Acid-Base Indicator Properties of Dyes from Local Flowers: *Cassia aungostifolia* Linn., *Thevetia peruviana* (Pers.) K. Schum and *Thevetia thvetiodes* (Kunth) K. Schum

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ABSTRACT

Indicators used in titration show well-marked changes of color in certain intervals of pH. Most of these indicators are organic dyes and are of synthetic origin. The environmental pollution caused by chemical industries in the synthesis of organic dyes had made the scientist in the developing country to enter in to an era, in which plant product serve as an alternative to synthetic products. The advantages of the plant products are local and easy accessibility, environmental friendly nature, and lower price compare to the synthetic products. Herbs are non-polluting renewable supplies of chipper products for the worlds growing population. Natural pigments in plants are highly colored substances and may show color changes with variation of pH. Curcumin isolated from *Curcuma longa* is as example of natural indicator used in analytical chemistry. Hence the work was carried out to study the indicator property of flowers *Cassia aungostifolia* Linn., *Thevetia peruviana* (Pers.) K. Schum and *Thevetia thvetiodes* (Kunth) K. Schum from ethanolic extract. It was found that the extract changes the color at different pH and can be used successfully as a compound indicator.

Key words: Acid-base indicator, *Cassia aungostifolia* Linn., *Thevetia peruviana*, *Thevetia thvetiodes*, Anthocynins.

INTRODUCTION

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 color 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 and Osahon et al., 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.[1,2] 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.[3,4] Ekandem and Eze et al. have also reported their findings on the use of some natural dye extracts as indicators in acid-base titrimetry.[5,6] 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.

_Cassia aungostifolia_ linn. commonly known Tinnevelly Senna or Tanner’s cassia, is a well known source of sennosides as belonging to family Caesalpiniaaceae. This herb contains...
anthraquinones, flavonoids and flavan-3-ol derivatives.[1] *Cassia aungostifolia* has been used as natural medicine for the treatment of Anti-viral, anti-cancer and hypoglycemic. The whole plant possesses medicinal properties useful in the treatment of skin diseases, inflammatory diseases, rheumatism, anorexia and jaundice.[8] *Thevetia peruviana* (Pers.) K. Schum commonly known as yellow oleander belonging to family Apocynaceae it contain a milky sap containing a compound called thevetin that is used as a heart stimulant but in natural from is extremely poisonous as are all part of plant.[9] *Thevetia thvetiodes* (Kunth) K. Schum commonly known giant thevetia as belonging to family Apocynaceae; The leaves and bark are used as an emetic and purgative. The flowers of the tree are cultivated for their seeds that contain a strong heart drug. All parts of the tree are poisonous and the latex is an irritant that causes blisters upon skin contact.[8] It seems that no work has been done on the suitability of *Cassia aungostifolia*, *Thevetia peruviana* and *Thevetia thvetiodes* as indicator in acid-base titration as compared to the relatively common Methyl Red and Phenolphthalein using acid-base titration. Hence the present vocation was attempted to appraise the flower as a natural indicator.

**MATERIAL AND METHOD**

**Material**

Fresh flower of were collected from the Rajkot region, Gujarat, and they were authenticated from NISCAIR, New Delhi, Ref No: NISCAIR/RHMD/Consult/2010-11/1468/69. All other ingredients were of analytical grade and purchased from Loba chemicals, Mumbai.

**Method**

The flower were cleaned by distilled water and cut into small pieces and macerated for two hours in 25ml of 90% ethanol. The extract was preserved in tight closed container and stored away from direct sun light.[11]

The experiment was carried by using the same set of glassware’s for all types of titrations. As the same aliquots were used for both titrations i.e. titrations by using standard indicators and flower extract, the reagents 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. A set of five experiments each for all the types of acid base titrations were carried out. The mean and standard deviation for each type of acid base titrations were calculated from results obtained. The extract was also analyses for its $\lambda_{\text{max}}$ in UV-Visible range on Systronics single beam spectrophotometer (Shimadzu UV 1800).

**RESULT**

The extract was found to contain compound anthocynins Table 2 as it gives blue color to aqueous sodium hydroxide solution, yellow orange color to concentrated sulphuric acid while red color which fed out on standing with magnesium-hydrochloric acid. The flowers of the tree are cultivated for their seeds that contain a strong heart drug. All parts of the tree are poisonous and the latex is an irritant that causes blisters upon skin contact.[8]

The extract was also analyses for its $\lambda_{\text{max}}$ in UV-Visible range on Systronics single beam spectrophotometer (Shimadzu UV 1800).

