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Volumetric Acid-Base Titration by using of Natural Indicators and Effects of Solvent and Temperature

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Abstract

In this work, many natural sources as acid-base indicators which are extracted from different parts of fruits, flowers and plants were investigated for volumetric acid-base titration at room temperature, 60°C, 92°C and 98°C. Pigments from some fruits and plants were extracted, separated, and purified in carbon tetrachloride, chloroform, ethanol, methanol and toluene as solvents. These indicators in acid-base titrations shown sharp color changes with variation of pH at the equivalence point and we could determine the pH range. For some indicators the color of indicator in different solvents was similar that suggested there was no obvious modification of chemical structure of indicators in different solvents. In addition, the effect of temperature on indicators and their stability were studied. The result proved to be acceptable in introducing natural pigments as suitable acid - base indicators. These natural indicators are found to be a very useful, economical, simple, accurate and nature-friendly.

Keywords: Acid- base indicator; Natural pigment; Solvents; Titration; pH

Introduction

Several types of synthetic chemical indicators are available for different types of titrimetric analyses. Acid-base indicators are known as pH indicators. Acid–base indicators are substances (dyes) which change color with pH. They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions. Volumetric analysis is one of the major quantitative techniques. In titrimetry, the equivalent point is usually determined by the end point in the titration. The end of point in traditional titrimetry is usually indicated by some substances added into the analyte solution, which change color immediately after the equivalent point has been attained. These substances are generally referred to as indicators. Several types of indicators are available for different types of titrimetric analyses. Most pH indicators are either weak organic acids or bases dyes which accept or donate electrons [1]. Although there are automated titration apparatus that determine the equivalent point between reacting species, indicators are still needed for teaching and research laboratories for simple titration [2]. Commercial indicators are expensive and some of them have toxic effects on users and can also cause environmental pollution [3]. For these reasons there has been an increasing interest in searching for alternative sources of indicators from natural origins. Historically, plants have been used for the extraction of a majority of natural dyes. As interest in natural dyes grew, information from the old literature was collected and traditional dyeing practices in different regions were documented and compiled by various researchers. The use of natural dyes as acid-base indicator was first reported by Sir Robert Boyle in collection of assays "Experimental History of Colors" in 1664 [4,5]. 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.* [6] and Osabohien *et al.* [7], 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. Natural dyes are derived from natural resources and based upon their source of origin; these are broadly classified as plant, animal, mineral, and microbial dyes although plants are the major sources of natural dyes. Recent environmental awareness has again revived interest in natural dyes mainly among environmentally conscious people. Natural dyes are considered eco-friendly as these are renewable and biodegradable. Ekandem *et al.* [8] and Eze *et al.* [9] have reported their findings on the use of some natural dye extracts as indicators in acid-basetitrimetry. In recent years, there are numerous natural acid-base indicators that can be obtained from common flowers, fruits and vegetables [3,10].

Among of natural dyes as acid-base indicator, Flavones, Flavonols, Anthocyanidins, Anthocyanins are some types of indicator, which have been studied in order to substitute these compound instead of synthetic indicators [11,12]. For example, the chemical structure forms and colors of an anthocyanin at different pHsare presented in Figure 1.

In this work, we report the findings of our investigations on the acid-base indicator properties of dyes obtained from parsley, coriander, borage, allium ampeloprasum, red cabbage, tulip petals, rose petals, rosa damascene, red onion skin, curcuma, cinnamon, ginger, saffron, black pepper, red pepper, yellow pepper, coffee, quince leaf, strawberry, sour berry, cornelian cherry, carrot, green walnut in different solvents at different temperature.

Materials and Methods

Flowers, plants and fruits materials

Parsley, coriander, borage, allium ampeloprasum, red cabbage, tulip petals, rose petals, rosa damascene, red onion skin, curcuma, cinnamon, ginger, saffron, black pepper, red pepper, yellow pepper, coffee, quince leaf, strawberry, sour berry, cornelian cherry, carrot

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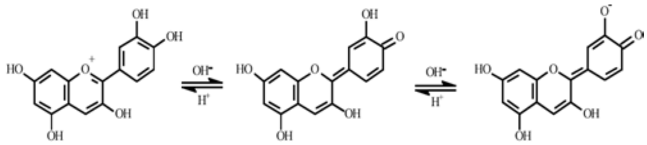

Figure 1: The chemical structure forms and colors of an anthocyanin at different pHs.

and green walnut were purchased from Agricultural Research Center Tabriz. Samples include flowers, plants leaves and petals and fruits skins. The samples were washed thoroughly under tap water, cleaned by distilled water, air-dried and powdered using mechanical blender.

