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On the use of *Hibiscus subdariffa* flower extract as natural acid-base indicator

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ABSTRACT

The use of *Hibiscus subdariffa* flower extract as a naturally occurring acid-base indicator was studied. This flower contains anthocyanine pigment whose colour depends on pH. The acid-base equilibrium of this pigment was investigated using spectrophotometric method. The pk_{In} values were found to be 2.8 and 7.3. The use of this extract in acid-base titration gave similar result(s) compared to methyl orange indicator.

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Introduction

Hibiscus subdariffa (Malvaceae) is a perennial herb growing up to 2 to 2.5m tall. The economic uses of the plant are as garden ornamentals and potherbs, used locally in Africa as source of dye and timber and as medicinal plant and drink.

In Africa, the water extract of *Hibiscus subdariffa* is taken as a hot or cold drink. The drink is known as *Wanjo* in the Gambia, *Zobo* in Nigeria, *Karkaday* in Egypt and Sudan and *Omutete* in Namibia. The plant is highly cultivated in the northern part of Nigeria probably because of the favourable climate.

The plant flower contains anthocyanine [1,2] i.e. a pigment usually responsible for pink, red, purple, violet and blue colours in flowering plants. The dye extracted from the flower of the plant changes its colour according to the hydrogen ion concentration of the solution. As such, may be utilized as an acid - base indicator in neutralization titrations.

The chief characteristic of pH indicators is that their colour change from a predominantly alkaline colour is not sudden but takes place within intervals of pH. This is termed the colour-change intervals of indicators [3]. The position of the colour-change intervals in the pH scale varies widely with different indicators. The indicator is weak acid (or base) and their equilibria in aqueous solution may be written as follows;

$$HInd + H_2O \rightleftharpoons H_3O^+ + Ind$$

$$Ind + H_2O \rightleftharpoons HInd^+ + OH^-$$

$$^aH_3O^+ = \frac{KH_{Ind} \bullet {}^aH_{Ind}}{{}^aInd}$$

where KH_{Ind} is known as the thermodynamic equilibrium constant.

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where $[H_{ind}]$ and $[Ind^-]$ are concentrations of the acidic and basic forms of indicator respectively $^-VH_{Ind}$ and V_{Ind} are their activity coefficient and a = activity.

$$pH = pKH_{Ind} - Log\frac{[H_{Ind}]}{[Ind]} - Log\frac{VH_{Ind}}{V_{Ind}}$$

Most acid - base indicators are organic compounds exhibiting the properties of weak acids or bases. The reactions of proton transfer for such substances are attended by structural changes with the formation, disappearance or change in the chromophoric groups. In monochromatic indicators, the chromophoric groups are contained in only one form of the indicator (protonated or deprotonated), while in dichromatic indicators, these groups are present in the structure of both forms [4].

The equilibrium indicator solution is mainly influenced by temperature and ionic strength of the

solution. A change in the ionic strength of the solution can shift equilibrium (the salt affect) and thereby change the intensity of the colour of one or both forms. Hence when making a colour comparison for the determination of the pH of a solution not only must the indicator concentration be the same in the two solutions but the ionic strength must also be equal. The colour - change equilibrium at any particular ionic strength (constant activity coefficient term) can be expressed by the modification equation.

$$pH = pK_{Ind} + Log\frac{[H_{Ind}]}{[H_{Ind}^{-}]}$$

where pK_{In} is termed the apparent indicator constant (equilibrium constant).

In the present work, the indicator constant was estimated using spectrophotometric method. The sensitivity of these indicators to detect the end point of acid-base titrations in the presence of the flower indicator was also evaluated in this study.

EXPERIMENTAL

Sample Collection

Dried flower (Zobo calyces) was purchased from Samaru-Zaria market. The dried flower was powdered in a mortar and then kept in plastic bottles.

Extraction of Pigment

0.25g of the dried powdered sample was extracted at room temperature with 25ml of distilled water, then centrifuged at 15000rpm for 15minutes. The extract solution was filtered off through a Whatman filter No.1 paper and then used for investigation (Spectrophotometric method).

Buffer Solution

Thiel - Schulzbuffers were prepared from oxalic, boric, succinic acids, sodium sulphate, borax and sodium carbonate to obtain the series of buffer solutions (5).

Determination of pK_{In} using Spectrophotometric Method

1ml of flower extract (pigment) and 1M $NaClO_4$ (0.5ml) were transferred into a volumetric flask (5ml) and made to the mark with each of the buffer solutions. The absorption spectrum of the solution was measured using UV-visible SP 8 - 100 spectrophotomer against blank buffer solution.