**Table 1: Standard chart for Phytochemical identification**

<table>
<thead>
<tr>
<th>Phytochemicals</th>
<th>Color with aq. NaOH</th>
<th>Color with Conc. H$_2$SO$_4$</th>
<th>Color with Mg-HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthocynins</td>
<td>Blue violet</td>
<td>Yellow to orange</td>
<td>Red (fades to pink)</td>
</tr>
<tr>
<td>Flavonones</td>
<td>Yellow</td>
<td>Yellow to orange</td>
<td>Yellow to red</td>
</tr>
<tr>
<td>Flavonones</td>
<td>Yellow to orange (cold)</td>
<td>Crimson Orange</td>
<td>Red, magenta, violet, blue</td>
</tr>
<tr>
<td>Isoflavones</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
</tr>
<tr>
<td>Leucoanthocyanins</td>
<td>Yellow</td>
<td>Crimson</td>
<td>Pink</td>
</tr>
</tbody>
</table>

**Table 2: Technological characterization for analysis of chemical test.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Poly-Phenolic compound</th>
<th>Flavonoid</th>
<th>Anthocynins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Color with FeCl$_3$</td>
<td>Color with Lead acetate</td>
<td>Shinoda test</td>
</tr>
<tr>
<td>CAI</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>TPI</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>TTI</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

+; Presence of compound
The Flower extract was screened for its use as an acid-base indicator in various acid-base titrations, and the results of this screening were compared with the results obtained by standard indicators methyl red, phenolphthalein and mixed indicator (methyl orange: bromocresol green (0.1:0.2) results are presented in Table 4, 5, 6, 7, 8. The titrations of strong acid with strong base (HCl & NaOH), strong acid with weak base (HCl & NH₄OH), weak acid with strong base (CH₃COOH & NaOH), and weak acid with weak base (CH₃COOH and NH₄OH) were carried out using standard indicators and flower extract. The results of these titrations are given in Table 5, 6, 7, 8. It could be due to these flavonoids and anthocyanins, the sharp end point appeared in the above mentioned titrimetric analyses. The flower extract of C. aungostifolia, T. peruviana and T. thevetiodes was found to have Poly-Phenolic, flavonoids, anthocyanins and is pH sensitive. The end point determination of acid base titrations by the traditional indicators, compared with flower extract indicator, it was observed that traditional indicators gave incorrect results due to addition of excess of titrant (base) after the neutralization reaction was completed, but flower extract indicator has given sharp end point because solutions give sharp color change at the equivalence points. Thus natural indicator employed in the acid base titrations was found economic, safe and an efficient alternative for traditional indicators. In comparison to this, chemical indicators were found more expensive and hazardous, which proves that flower extract of C. aungostifolia, T. peruviana and T. thevetiodes, as a natural indicator is more worthy.

Table 3: Determination of UV Visible absorption

<table>
<thead>
<tr>
<th>Sample code</th>
<th>UV λmax</th>
<th>Visible λmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAI</td>
<td>275</td>
<td>596</td>
</tr>
<tr>
<td>TPI</td>
<td>338</td>
<td>555</td>
</tr>
<tr>
<td>TTI</td>
<td>291</td>
<td>537</td>
</tr>
</tbody>
</table>

Table 4: Technological characterization for analysis and comparisons of color change.

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Titrate</th>
<th>Indicator Color Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>NaOH</td>
<td>Yellow - pink (11.19-1.04) Greenish yellow-Colorless (12.72-2.32) Light Green to Colorless (12.72-5.37)</td>
</tr>
<tr>
<td>HCl</td>
<td>NH₄OH</td>
<td>Pink -Colorless (10.98-6.74) Yellow- Colorless (11.29-1.28) Greenish yellow-Colorless (11.05-2.0) Light Green to Colorless (11.0-2.69)</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>NaOH</td>
<td>Yellow- light red (12.95-6.12) Yellow- Colorless (11.31-5.10) Greenish yellow-Colorless (11.05-6.7) Light Green to Colorless (10.95-5.92)</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>NH₄OH</td>
<td>Orange to blue-green (4.73-2.86) Yellow- Colorless (12.33-6.01) Greenish yellow-Colorless (12.67-5.99) Light Green to Colorless (10.95-5.92)</td>
</tr>
</tbody>
</table>


Table 5: Technological characterization of acid-base titration using standard indicator.