Chemicals required

Carbon tetrachloride, chloroform, ethanol, methanol, toluene, NaOH and HCl were purchased from Sigma- Aldrich chemical. All other chemicals were of analytical reagent grade and were purchased from Merck. All solutions were prepared using double distilled water.

Apparatus

Reagent bottle, weighing balance, spatulas, hot plate, shaker, oven, electric grinder, test tubes, test tube stand, droppers, 50mL burettes, wash bottle, beaker, spatula, pipettes, pipette filler, funnel, clamp stand, tissue paper, magnetic stirrer, watch glass, volumetric flasks of 25mL & 50mL, conical flask, pH paper, A digital pH meter (Switzerland OHAUS2100) with glass and calomel electrodes, measuring cylinders.

Preparation of flowers, plants and fruits extract in different solvents

2 grams of samples powder were mixed with 50mL of carbon tetrachloride, chloroform, ethanol, methanol and toluene as solvents for 48h with stirring. The solution was shaken and swirled well, until the entire compound dissolved. The extract is filtered with suction using a Buchner funnel, filter paper and the filter flask [13,14]. The resulted aqueous extract was evaporated to one-fifth of its original volume and then used as natural indicator for acidimetric and alkalimetry. The extract was preserved in light closed container and stored away from direct sunlight.

Change of color samples in equivalent points at different solvents

Prepared natural indicator samples were used for titration. The experimental work was carried out using the same set of glass wares in the order of strong acid versus strong base with five drops of natural indicator at room temperature. 5.0 mL of 0.1 M NaOH was separately titrated with 0.1 M HCl using the natural indicators extracted from samples in order to determine equivalent points.

Results and Discussion

Change of color samples in equivalent point at different solvents

Prepared natural indicator samples were used for titration. The experimental work was carried out using the same set of glass wares in the order of strong acid versus strong base with five drops of natural indicator at room temperature. 5.0 mL of 0.1 M NaOH was separately titrated with 0.1 M HCl using the natural indicators extracted from samples in order to determine equivalent points. The results of titration with colors observed in acidic and alkali media are summarized in Table 1. And volume of acid consumed is reported in Table 2. For example, it was observed that the natural indicator (Curcuminoidsextracted from curcuma dissolved in Ethanol) when added to the acid produced a sharp yellow color as indicated in Table 1. After titration by strong base was observed distinctive and sharp color change that shown equivalent point in this sample. The presence of Curcuminoids in curcuma and anthocyanins were responsible of sharp color changes in red cabbage, red onion skin, tulip petals, borage occurred at the end point of the titrations [11,15]. Therefore, we can say that it is always beneficial to use these natural indicators in acid base titrations because of its economy, simplicity and availability.

The pH range of indicators

We were performed this investigation for three samples curcuma, borage and tulip petals. Initially, pH meter shown pH=12/8 for strong

Table 1: Natural indicator samples in different solvents and color observed in acidic and alkaline condition.

Solvent	Media	Samples																			
		Cur-cuma	Cinna-mon	Ginger	Saffron	Black pepper	Yellow pepper	Red pepper	Coffee	Quince leaf	straw-berry	Corne-lian cherry	Green walnut	Carrot	Egg-plant skin	Red onion skin	Rosa dama-scene	Tulip petals	Borage	Coria-nder	Parsley
Toluene	Acidic	Yellow	Brown	Yellow	Yellow	Green	Yellow	Red	Brown	Green	Orange	Green	Dark Brown	Orange	Purple	Purple	Pink	Red	Pink	Green	Green
	Alkaline	Red	Brown	Yellow	Yellow	Green	Yellow	Orange	Brown	Brown	Orange-pink	Brown	Dark Brown	Orange	Green	Green	Brown	Red	Green	Green	Green
Tetra-chloride	Acidic	Yellow	Light Brown	Yellow	Yellow	Green	Yellow	Red	Brown	Green	Orange	Red	Yellow-Green	Orange	Purple	Purple	Pink	Red	Pink	Green	Green
	Alkaline	Red	Dark Brown	Yellow	Yellow	Green	Yellow	Red-Orange	Brown	Green-Brown	Orange-Pink	Brown	Yellow	Orange	Green	Green	Brown	Red	Green	Green	Green
Chloro-form	Acidic	Yellow	Brown	Yellow	Yellow	Green	Yellow	Red	Brown	Green	Orange	Red	Green	Orange	-	Red	Red	-	Red	Green	Green
	Alkaline	Red	Brown	Yellow	Yellow	Green	Yellow	Red	Brown	Green	Orange-Pink	Brown	Green	Orange	-	Red	Red	-	Red	Green	Green
Ethanol	Acidic	Yellow	Light Brown	Yellow	Yellow	Green	Yellow	Red	Very Light Brown	Green	Orange	Red	Yellow-Green	Orange	Purple	Purple	Purple	-	-	Green	Green
	Alkaline	Red	Dark Brown	Yellow	Yellow	Green	Yellow	Red	Very Dark Brown	Green-Brown	Orange-Pink	Red	Yellow-Green	Orange	Green	Green	Yellow-Green	-	-	Green	Green
Metha-nol	Acidic	Yellow	Brown	Yellow	Yellow	Green	Yellow	Red	Brown	Pale Green	Orange	Orange	Yellow-Green	Orange	Purple	-	Pink	Red	Purple	Green	Green
	Alkaline	Red	Brown	Yellow	Yellow	Green	Yellow	Red	Brown	Medium Spring Green	Orange-Pink	Very Light Brown (Wheat)	Dark Brown	Orange	Green	-	Brown	Purple	Green	Green	Green

