ANALYTICAL POTENTIALS OF DYE EXTRACTS FROM *ASPILIA AFRICANA* (ORAMEJULA) FLOWERS

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ABSTRACT

Sequel to the increasing interest in the use of organic dyes and pigments because of safety, cost, and environmental considerations, the analytical potentials of ethanol, cold and hot water extracts of the flowers of Aspilia Africana was evaluated. The present study was part of a group of studies designed to evaluate the flower extracts of some readily available common plants to assess their analytical and industrial potentials. The flowers of Aspilia Africana was collected, dried, ground and dye extracts obtained by solvent extraction using ethanol, cold and hot water. 3 drops of the dye extract were dropped in 10ml of 0.1M H_2SO_4. This was titrated against 0.1M NaOH until the colour changed from light lemon green to light orange for ethanol extract of Aspilia Africana while the cold water and hot water extract gave the same colour changes at end point from light orange to light lemon green. The titration was repeated using standard indicators such as phenolphthalein, methyl orange, bromothymol blue and methyl red for weak acid/ strong base, strong acid/ strong base, strong acid /weak base and weak acid /weak base. The same acid and base of same strength were assessed using potentiometric titration. These results indicated that flower extracts of this plant can be used as acid-base indicator in all titration. The pH of these indicators was also determined. The rationale behind using these natural indicators in preference to synthetic indicators is its easy availability, biodegradability, more compatibility with the environment, inertness, ease of preparation and cost effectiveness.

Keywords: Aspilia Africana, dye extracts acid-base titration, potentiometric titration, pH, natural indicator

INTRODUCTION

A pH indicator is a halochromic chemical compound that is added in small amounts to a solution so that the pH (acidity or alkalinity) of the solution can be determined easily. An acid- base indicator is usually a weak organic acid denoted as (HIn) that has a different colour than its conjugate base (In^-) (Silberberg, 2006). Hence pH indicators are chemical detectors for hydronium ions (H_3O^+) (or Hydrogen ions (H^+) in the Arrhenius model). Normally, the indicator causes the colour of the solution to change depending on the pH. An indicator changes colour over a range of pH (Ikoku *et al,* 1984)

Commercial indicators are expensive and some of them have toxic effects on users and can also cause environmental pollution (Pathade, 2009). For these reasons there has been an increasing interest in searching for alternative sources of indicators from natural origins as alternatives. These alternatives would be cheaper, more available, simple to extract, less toxic to users and environmentally friendly. Volumetric analysis is one of the key quantitative techniques used to analytically determine both inorganic and organic acid interaction with strong or weak acids and bases in raw materials, intermediates and finished products for

quality assurance purposes. This is accomplished via the use of appropriate weak organic dyes or acids pH indicators.

Most pH indicators are either weak organic acids or bases dyes which accept or donate electrons. The change in colour at a marginal range is attributed to their acidity or basicity properties. Although there are automated titration apparatus that determine the equivalent points between reacting species, indicators are still needed for teaching and research laboratories for simple titration (Nwosu, 2004). Natural indicators have been extracted from Hibiscus (red species), Bougainvillea and rose flowers (Nwosu, 2004). Eze and Okereafor, 2002 also investigated the industrial and analytical potentials of dye extracts from the fruit of *Telfairoccidentalis* .In a previous study carried out by Azundo 2006 (Unpublished data), dyes were extracted from the guinea corn leaves and used for titration. However, the data was not consistent and little is known about whether the dyes could react well with all types of reacting species (strong bases versus strong acids and or weak acids versus strong base or the vice versa.

Several other studies by other authors have reported on the effectiveness of natural indicators in acid-base titrations e.g. *Nerium odorum*, *Thespesia populnea* extract used as indicators (Patil, 2009); *Morus alba* linn fruit extract indicator (Pathade, 2009) and *Ixora coccinea*, *Datura stramonium,* Sun flower (*Helianthus annus*), pride of Barbados (*Caesalpinia pulcherrima*) and rail creeper (*Ipomoea palmate)* flower petal extracts (Nwosu, 2004). Natural dyes are also applied in the colouring of foods, textiles and cosmetics apart from their use in acid base titrations as indicators (Gruden, 1970, Akpuaka *et al*, 1998). Some synthetic dyes are carcinogenic. An example is the dye that was used in colouring magarine called butter yellow. Butter yellow which is an azo dye was found to be carcinogenic. Magarine is now coloured with β-carotene which is a natural dye.(Bruice,2007)

The natural indicator sources investigated in these papers have been extracted and prepared using ethanol, hot water, or cold water or weak acids versus weak bases). In this study we observed the reaction of flower extract in different pH conditions and compared natural indicator to commercial indicators with measurement of pH

There is little evidence available with regards to the pH ranges of the indicator, its optimum function and its possibilities of replacing some expensive commercial indicators. Unlike some commercial indicators that are known to have detrimental effects, we anticipate that indicators from natural sources could reduce both environmental pollution and the toxic effect on users. This will also encourage the cultivation of the crop in large scale for multipurpose uses.

