to compensate for the light absorption characteristics due to the turbidity alone, the percentage transmissions of blank solutions, *i.e.*, solutions exactly similar to the test solutions but without the indicator being present, were measured separately. The difference between the percentage transmission of water and each of the above blank solutions (buffer + wetting agent) was found out and added on to the percentage transmission of the test solution (buffer + wetting agent + indicator), thus making good the error due to the turbidity, provided it is simply additive and does not produce other complications. The apparent Δ pH values (the difference between the Sorenson value and the pH by spectrophotometric method) as calculated from such corrected data do not appear to vary regularly with increasing amounts of the wetting agent (Table I, Column 3). Other corrections were therefore applied.

Normally acid standard, as used for such purposes should have a pH = $pk - 2$. But as the pk value for thymol blue is $1 \cdot 7$,[5] no such acid standard is practicable. Further, it would be seen that the acid standard initially used by us as well as Krishnappa *et al.* had a pH of about $0 \cdot 5$ or more. But when the wetting agent is present the apparent pH is diminished to a value roughly equal to $pk - 2$, thereby compensating and giving an absorbance value which may be taken as a_a. It is on account of this factor that Krishnappa *et al.* could get coherent results even when using an acid standard solution of pH as high as $0 \cdot 5$–$0 \cdot 7$. The same procedure was adopted by us also and gave reasonable results at low concentration of wetting agent (WA $0 \cdot 02\%$). However, when higher concentrations of WA were used to make up the acid standards, they became turbid and so this method of compensation could not be applied. The a_a value for pure acid standard free of WA also did not lead to satisfactory results as Δ pH became imaginary as a_x, often came out to be greater than a_a. In order to apply the necessary correction, therefore, a theoretical value of a_a was computed as shown below:—

pH (Sorenson value) of the acid standard $= 0 \cdot 4942$

The absorbance of the acid standard (observed) $a_a = 1 \cdot 4500$

The absorbance of the basic standard $= 0 \cdot 0375$

$$pH = pk - \log_{10} \frac{HA}{A}$$

$$0 \cdot 4942 = 1 \cdot 7 - \log_{10} \frac{HA}{A}$$

$$\therefore \quad \log \frac{HA}{A^-} = 1 \cdot 7 - 0 \cdot 4942 = 1 \cdot 2058$$

TABLE I

a_e (Corrected) $= 1 \cdot 5380$
a_b $= 0 \cdot 0375$
pH (Sorenson Value) of the acid standard $= 0 \cdot 4942$

Conc. of WA	Manoxol OT				Dodecyl benzene sodium sulfonate			
	Ionic St. ·5		Ionic St. ·02		Ionic St. ·02		Ionic St. ·2	
	pH by QH	Δ pH by spectrophotometer	pH by QH	Δ pH by spectrophotometer	pH by QH	Δ pH by spectrophotometer	pH by QH	Δ pH by spectrophotometer
1	2	3	4	5	6	7	8	9
·39	1·93	−0·19	2·68	−0·98	3·12	−2·26	..	..
·30	1·91	−0·24	2·74	−0·81	3·11	−2·13	2·33	..
·20	1·91	−0·44	2·71	−0·60	2·97	−1·88	2·33	−1·84
·15	1·90	−0·415	2·64	−0·52	3·02	−1·86	2·31	−1·84
·10	1·87	−0·17	2·58	−0·23	3·02	−1·63	2·31	−1·60
·08	1·85	−0·15	2·78	−0·15	3·06	−1·51	2·31	−1·52
·05	1·80	+0·12	2·62	+0·20	3·04	−1·00	2·31	−1·25
·02	1·76	+0·45	2·58	+0·36	2·99	−0·39	2·31	−0·57
·00	..	..	2·81	..	..	..	..	..