Table 2: Volume (mL) of acid used to reach the equivalent point of acid-base titrations and color change in titration.

	Material	Alkaline	NaOH as Titrate (mL)	Acidic	HCl as Titrant (mL)
1	Curcuma	Red	5	Yellow	5
2	Red cabbage	Purple	5	Red	5
3	Red onion skin	Green	5	Purple	3.9
4	Tulip petals	Purple	5	Red	4.6
5	Borage	Light Green	5	Colourless	5

Table 3: Volume (ml) of acid used to reach the equivalent point of acid-base titrations and pH range of indicators.

	Natural Indicator	Base (mL)	Acid (mL)	pH range
1	Curcuma	10	9.8	8/52-5/87
2	Borage	10	11.2	6/88-4/68
3	Tulip petals	10	9.8	8/70-4/43

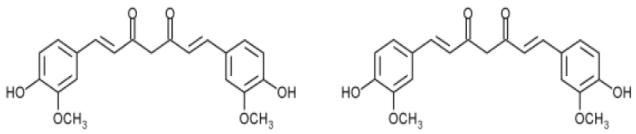

Figure 2: The chemical structure forms of curcumin in enol (a) and keto (b).

Figure 3: The colors of curcumin at different pHs.

base. When acid added little by little, the pH range was between 8/52 (alkaline) to 5/87 (acidic) after titration in case of curcuma. In case of borage, the pH range was between 6/88 (alkaline) to 4/68 (acidic) and tulip petals shown the pH range 8/70 (alkaline) to 4/43 (acidic). The results pH range of indicators is shown in Table 3. The possible factors that might have contributed to the pattern of the pH variation as well as titer value could be temperature, ionic strength, colloidal particles and organic solvents [2]. Another reason could be the chemical composition of the natural indicators. Curcuminoids have the capacity to produce sharp color changes at certain pH ranges as compared to non-curcuminoids derivatives because of the functional groups (e.g. o-methoxy phenolic groups and keto and enol forms in solid phase and solution) in flavonoids and tannins. The chemical structure of curcumin is shown in Figure 2. It can exist at least in two tautomeric forms, keto and enol. The keto form is preferred in solid phase and the enol form in solution. Curcumin is a pH indicator. In acidic solutions (pH <7.4) it turns yellow whereas in basic (pH >8.6) solutions it turns bright red [15,16]. The colors of curcumin at different pHsare presented in Figure 3. In borage and tulip petals Flavonoids have the capacity to produce sharp color changes at certain pH ranges as compared to non-flavonoid derivatives because of the functional groups (e.g. OH) inflavonoids. The plants and fruits such as borage and tulip petals have a mixture of anthocyanins and other pigments that indicate a wide range of pH [11] Figure 1.

Table 4: The effect of temperature on the color indicator.

	Natural Indicator	Temperature (°C)	Color change
1	Curcuma	98	No color change
2	Borage	60	Red-purple
3	Tulip petals	92	No color change

The effect of temperature on the color indicator

The anthocyanin and curuma stability can be affected by many factors. Therefore, the effect of temperature on the three samples (Curcuma, Tulip and Borage) was studied at 98 °C, 92 °C and 60 °C. The obtained results are shown in Table 4. The color of curcuma and tulip petals showed a good resistance to heat.

Conclusion

Many natural sources as acid-base indicators which are extracted from different parts of fruits, flowers and plants were investigated for volumetric acid-base titration at room temperature, 60 °C, 92 °C and 98 °C. Pigments from some fruits and plants were extracted, separated, and purified in carbon tetrachloride, chloroform, ethanol, methanol and toluene as solvents. These indicators in acid-base titrations shown sharp color changes with variation of pH at the equivalence point and we could determine the pH range. For some indicators the color of indicator in different solvents was similar that suggested there was no obvious modification of chemical structure of indicators in different solvents. In addition, the effect of temperature on indicators and their stability were studied. The result proved to be acceptable in introducing natural pigments as suitable acid - base indicators.

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