Acid-base indicator properties of dyes from local plants I: Dyes from *Basella alba* (Indian spinach) and *Hibiscus sabdariffa* (Zobo)

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**ABSTRACT**: The acid-base indicator properties of aqueous and ethanol extracts from calyces of *H. sabdariffa* (Zobo) and a dye obtained from the ripe fruits of *Basella alba* (Indian spinach), two local plants, were investigated. A purple coloured dye obtained from the ripe fruits of *Basella alba* showed a $\lambda_{\text{max}}$ at 580nm, absorptivity of 0.2269 and was found to be photochemically unstable. A deep red coloured dye obtained from aqueous and ethanol extracts of *H. sabdariffa* had $\lambda_{\text{max}}$ of 520nm and 540nm and absorptivities of 0.1909 and 0.1187 respectively. The peaks are associated with $\pi \rightarrow \pi^*$ transitions. In strong acid/strong base titrations using the dyes as indicators, the end-points obtained agreed well with those obtained using conventional indicators. The dyes were found not suitable for weak acid/weak base titrations. The $K_a$ of the purple dye from *Basella alba* was of the order of $10^{-5}$ while that of the red dye from *H. sabdariffa* was of the order of $10^{-6}$. @JASEM

In spite of the numerous instrumental techniques currently available for the chemical analyses of various samples, conventional methods of analyses are still relevant and find application in many situations. Some conventional analytical techniques that are still popular include gravimetry and titrimetry. In titrimetry, the equivalence point is usually determined by the end point in the titration. The end point in traditional titrimetry is usually indicated by some substances added into the analyte solution, which change colour immediately after the equivalence point has been attained. These substances are generally referred to as indicators. Several types of indicators are available for different types of titrimetric analyses. For acid-base titrations, organic dyes, which are either weak acids or bases, serve excellently as indicators.

A large number of dyes are obtainable as natural products. In Nigeria, several workers have extracted a number of dyes from a variety of local plants. According to Akpuaka et al. (1998), Osabohien et al. (2002), the local plants - Camwood, Redwood, Henna, Annato, Rothmania, Terminalia, Indiqovine, Kola, Banana, Tumeric, Roselle and Ginger all contain different types of dyes which are used for various purposes. The suitability of some of these dyes for dyeing purposes has been investigated on different types of fabrics. An evaluation of other properties of a number of dyes including synthetic dyes have also been reported by a number of workers (Obanda et al., 1997; Dambata et al., 1997). Ekandem et al. (1997) and Eze et al. (2002) have also reported their findings on the use of some natural dye extracts as indicators in acid-base titrimetry. Other than these few reported cases, very little attention has been paid to the use of local dye extracts as indicators in acid-base titrimetry.

*Basella alba* (Indian spinach), called *Ogborogi* by the Izon people of the Niger Delta, is a very popular vegetable in many coastal communities of southern Nigeria. Recently, Odilora et al. (2002) extracted a purple dye from the ripe fruits of *B. alba* with several solvents including methanol and ethanol. The purple dye was applied on 100% cotton and polyester fibres and the wash fastness, heat fastness and light fastness properties of the dye were evaluated, but the acid-base indicator properties of this purple dye were, however, not reported. Ekandem et al. (1997) reported the acid-base indicator properties of ethanol extracts from flowers of *Hibiscus rosasinensis*, a Roselle plant. The acid-base indicator properties and other industrial applications of hexane extracts of *Telfairia occidentalis* (Fluted pumpkin) have also been recently reported (Eze et al., 2002). The acid-base properties of *H. sabdariffa* (also a Roselle plant) have, however, not been reported. The calyx of *H. sabdariffa* (commonly known as Zobo in the northern communities of Nigeria) is popular, mostly as a beverage drink. The acid-base indicator properties of the calyx of this variety of the Hibiscus have also not been reported. In this paper, we report the findings of our investigations on the acid-base indicator properties of dyes obtained from these two plants, *Basella alba* and *Hibiscus sabdariffa*, the Roselle plant (Zobo).

