JASEM ISSN 1119-8362

Full-text Available Online at www.bioline.org.br/ja

J. Appl. Sci. Environ. Mgt. *March*, 2006
Vol. 10 (1) 5 - 8

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

IZONFUO, W-A L; FEKARURHOBO, G K; OBOMANU, F G; DAWORIYE, L T

Department of Chemistry, Rivers State University of Science and Technology, P M B 5080, Port Harcourt, Nigeria

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 λ_{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 λ_{max} of 520nm and 540nm and absorptivities of 0.1909 and 0.1187 respectively. The peaks are associated with n→JI* 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 *Telfaira 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

* *Corresponding author E-mail:* welfordabbey@yahoo.com

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 Table1) . 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 λ_{max} at 520nm while that of the ethanol extract has a λ_{max} at 540nm. Ekandem *et al.* (1997) also obtained a λ_{max} of 520nm for the ethanol extracts of *Hibiscus rosasinensis*. The λ_{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 λ_{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 λ_{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.

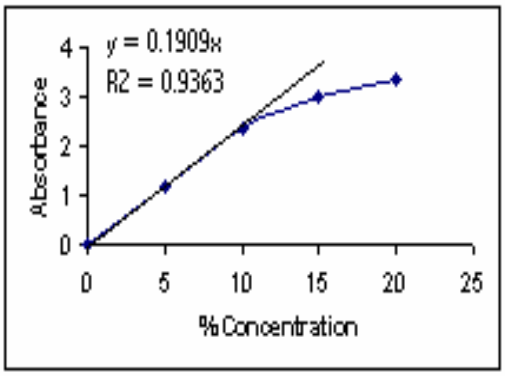

Fig. 1: H. Sabdariffa / water

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 only 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→Л* transition as Л→Л* transitions are usually characterized by very high absorptivities (Skoog *et al*, 1998).

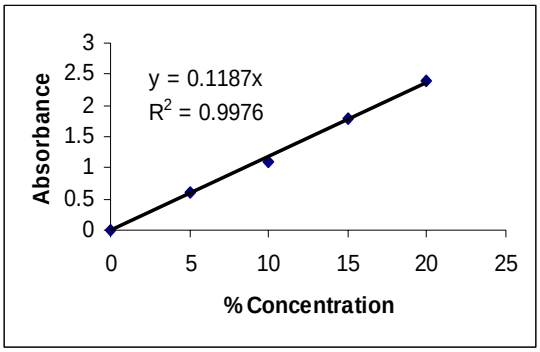

Fig 2: H. Sabdariffa / ethanol

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.

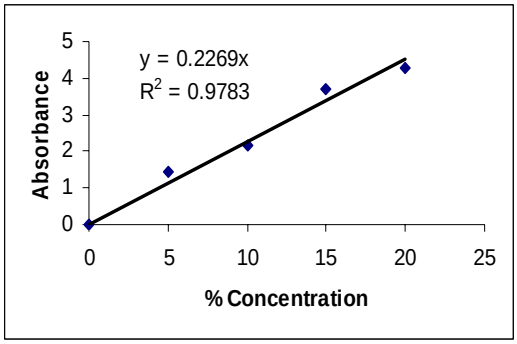

Fig. 3: B. Alba

Table 1. Titration end points (25.00ml of 0.1M of the base was titrated against 0.1M solution of the acid in each case)

Indicators	HCℓ / NaOH	HAc / NaOH	HCℓ / NH_4OH	HAc / NH_4OH
Methyl orange	24.80	3.50	22.50	5.60
Methyl red	24.90	21.10	22.60	18.70
Phenolphthalein	25.10	24.90	21.60	21.00
H. sabdariffa (aqueous extract)	24.20	23.80	22.80	24.70
H. sabdariffa (ethanol extract)	24.30	4.80	22.20	4.30
Basella alba	24.50	23.60	**	8.25

** = not evaluated

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 tritrations. 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).

$$pH = pK_a + \log\frac{[\ln^-]}{[H\ln]} \quad 1$$

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

$$pH = pK_a \quad 2$$

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 pK_a and K_a 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 pK_a and K_a values as 5.56 and 2.75 x 10^{-6} respectively. The pK_a value obtained for *H. sabdariffa* is very similar to that reported for *H. rosasinensis*. The order of magnitude of the K_a values are also comparable. The Pk_a and K_a 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 photoinstability 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).

Acknowledgement: The authors are grateful to Prodec-Fugro Ltd, Port Harcourt for the spectroscopic analyses.

REFERENCES

Akpuaka, MU; Chukwuneke, C; Agbo, G. (1998). The dyeing of textile fabrics with natural dyes from some local trees. J. Chem. Soc. Nig. 23, 47-52.

Dambata, BB; Gumel, SM (1997). Dye-fibre bond stabilities of some reactive dyes on nylon. J. Chem. Soc. Nig. 22, 121-131.

Dambata, BB; Obande, OD; Kazaure, MA (1996). Evaluation of the dyeing properties of some heterocyclic disperse dyes in perchloroethylene and water. J. Chem. Soc. Nig. 21, 57-64.

Ekandem, JE; Owor, AU (1997). Local flower extracts as simple acid-base indicators. J. Chem. Soc. Nig. 22, 98-103.

Eze, SO; Okereafo, A (2002). Industrial and analytic potentials of dye extracts from *Telfaira occidentalis* (Fluted pumpkin). J. Chem. Soc. Nig. 27, 143-146.

Obanda, OD; Dambata, BB; Ukpumwan, DO (1995). Predicting light fastness of dyes on textiles from spectra of their photofading in solutions - A preliminary report. J. Chem. Soc. Nig. 20, 8-17.

Odilora, CA; Ozabor, WC; Ugiagba, B (2002). Extraction and colouring effect of the dye from *Basella alba* (Indian spinach) on cotton and polyester fibres. Proceedings of the Annual Conference of the Chemical Society of Nigeria held in Calabar.

Osabohien, E; Ukpumwan, DO (2002). Extraction of natural dyes from some local plants. J. Chem. Soc. Nig. 27, 2, 139-142.

Skoog, DA; Holler, FJ; Nieman, TA (1998). Principles of instrumental analysis. 5th ed. Harcourt Brace College Publishers, Sea Harbor Drive, Orlando, Florida.