Universal pH Indicator as a Colorimetric Reagent for Differentiating Inorganic Anions

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ABSTRACT

A simple colorimetric approach using a universal pH indicator to differentiate inorganic anions according to their relative acidity or basicity is presented. Anions caused changes in the pH of the solution, producing various colors of the universal indicator. Among halides, F\(^-\) was differentiated from Cl\(^-\), Br\(^-\) and I\(^-\). The indicator was also used on conjugate acid-base pair anions to distinguish HCO\(_3\)\(^-\) from CO\(_3\)\(^2-\), HSO\(_4\)\(^-\) from SO\(_4\)\(^2-\), HSO\(_3\)\(^-\) from SO\(_3\)\(^2-\), and various phosphate species. Oxyanions SO\(_3\)\(^2-\), HSO\(_3\)\(^-\), ClO\(_3\)\(^-\), ClO\(_2\)\(^-\) and NO\(_2\)\(^-\) can be differentiated from oxyanions with more oxygens attached, namely, SO\(_4\)\(^2-\), HSO\(_4\)\(^-\), ClO\(_3\)\(^-\), ClO\(_2\)\(^-\) and NO\(_3\)\(^-\) respectively. Results can be correlated with the acid ionization constant \(K_a\) and/or base hydrolysis constant \(K_b\) of the anion.

Keywords: Colorimetric, Universal pH Indicator, Anion differentiation, pH, Ionization constants.

INTRODUCTION

Acid-base indicators or pH indicators are a class of dyes that are common in most chemistry laboratories. These are weak acids or bases of which its undissociated form exhibits a color different from its ionic form.\(^1\) It has been developed, primarily, for determining the pH of solutions. However, its application has expanded to include sensing various analytes such as gases,\(^5-7\) organic compounds\(^8,9\) and cations.\(^10,11\)

Recently, our group has shown that anions can be differentiated based on its acidic or basic properties. Using flower pigments\(^12\) or common laboratory pH indicators,\(^13\) different anions change the color of the indicator depending on the pH produced in solution. This approach has been applied to differentiate conjugate acids and bases such as carbonates, sulfates and phosphates. While flower pigments can be extracted easily from natural sources, its color was found to be unstable for long periods of time and tend to vary depending on the extraction procedure and its source. Common laboratory pH indicators, on the other hand, are more stable and are readily available. However, the pH range of individual indicators is limited; thus, requiring several indicator solutions to perform the analysis.
In this study, a universal pH indicator serves as a “single” colorimetric reagent for the qualitative profiling of anions. This approach is simple, easy to conduct, and requires small amounts of reagents for analysis. The method can have practical applications in chemical education. It can serve as a teaching demonstration or microscale laboratory experiment in senior high school or undergraduate general chemistry, or analytical chemistry class to illustrate solution properties of anions, understand the nature of amphiprotic anions, and relate the effect of equilibrium constants $K_a$ and $K_b$ to varying anionic species.

**MATERIALS AND METHODS**

**Materials and Equipment**

Analytical grade sodium and potassium salts used in this study, namely NaF, NaI, Na$_2$SO$_4$, NaHSO$_4$, Na$_2$SO$_3$, NaClO, NaClO$_2$, NaNO$_3$, NaNO$_2$, Na$_3$PO$_4$, Na$_2$HPO$_4$, KCl, KBr, KH$_2$SO$_4$, and KClO$_3$ were purchased from commercial sources and used without further purification. The universal pH indicator (pH 4-10) was purchased from Sigma-Aldrich™.

**Reagent and Microplate Colorimetry Preparations**

1.5 mL of 0.1M salt solutions in distilled or deionized water were prepared. 0.3 mL of each solution were placed into 96-well microplates, with one column composed of three wells serving as the three trials for each salt. A separate column was used for the control group (water only). 15.6 μL of the universal pH indicator was added into each test solution.

**RESULTS**

One of the most versatile acid-base indicators developed is the universal pH indicator.$^{14}$ Also known as Yamada Universal Indicator, this solution consists of thymol blue, bromothymol blue, phenolphthalein and methyl red.$^{15}$ It operates at long pH ranges (pH 4-10). In this study, a universal pH indicator was used as a “single” reagent for differentiating anions. The addition of the universal pH indicator to individual solutions of anions led to color changes as shown in Figure 1.

Among the halides, F$^-$, Cl$^-$, Br$^-$, and I$^-$, only F$^-$ was generally distinct from the others. F$^-$ led to an olive-green solution while other halides have colors similar to the control solution at 0.1M concentration. At a higher concentration (1M), F$^-$ is still significantly different from Cl$^-$, Br$^-$, and I$^-$, but the color has turned to blue. Moreover, I$^-$ could now be distinguished from the other halides with a color change from yellow to olive-green. This observation may be attributed to an increase in ionic strength of halide solutions which caused a shift in the color of the indicator. This behavior has also been noted by Rodriguez and Mirenda$^{16}$ in which an increase in salt concentration led to a shift of the pH indicator towards the basic form. Thus, it is important to compare anions with the same concentration and under dilute conditions.

Conjugate acids/bases were also distinguished from each other. It was observed that the color of the SO$_4^{2-}$ solution is yellow while that of HSO$_4^-$ is red. Meanwhile, SO$_3^{2-}$ was notably violet while HSO$_3^-$ was red-orange. Different phosphate species exhibited different colors: PO$_4^{3-}$ is violet, HPO$_4^{2-}$ is blue, and H$_2$PO$_4^-$ is orange. It was also observed that CO$_3^{2-}$ is violet while HCO$_3^-$ is blue. As expected, the conjugate acid form of the anion tends to shift the color of the indicator towards the acidic color relative to its basic color.