or

$$\frac{HA}{A^-} = 10^{1\cdot 2058} = 16\cdot 06$$

$$\therefore \quad 16\cdot 06 = \frac{a_b - a_x}{a_x - a_a},$$

Substituting the value of a_a (obs.) for a_x

i.e., $\qquad 16\cdot 06 = \dfrac{0\cdot 0375 - 1\cdot 450}{1\cdot 450 - a_a}$

i.e., $\qquad a_a$ (corrected) $= 1\cdot 5380.$

It is interesting and reassuring to see that the a_a value both by the addition of WA (0·02%) to acid standard and by calculation comes to be very nearly the same, although at higher concentration of WA this is disturbed by the turbidity effect. This theoretical and corrected value of a_a was employed in calculating $\varDelta$ pH in the above set of experiments. However, when in spite of this correction, the apparent pH shifts experimentally obtained with manoxol-OT were not found to be coherent, it was surmised that the turbidity effect might not be simply additive, but interfering in nature. Hence, another method of applying the turbidity correction was tried. This was based on the theory of isobestic point at which each indicator has the same absorbance irrespective of pH. It was, therefore, thought that the pH shifts and the resultant colour changes will not be able to change the absorbance at the isobestic point. As such, if for a particular buffer concentration and test solution, it could experimentally be ascertained that there was not much difference between the absorbancies of (indicator + buffer) and (indicator + buffer + wetting agent), then it may reasonably be assumed that there is not much micelle formation and that the turbidity effect is negligible. When a search for such conditions was made, it was experimentally found that a diluted buffer of the composition shown below gave the desired results:

Buffer composition :   1·1 c.c. of 1 N — Na Ac + 1·18 c.c. of
0·9868 N — HCl in 50 c.c. of test solution.

Test solutions made with the above buffer + indicator gave the same absorbance at a wavelength corresponding to isobestic point for thymol blue (482 $m\mu$) both in the absence and presence of WA (0·2%).

Accordingly, another set of experiments was carried out with above buffer and the apparent pH shifts thus computed and shown in Table I, Column 5 indicate a more regular behaviour. A diluted buffer such as this also avoids any complications due to the salt effect and high concentration of buffer.

It may be noted that in this case Δ pH gradually tends to become less negative as the concentration of the surface active agent decreases till finally at very low concentration of wetting agent (in the region of 0·05–0·02%) it becomes positive. It is worthwhile to note that none of the theories so far propounded are able to explain such behaviour and change in the sign of Δ pH.

Teepol.—A 1% (by volume) stock solution of teepol in water was prepared and was used as the stock solution. A buffer of pH 2·00 was employed. A 0·1% solution (by volume) of this detergent gives an apparent pH shift of 1·20. In view of the fact that its constitution and molecular weight could not be definitely ascertained, further work with this substance was not continued.

Dedocyl benzene sodium sulfonate.—A set of experiments with varying amounts of this detergent was carried out with buffers (made out of sodium acetate and hydrochloric acid) of different pH and ionic strengths. Unlike Manoxol-OT, this detergent is found to give quite clear test solutions and also the solubility is much higher. With the same experimental procedure, the absorbancies of standards and test solutions were measured. The apparent pH shifts were calculated and are presented in Table I, Columns 7 and 9.

It was observed in all the above cases that the apparent pH is always less than the Sorenson value and the pH shift increases continuously with increasing amounts of the wetting agent.

Discussion.—When an attempt is made to give a quantitative interpretation of these results on the lines of Krishnappa *et al.*, it is found that the respective values of K_1 and K_2 the stability constants, calculated from two different pairs of readings in the same set of experiments do not agree with each other (*see* Table II).

Further, the apparent pH calculated from the values of k_1 and k_2 (Table II) are quite different from the ones experimentally observed.

In the case of dodecyl benzene sodium sulfonate, the calculated value of k_1 comes out to be negative in all cases. So it appears that this surface active agent as well corresponds more to the case of Nekal BX[4] which did not follow the equation

$$- \Delta \, pH = \log_{10} \frac{1 + k_2 \, C_w}{1 + k_1 \, C_w}$$

TABLE II

Surface active agent	pH of the test solution used (Sorenson value)	Values calculated from the equation $-\Delta\, pH = \log_{10} \dfrac{1 + k_2\, C_u}{1 + k_1\, C_u}$		Reference to Table I
		k_1	k_2	
Manoxol-OT	2·7	33·18	794·75	Vide items 3 and 4 of column 5
	2·7	52·08	1145·10	Vide items 1 and 2 of column 5
Dodecyl Benzene Sodium Sulfonate	3·0	− 83·24	10971·5	Vide items 5 and 6 of column 7
	2·3	−148·70	9052·0	Vide items 5 and 6 of column 9

than to the case of Igepon T which followed the equation. Further work, therefore, seems to be necessary to clarify the phenomenon and to give a more generally applicable quantitative treatment by taking into account some factors, most important of which appears to be micelle formation, which have perhaps so far been not fully considered.

ACKNOWLEDGEMENT

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