MATERIAL AND METHODS

The reagents used for this work were of analytical grade and were used as such without further purification. These include sodium hydroxide (NaOH), Sulphuric acid (H_2SO_4), Oxalic acid $(COOH)_2 2H_2O$, Sodium hydroxide (NaOH), and Amonium hydroxide (NH_4OH). The commercial indicators were methyl red, phenolphthalein, methyl orange, bromothymol blue, and the flower extract of *Aspilia Africana*, 6 filter papers. The following apparatus such as; pH meter, volumetric flasks (100 ml, 500 ml and 1000 ml), conical flask with volume size of 50 ml, burette of 50 ml, and graduated measuring cylinders of volume size 10, 50, 100 and 500 ml were used to carried out the experiment. Analytical grade reagents were made available by Abia State University, Uturu.

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Sample Collection and Preparation

Aspilia Africana flowers were collected from plants growing wild in Okigwe bushes. The flowers were collected and were kept at room temperature. They were dried to minimize oxidative loss before pounding into fine powder with mortar and pestle. The resulting powders were sieved. The natural indicator extract was prepared by weighing approximately 2 g of a powdered sample flowers into 50ml beaker and 20.0 ml of ethanol, hot water, and cold water was added. The mixture was vortexed for 5 minutes at ambient temperature (25°C) and then filtered using Whatman No. 1 filter paper into a new culture test tube of (20 × 250 mm), capped with a Teflon cap and store for use on the same day.

The experimental work was carried out by using the same set of glass wares for all type of titrations. As the same aliquots were used for both titrations i.e. titration by using standard indicators and flower extract, the reagent were not calibrated. The equimolar titrations were performed using 10 ml of titrant with three drops of indicator. All the parameters for experiment are given in Table 1.1. A set of three experiments was carried out and mean and standard deviation were calculated from results.

Experimental Procedure

Experiment with Natural Indicators

Approximately 10.0 ml of 0.1 M H_2SO_4 or 0.1 M $(COOH)_2 2H_2O$ was titrated with 0.1 M NaOH using the dyes, extracted from the *Aspilia Africana* in the order of strong acid versus strong base and weak acid versus strong base respectively, and then 10.0 ml of 0.1 M H_2SO_4 or 0.1 M $(COOH)_2 2H_2O$ was also titrated against the weak base 0.1 M NH_4OH in the order of (H_2SO_4 v/s NH_4OH, $(COOH)_2 2H_2O$ v/s NH_4OH). Three drops of the extracted indicator were added to each volume of acid used for the titration. The experiment was conducted in triplicates. The acid-base titration was carried out at room temperature.

Experiment with Standard Indicators

For the purposes of comparison, the standard commercial indicators were used for the same titrations instead of the dye extracts. The procedure used for the commercial indicators (standard indicators) was the same as described above for the natural indicators. The experiment was conducted in triplicates and the results were analyzed with simple Microsoft excel 2010 and SPSS statistical software. The statistics generated were used to discuss the results.

Potentiometric Titration with Natural Indicators

The pH meter was calibrated to 4.0, approximately 10.0 ml of 0.1 M H_2SO_4 or 0.1 M $(COOH)_2 2H_2O$ was titrated with 0.1 M NaOH using the natural indicator, extracted from the Urena Lobata and Aspilia Africana in the order of strong acid versus strong base and weak acid versus strong base respectively, as the pH of the acid was recorded before titrating. The base (NaOH) was being added in 1ml each as the pH reading is being recorded, at a point there will be a sudden change in pH and colour change. The titration continues with 1ml each, until there is little or no change in pH. And then 10.0 ml of 0.1 M H_2SO_4 or 0.1 M $(COOH)_2 2H_2O$ was also titrated against the weak base 0.1 M NH_4OH in the order of (H_2SO_4 v/s NH_4OH, $(COOH)_2 2H_2O$ v/s NH_4OH), as the pH of the acid was recorded before titrating. The base (NH_4OH) was being added in 1ml each as the pH reading is being recorded, at a point there will be a sudden change in pH and colour change. The titration continues with 1ml each, until there is little or no change in pH. Three drops of the extracted indicator were

added to each volume of acid used for the titration. The result of this experiment is shown in chapter four of this work.

Potentiometric Titration with Standard Indicators

For comparison, the procedure used for the commercial indicators (standard indicators) was the same as described above for the natural indicators. The results were analyzed with simple Microsoft excel 2010 and SPSS statistical software. The statistics generated were used to discuss the results.

RESULT AND DISCUSSION

pH Range of Indicators

The results of the titre values obtained using the natural indicator (*Aspilia Africana* extract) and standard indicators are presented in Table 1.