**EXPERIMENTAL**

Fresh ripe fruits of *B. alba* were obtained from a community in Bayelsa State, Nigeria. The fruits were washed with distilled water and mopped dry with...
absorbent paper to remove surface water. Some of the fruits were transferred into a 600ml beaker and macerated with a pestle. The purple liquid dye obtained after maceration was carefully decanted and stored in two storage bottles: an amber storage bottle and a transparent storage bottle. The dried calyces of *H. sabdariffa*, were obtained from a market in Port Harcourt and pre-treated to remove dirt. A 2g portion of the dried calyces was soaked in 200ml water and the procedure repeated using ethanol. Each extract was allowed to stand for 48 hrs, decanted and stored as previously described. A deep red and a purplish-red coloured dye were obtained from the water and ethanol extracts respectively.

The visible spectra of all the dye solutions were obtained immediately after extraction using a Unicam UV/Visible spectrometer, model number 040502. Visible spectra of the dyes stored in the transparent storage bottles were also obtained after 72 hours. Different percentage concentrations of the dye solutions (0, 5, 10, 15 and 20) were obtained by appropriate dilution with the extracting solvent. In the case of *B. alba* dilutions were made with water. The absorbances of the diluted solutions were measured at the respective wavelengths of maximum absorption determined from the spectra of the dyes.

Demonstrated acid-base titrations were performed with different types of acids and bases using the dyes as indicators (see Table 1). Similar titrations were performed using commercially available indicators. All reagents used for the demonstrations were of analytical grade and were used without further purification. The pH ranges over which the dyes change colour were also measured with an Orion model 310 pH meter.

**RESULTS AND DISCUSSION**

The dye obtained from the water extract of the *H. sabdariffa* L. has a $\lambda_{max}$ at 520nm while that of the ethanol extract has a $\lambda_{max}$ at 540nm. Ekandem *et al.* (1997) also obtained a $\lambda_{max}$ of 520nm for the ethanol extracts of *Hibiscus rosasinensis*. The $\lambda_{max}$ of the dye obtained from the 1:1 solvent mixture of water and ethanol was recorded at 536nm, while the value of 520nm obtained for the ethanol extract of *H. Sabdariffa* is identical to the $\lambda_{max}$ of the ethanol extract of *H. rosasinensis*. The peaks at 520nm and 540nm respectively obtained from the water and ethanol extracts may be due to solvent polarity differences which can bring about a hyposochromic or blue shift (Skoog *et al.*, 1998). The $\lambda_{max}$ of the dye obtained from *B. alba* is 580nm. The visible absorption spectra of the dyes stored in the transparent bottles were recorded after 72 hours of exposure to light. These indicate that the aqueous and ethanol extracts of *H. sabdariffa* are stable to light while the purple dye obtained from *B. alba* is photochemically unstable, as indicated by the disappearance of the peak which was at 580nm in the fresh dye.

![Fig. 1: H. Sabdariffa / water](image1)

Lambert-Beer law plots obtained from absorbance data of several diluted solutions of the dyes are shown in figs. 1-3. The absorbances of the ethanol and aqueous extracts of *H. sabdariffa* obey Lambert-Beer’s law up to 20% and 10% respectively. The absorbances of the purple dye obtained from *B. Alba* obey Lambert-Beer’s law up to concentrations of 20% of the purple dye. From the plots, the absorptivities of the aqueous and ethanol extracts of *H. sabdariffa* were found to be 0.1909 and 0.1187 respectively while that of the purple dye obtained from *B. alba* was 0.2269. The low values of the absorptivities suggest that the peaks are associated with n→$\pi^*$ transition as $\pi→\pi^*$ transitions are usually characterized by very high absorptivities (Skoog *et al.*, 1998).

![Fig 2: H. Sabdariffa / ethanol](image2)