<table>
<thead>
<tr>
<th>Titration (Titrant v/s Titrate)</th>
<th>Strength in moles</th>
<th>Indicator</th>
<th>Mean ± S.D.*</th>
<th>Color</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH v/s HCl</td>
<td>0.1</td>
<td>MR</td>
<td>12.3 ± 0.12</td>
<td>Yellow to pink</td>
<td>12.32-5.77</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>MR</td>
<td>11.2 ± 0.16</td>
<td>Yellow to pink</td>
<td>12.55-4.87</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>MR</td>
<td>11.2 ± 0.15</td>
<td>Yellow to pink</td>
<td>12.63-3.30</td>
</tr>
<tr>
<td>HCl v/s NH₄OH</td>
<td>0.1</td>
<td>PT</td>
<td>05.9 ± 0.01</td>
<td>Pink to colorless</td>
<td>10.50-6.74</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>PT</td>
<td>06.6 ± 0.08</td>
<td>Pink to colorless</td>
<td>10.61-8.28</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>PT</td>
<td>06.5 ± 0.16</td>
<td>Pink to colorless</td>
<td>10.98-8.29</td>
</tr>
<tr>
<td>CH₃COOH v/s NaOH</td>
<td>0.1</td>
<td>MR</td>
<td>12.0 ± 0.11</td>
<td>Yellow to light red</td>
<td>12.33-6.01</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>MR</td>
<td>11.9 ± 0.14</td>
<td>Yellow to light red</td>
<td>12.56-5.96</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>MR</td>
<td>12.0 ± 0.09</td>
<td>Yellow to light red</td>
<td>12.67-5.99</td>
</tr>
<tr>
<td>CH₃COOH v/s NH₄OH</td>
<td>0.1</td>
<td>MI</td>
<td>05.0 ± 0.05</td>
<td>Orange to green</td>
<td>03.25-4.52</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>MI</td>
<td>05.6 ± 0.19</td>
<td>Orange to green</td>
<td>02.81-4.68</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>MI</td>
<td>06.1 ± 0.17</td>
<td>Orange to green</td>
<td>02.86-4.73</td>
</tr>
</tbody>
</table>

*All values are mean ± S.D. for n=3

### Table 6: *Cassia aungostifolia* as indicator

<table>
<thead>
<tr>
<th>Titration (Titrant v/s Titrand)</th>
<th>Strength in moles</th>
<th>Indicator</th>
<th>Mean ± S.D.</th>
<th>Color</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH v/s HCl</td>
<td>0.1</td>
<td>CAI</td>
<td>13.1 ± 0.11</td>
<td>Yellow to colorless</td>
<td>11.19-3.14</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>CAI</td>
<td>10.0 ± 0.18</td>
<td>Yellow to colorless</td>
<td>11.62-1.65</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>CAI</td>
<td>10.7 ± 0.12</td>
<td>Yellow to colorless</td>
<td>11.36-1.04</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>CAI</td>
<td>19.0 ± 0.18</td>
<td>Yellow to colorless</td>
<td>10.46-2.01</td>
</tr>
<tr>
<td>HCl v/s NH₄OH</td>
<td>0.5</td>
<td>CAI</td>
<td>12.6 ± 0.05</td>
<td>Yellow to colorless</td>
<td>11.34-1.28</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>CAI</td>
<td>6.0 ± 0.03</td>
<td>Yellow to colorless</td>
<td>11.29-1.31</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>CAI</td>
<td>11.5 ± 0.13</td>
<td>Yellow to colorless</td>
<td>12.83-1.12</td>
</tr>
<tr>
<td>CH₃COOH v/s NaOH</td>
<td>0.5</td>
<td>CAI</td>
<td>10.6 ± 0.17</td>
<td>Yellow to colorless</td>
<td>12.95-6.32</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>CAI</td>
<td>10.3 ± 0.08</td>
<td>Yellow to colorless</td>
<td>12.18-6.17</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>CAI</td>
<td>4.4 ± 0.16</td>
<td>Yellow to colorless</td>
<td>09.28-7.35</td>
</tr>
<tr>
<td>CH₃COOH v/s NH₄OH</td>
<td>0.5</td>
<td>CAI</td>
<td>8.4 ± 0.05</td>
<td>Yellow to colorless</td>
<td>10.18-5.35</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>CAI</td>
<td>8.9 ± 0.06</td>
<td>Yellow to colorless</td>
<td>11.31-5.10</td>
</tr>
</tbody>
</table>

*All values are mean ± S.D. for n=3
HCl: Hydrochloric acid, CH₃COOH: Acetic Acid, NaOH: Sodium Hydroxide, NH₄OH: Ammonium Hydroxide, CAI: *C. aungostifolia*