Table 1. Mean volume (in ml) of base used to reach the equivalent point of acid-base titrations

Indicator Type	*Reaction Type*			
	H_2SO_4/ NaOH	$(COOH)_2 2H_2O$ / NaOH	H_2SO_4/ NH_4OH	$(COOH)_2 2H_2O$ / NH_4OH
Ethanol Extract	23.5 ± 0.17	21.2 ± 0.21	3.5 ± 0.29	4.6 ± 0.24
Hot water extract	23.7 ± 0.12	21.2 ± 0.22	3.4 ± 0.33	4.3 ± 0.12
Cold water extract	23.4 ± 0.16	Nd	3.5 ± 0.40	4.6 ± 0.21
Bromothymol blue	23.1 ± 0.12	21.0 ± 0.12	3.4 ± 0.33	4.1 ± 0.14
Methyl Red	22.9 ± 0.12	20.7 ± 0.14	4.0 ± 0.16	3.8 ±0.24
Methyl Orange	21.1 ± 0.08	20.0 ± 0.38	3.5 ± 0.21	3.7 ± 0.12
Phenolphthalein	23.1 ± 0.1	23.3 ± 0.12	3.5 ± 0.24	3.5 ± 0.24

Means plus standard deviation determination, and nd: not determine. Concentration of H_2SO_4 0.1 M, NaOH = 0.1 M, $(COOH)_2 2H_2O$ = 0.1 M, and NH_4OH = 0.1 M.

The results show that the ethanol, cold and hot water extracts of *Aspilia Africana* gave similar equivalent points ranging from 23.4±0.16-23.7±0.12 which were clse to the equivalent points obtained using phenolphthalein and bromothymol blue and so the natural plant extracts can be used in place of phenolphthalein and bromothymol blue in acid-base titrations involving a strong acid/strong base.

Also for weak acid/ strong base the result the ethanol and hot water extract did not show any significant difference in their equivalent points (21.0±0.12 and 21.2±0.22) and were closest to bromothymol blue (21.0±0.12) and so the natural dye extracts can replace the commercial indicator bromothymol blue.

Similarly on the same principles, for strong acid /weak base the ethanol and cold water extracts can be used in place of methyl orange and phenolphthalein while the hot water extract can replace bromothymol blue in acid –base titrimetry.

For weak acid/ weak base, the closest end points of the extracts and the commercial indictors was that of the hot water extract and bromothymol blue

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The colour changes of the dye extracts at the equivalent points and that of the commercial indicators is shown in table 2. For the titration using strong acid / strong base, the colour change was quite distinct but none has the same colour change with the commercial indicators. However for weak acid/ strong base, the ethanolic extract of Aspilia Africana has an end point colour (light lemon green to light orange) close to methyl red (light pink to orange).Also for weak acid / weak base, and strong acid / weak base, the hot and cold water extracts gave the same end point colour with methyl red.

It was observed that the natural indicator (*Aspilia Africana*) the ethanol extract changes from light lemon green to light orange, the hot water and cold water extract changes from pale orange to pale lemon green as indicated in table 2. It was observed that the pH range of the acid was affected by the indicator added because of the nature of the indicator as shown in table 3. Methyl red has the pH range of 1.14 – 2.77; due to its acidic nature it reduces the pH of the acids most even to 0.00 like in Oxalic vs NH_4OH. The possible factors that might have contributed to the pattern of the pH variation as well as titre value could be temperature, ionic strength, colloidal particles and organic solvents (Skoog, 1994).

Equivalent Points

The average titre values obtained for the extract was comparable to methyl orange, phenolphthalein methyl red and bromothymol blue indicator used as indicated in table 1. It was interesting to observe that for the weak acid versus strong base the titre values of Aspilia Africana, cold water extract has similar value with methyl red. For weak acid versus weak base the methyl orange were quite different to the natural indicator extract and synthetic indicator, as presented in table 1.

The pH of the natural indicators and those of the commercial indicators are shown in table 3.

Table 3. The pH range of both the natural and synthetic indicator

Indicator type	*pH Range*	*Colour Change*
Phenolphthalein	12.84 – 13.28	Colourless to pink
Methyl Orange	1.14	Reddish to yellow
Methyl red	1.14 – 2.77	Light pink to orange
Bromothymol Blue	6.87 – 13.21	Yellow to blue
Ethanol extract of Aspilia Africana	12.84 – 13.28	Light lemon green to light orange
Hot water extract of Aspilia Africana	12.84 – 13.28	Light orange to light lemon green
Cold water extract of Aspilia Africana	12.84 – 13.28	Light orange to light lemon green

The pH ranges of the ethanolic, hot and cold water extracts were the same (12.84-13.28). They show the same pH range with phenolphthalein (12.84-13.28). Therefore the dye extracts from *Aspilia Africana* can generally replace phenolphthalein in acid –base titrations. The pH ranges of the indicators are related to the nature of the compounds. Order of acidity of the commercial indicators is methyl orange > methyl red > bromothymol blue > Phenolphthalein

CONCLUSION

The analytical potentials of dye extracts from *Aspilia Africana* was successfully evaluated. The ethanol, cold and hot water extracts of the dyes from the plant flowers can replace the commercial standard indictors. All the dye extracts in the different solvents can be used in place of phenolphthalein.

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