In order to evaluate the potential for the use of the dyes as indicators in acid-base titrimetry, a number of demonstrated titrations were conducted. The end points of the demonstrated titrations using 2 to 3 drops of the dyes are reported in Table 1. The end points of the demonstrated acid-base titrations using commercially available indicators are also reported in the table.
The results in the table show that the end points obtained with the aqueous and ethanol extracts of *H. sabdariffa* in 0.1M solutions of hydrochloric acid and sodium hydroxide (i.e. strong acid/strong base) are comparable to those obtained using traditional indicators (methyl orange, methyl red and phenolphthalein). The end points obtained using the extracts of *H. sabdariffa*, in titrations involving 0.1M hydrochloric acid and 0.1M ammonium hydroxide solutions (i.e. strong acid/weak base) are also fairly comparable to the end points obtained using the commercial indicators. The end points obtained with the extracts of *H. sabdariffa* in 0.1M acetic acid versus 0.1M ammonium hydroxide titrations are not comparable to any of the end points obtained using the traditional indicators except for the aqueous extract of *H. sabdariffa* which demonstrated an end point slightly close to that of phenolphthalein in this medium. This suggests that the aqueous and ethanol extracts of *H. sabdariffa* are generally not suitable indicators in weak acid/weak base titrations. The end point obtained with the aqueous extract of *H. sabdariffa* appears fairly comparable with the results obtained using phenolphthalein and methyl red but is obviously different from the end point obtained with methyl orange in the titrations involving 0.1M acetic acid and 0.1M sodium hydroxide solutions (weak acid/strong base). Using *H. rosasnensis* as indicator in 0.1M hydrochloric acid/0.1M sodium hydroxide titrations, Ekandem et al. (1997) obtained end points comparable to those obtained using methyl red and phenolphthalein. In 0.1M hydrochloric acid and 0.1M ammonium hydroxide, they obtained comparable end points with those using methyl orange and methyl red. The end point obtained using ethanol extract of *H. sabdariffa* in the weak acid/strong base titration is not totally in agreement with those obtained using the aqueous extract of *H. sabdariffa* and the conventional indicators used in the study. The end points recorded with the fresh purple dye obtained from *B. alba* are comparable with those obtained for the aqueous and ethanol extracts of *H. sabdariffa* and all the conventional indicators used in the strong acid/strong base titrations. Comparable end points were also obtained using *B. alba* and *H. sabdariffa* and two conventional indicators (methyl red and phenolphthalein) in titrations involving weak acid/strong base. Again, the end points obtained using *B. alba* and the aqueous extracts of *H. sabdariffa* were very comparable in the weak acid/strong base titrations. The results obtained using the purple dye of *B. alba* in titrations involving weak acid and a weak base were not in agreement with the end points obtained with other indicators. This observation suggests that the purple dye of *B. alba* cannot serve as a suitable indicator in acid/base titrimetry involving a weak acid and a weak base.

The pH sensitivities of the dyes were evaluated by measuring the pH of the medium just before and after colour change has occurred. The two pH values were taken as the pH range over which colour change occurred to indicate the end point. The relationship between the pH of an indicator, its dissociation
constant and the concentrations of the conjugate base and acid forms of the indicator is mathematically expressed by the following equation (Eq. 1) (Skoog et al, 1998).

\[
pH = pK_a + \log \frac{[\text{In}^-]}{[H\text{In}]}\]

where In⁻ and HIn are the two forms of the indicator which usually have different colours. At the equivalence point, the concentrations of the two forms, In⁻ and HIn, are equal. Equation (1) therefore reduces to

\[
pH = pK_a\]

The aqueous extract of H. sabdariffa changes colour from pink to green in the pH range of 3.79 to 7.70 in the titration involving 0.1M HCl and 0.1M NaOH solutions. The purple dye of B. alba changes colour also from pink to green in the pH range of 6.68 to 8.66. Therefore the pKₐ and Kₐ of H. sabdariffa are 5.74 and 1.82 x 10⁻⁶ respectively. Ekandem et al. (1997) reported a pH range of 4.78 to 6.35 over which the ethanol extract of H. rosasinensis changed colour. They also reported the pKₐ and Kₐ values of H. rosasinensis as 5.56 and 2.75 x 10⁻⁶ respectively. The pKₐ value obtained for H. sabdariffa is very similar to that reported for H. rosasinensis. The order of magnitude of the Kₐ values are also comparable. The pKₐ and Kₐ values of B. alba are 5.57 and 2.69 x 10⁻⁶ respectively.

It can be concluded from the results of this study that aqueous and ethanol extracts of H. sabdariffa and the purple dye of B. alba can serve as suitable indicators in acid-base titrimetry involving a strong acid and a strong base. The extracts from H. sabdariffa and the dye from B. alba were found completely unsuitable for weak acid versus weak base titrimetry. The purple dye of B. alba also proved fairly suitable as indicator in weak acid/strong base titrimetry. The ethanol and aqueous extracts of H. sabdariffa were also shown to be suitable indicators in strong acid/weak base titrimetry. Except for the photostability of the chromophore in the purple dye of B. alba which is responsible for the disappearance of the peak at 580nm, the dye of B. alba can be used as suitable indicator in all acid-base titrimetry (except weak acid versus weak base).

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REFERENCES


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