### Table 7: *Thevetia thvetiodes* as indicator

<table>
<thead>
<tr>
<th>Titration (Titrant v/s Titrand)</th>
<th>Strength in moles</th>
<th>Indicator</th>
<th>Mean ± S.D.</th>
<th>Color</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH v/s HCl</td>
<td>0.1</td>
<td>TTI</td>
<td>11.6 ± 0.06</td>
<td>Light green to colorless</td>
<td>12.33-6.48</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>TTI</td>
<td>10.1 ± 0.05</td>
<td>Light green to colorless</td>
<td>12.46-6.43</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>TTI</td>
<td>10.0 ± 0.12</td>
<td>Light green to Colorless</td>
<td>12.72-5.37</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>TTI</td>
<td>6.5 ± 0.08</td>
<td>Light green to Colorless</td>
<td>10.38-4.60</td>
</tr>
<tr>
<td>HCl v/s NH₄OH</td>
<td>0.5</td>
<td>TTI</td>
<td>7.3 ± 0.18</td>
<td>Light green to Colorless</td>
<td>10.78-2.69</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>TTI</td>
<td>7.0 ± 0.16</td>
<td>Light green to Colorless</td>
<td>11.0-5.42</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>TTI</td>
<td>10.9 ± 0.13</td>
<td>Light green to Colorless</td>
<td>12.36-9.20</td>
</tr>
<tr>
<td>CH₃COOH v/s NaOH</td>
<td>0.5</td>
<td>TTI</td>
<td>11.5 ± 0.17</td>
<td>Light green to Colorless</td>
<td>12.73-6.52</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>TTI</td>
<td>11.3 ± 0.18</td>
<td>Light green to Colorless</td>
<td>12.76-6.55</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>TTI</td>
<td>6.6 ± 0.05</td>
<td>Light green to Colorless</td>
<td>10.20-6.62</td>
</tr>
<tr>
<td>CH₃COOH v/s NH₄OH</td>
<td>0.5</td>
<td>TTI</td>
<td>7.5 ± 0.03</td>
<td>Light green to Colorless</td>
<td>10.73-5.99</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>TTI</td>
<td>8.0 ± 0.11</td>
<td>Light green to Colorless</td>
<td>10.95-5.92</td>
</tr>
</tbody>
</table>

*All values are mean ± S.D. for n=3
HCl: Hydrochloric acid, CH₃COOH: Acetic Acid, NaOH: Sodium Hydroxide, NH₄OH: Ammonium Hydroxide, TTI: *T. thvetiodes*

### Table 8: *Thevetia peruviana* as indicator

<table>
<thead>
<tr>
<th>Titration (Titrant v/s Titrand)</th>
<th>Strength in moles</th>
<th>Indicator</th>
<th>Mean ± S.D.</th>
<th>Color</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH v/s HCl</td>
<td>0.1</td>
<td>TPI</td>
<td>11.5 ± 0.06</td>
<td>Greenish yellow to Colorless</td>
<td>12.33-6.97</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>TPI</td>
<td>10.5 ± 0.05</td>
<td>Greenish yellow to Colorless</td>
<td>12.47-4.81</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>TPI</td>
<td>10.5 ± 0.12</td>
<td>Greenish yellow to Colorless</td>
<td>12.72-2.32</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>TPI</td>
<td>8.3 ± 0.08</td>
<td>Greenish yellow to Colorless</td>
<td>10.29-6.35</td>
</tr>
<tr>
<td>HCl v/s NH₄OH</td>
<td>0.5</td>
<td>TPI</td>
<td>7.3 ± 0.18</td>
<td>Greenish yellow to Colorless</td>
<td>10.88-2.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>TPI</td>
<td>7.1 ± 0.16</td>
<td>Greenish yellow to Colorless</td>
<td>11.15-2.36</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>TPI</td>
<td>11.4 ± 0.13</td>
<td>Greenish yellow to Colorless</td>
<td>12.55-7.35</td>
</tr>
<tr>
<td>CH₃COOH v/s NaOH</td>
<td>0.5</td>
<td>TPI</td>
<td>10.7 ± 0.17</td>
<td>Greenish yellow to Colorless</td>
<td>12.82-8.08</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>TPI</td>
<td>11.5 ± 0.18</td>
<td>Greenish yellow to Colorless</td>
<td>12.78-7.22</td>
</tr>
</tbody>
</table>

*All values are mean ± S.D. for n=3
HCl: Hydrochloric acid, CH₃COOH: Acetic Acid, NaOH: Sodium Hydroxide, NH₄OH: Ammonium Hydroxide, TPI: *T. peruviana*
CONCLUSION

The results obtained in all the types of acid-base titrations lead us to conclude that, it was due to the presence of flavonoids and anthocyanins, sharp color changes occurred at end point of the titrations. We can also conclude that, it is always beneficial to use *C. aungostifolia*, *T. peruviana* and *T. thvetiodes* flower extract as an indicator in all types of acid base titrations because of its economy, simplicity and wild availability.

REFERENCES