Acid - Base Titration

To compare the sensitivity of the flower pigment with the synthetic acid-base indicators, different concentrations (0.01, 0.1 and 1M) of HCl were prepared and then titrated against NaOH using methylorange indicator and flower extract (pigment).

RESULTS AND DISCUSSION

Determination of Indicator Equilibrium Constant

The electronic spectrum of the flower indicator in the presence of various buffer solutions is given in Fig. 1. The figure shows that there were continuous changes in the absorbance values at different pH conditions when measured at wavelength of 560nm. The change of colour from greenish blue to red occurred in the flower extract.

The variation in absorbance (A) with pH could be used to calculate the pKa value (indicator constant) of the flower pigment indicator (6). The pK_{In} values are equal to the value of pH at half height of absorbance pH curves (Fig. 1).

$$pK_{In} = pH \text{ at } A_{½} > 1$$

$$A_{1/2} = \frac{A_{max} - A_{min}}{2} + A_{min}$$

where A_{max} and A_{min} are the maximum and minimum absorbance on absorbance - pH graph. The calculated pk_{In} values are presented in Table 1.

Table 1: Calculated pk_{In} values (indicator constants) for flower indicator and methyl – orange obtained from variation in Absorbance - pH relationship

Indicator	λnm	Pka
Hibiscus subdariffa	510, 560	2.8, 7.3
Methyl orange	509, 560	2.8, 7.4

synthetic indictor changed colour when the pH was about 4.3. This is satisfactory when titrating strong acid with a strong base in view of the sudden and very wide swing in pH at the equivalence – point. Thus the flower indicator and the methyl-orange both changed colour at about the same time in this type of titration.

Table 2: Acid- base Titration Results using Methyl orange as indicator

Titration	Rough	1	2
Final burette reading (ml)	2.4.60	48.80	40.30
Initial burette reading (ml)	.0.00	24.90	16.50
Volume of acid used	24.60	23.90	23.80

Average volume of acid used = 23.85 ml

Table 3: Acid -base titration results using flower indicator

Titration	Rough	1	2
Final burette reading (ml)	25.70	49.60	30.90
Initial burette reading (ml)	.0.00	25.90	7.30
Volume of acid used	25.70	23.70	23.60

Average volume of acid used = 23.65 ml

Acid - Base Titrations Using Flower Indicator

The investigated flower indicator (*Hibiscus sabdariffa*) was used to detect the end point of NaOH - HCl titrations with concentrations 0.01, 0.1 and 1 mol/litre. The results obtained were compared with those of methyl-orange indicator (Tables 2 and 3). From the titration both the flower indicator and the

The application indicates that the results were concordant with a percentage error ranging from 0 to 1.4% in the case of 0.1 and 1 mol titrants. However, the titrant 0.01M NaOH - HCl exhibited an obvious error in reaching more than 20% for the flower indicator. The error resulted from the effect of flower indicator's acidity on the titrant at this concentration (0.01M), in addition to a decrease of the inflection in pH of the

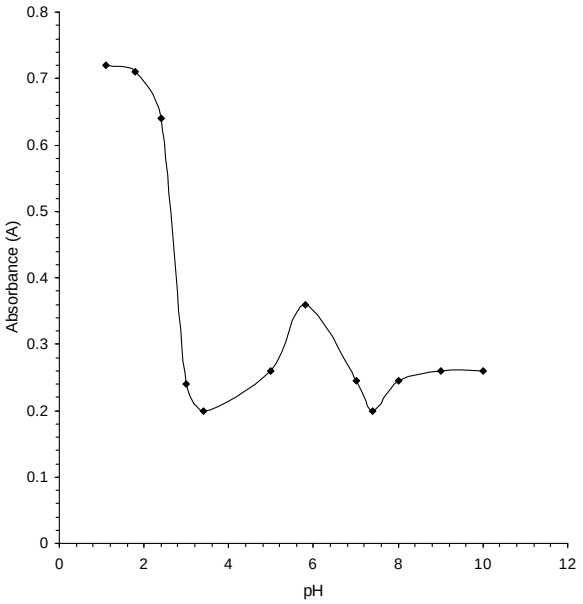

Figure 1: Determination of pKind of Habiscus subdariffa indicator

diluted system than concentrated system (from 5.3 to 8.7 instead of 3.0 to 10.5) (7). This is apart from the pH range of this indicator.

CONCLUSION

The *Hibiscus subdariffa* indicator exhibited high potential of being a cheep supplement in acid – base titrations. This flower indicator exhibited high accuracy in detecting the end - point in acid - base titrations, when the titrants were in the range 0.1 to 1M, but low sensitivity at low titrant concentrations ($\leq$ 0.01M).

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