Finally, oxyanion pairs sulfate-sulfite, bisulfate-bisulfite, nitrate-nitrite, and oxychlorides were also differentiated from each other. Less-oxygenated oxyanions SO$_3^{2-}$ and ClO$_2^-$ resulted in blue to violet colors. ClO$_3^-$, at the onset, is violet but
eventually turns to light green, then colorless. It should be noted that hypochlorite, ClO\textsuperscript{-}, is a widely-used bleach and a strong oxidant, and is known to degrade dyes.\textsuperscript{17,18} Meanwhile, oxanions with a higher number of oxygen atoms attached, SO\textsubscript{4}\textsuperscript{2-}, ClO\textsubscript{3}\textsuperscript{-}, and ClO\textsubscript{4}\textsuperscript{-}, result in a yellow solution. On the other hand, for oxanions NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-}, nitrate exhibited a dark green color, while nitrite ion yielded a yellow-green solution.

The analysis was also performed in degassed distilled and degassed deionized water. Similar results were obtained as those for simple distilled water. This implies that minimal impurities like dissolved gases in the air do not significantly affect the results of the analysis.

**DISCUSSION**

The colors observed for anion solutions correlate well to the colors of the indicator at a given pH of the solution. This was verified using a pH meter. Conjugate bases and less oxygenated oxychlorides ClO\textsubscript{2}\textsuperscript{-}, ClO\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-} and PO\textsubscript{4}\textsuperscript{3-} with pH of 10 or greater exhibited a violet color. SO\textsubscript{4}\textsuperscript{2-} and HPO\textsubscript{4}\textsuperscript{2-} with pH 9 to less than 10 imparted a yellow solution. HCO\textsubscript{3}\textsuperscript{-} with pH ranging from 8 to less than 9 yielded a blue-green color. On the other hand, NO\textsubscript{3}\textsuperscript{-} and F\textsuperscript{-} with pH 7 to less than 8 presented a green color. Oxanions SO\textsubscript{4}\textsuperscript{2-}, ClO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} with pH from 6.4 to less than 7 displayed a yellow-green solution. Meanwhile, halides I\textsuperscript{-}, Cl\textsuperscript{-}, and Br\textsuperscript{-} with pH from 6 to less than 6.4 imparted a yellow color. For protonated anions, H\textsubscript{3}PO\textsubscript{4}\textsuperscript{-} (pH 4-5) gave off orange color, while HSO\textsubscript{3}\textsuperscript{-} and HSO\textsubscript{4}\textsuperscript{2-} (pH < 4) yielded red-orange or red, respectively.

Aside from pH, the color of the solution imparted by anions can be correlated to its acid ionization constant ($K_a$) or base hydrolysis constant ($K_b$).\textsuperscript{19} This allows grouping of anions based on its acidic or basic properties as shown in Fig. 2. Anions which turn the pH indicator to red or red-orange (HSO\textsubscript{4}\textsuperscript{2-}, HSO\textsubscript{3}\textsuperscript{-} and H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}) are protonated species and were found to have $K_a$ values greater than its $K_b$ (Table 1). Thus, these anions tend to produce more H\textsubscript{3}O\textsuperscript{+} in solution via acid ionization than OH\textsuperscript{-} ions produced via base hydrolysis, as exemplified by HSO\textsubscript{4}\textsuperscript{2-} in Figure 3.

**Table 1: Acid ionization and base hydrolysis constants for protonated anions**

| Anion       | Acid ionization constant ($K_a$) | Base Hydrolysis constant ($K_b$) |
|-------------|---------------------------------|----------------------------------|
| HSO\textsubscript{4}\textsuperscript{2-} | 1.2x10\textsuperscript{2}       | Very small                       |
| HSO\textsubscript{3}\textsuperscript{-} | 6.3x10\textsuperscript{5}       | 8.3x10\textsuperscript{-13}      |
| H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} | 6.2x10\textsuperscript{6} | 1.3x10\textsuperscript{-12}      |

*Calculated from $K_b = K_a/K_w$ where $K_w$ is the ionization constant of water, and $K_a$ is ionization constant of the conjugate acid of the anion.

$$\text{HSO}_4^- (aq) + H_2O(l) \rightleftharpoons SO_4^{2-} (aq) + H_3O^+ (aq)$$

**acid ionization**

$$\text{HSO}_4^- (aq) + H_2O(l) \rightleftharpoons H_2\text{SO}_4 (aq) + OH^- (aq)$$

**base hydrolysis**

**Fig. 3. Acid ionization and base hydrolysis reactions involving HSO\textsubscript{4}\textsuperscript{2-}**

On the other hand, anions that turn the pH indicator to yellow or yellow-green (Cl\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-} and ClO\textsubscript{3}\textsuperscript{-}) or green (F\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-}) were found to have $K_a$ values less than 10\textsuperscript{-11}. Finally, anions that turn the pH indicator to blue or violet (ClO\textsubscript{2}\textsuperscript{-}, SO\textsubscript{3}\textsuperscript{2-}, HPO\textsubscript{4}\textsuperscript{3-}, PO\textsubscript{3}\textsuperscript{-}, HCO\textsubscript{3}\textsuperscript{-}, CO\textsubscript{2}\textsuperscript{-} and ClO\textsubscript{4}\textsuperscript{-}) are relatively basic. These anions, except for ClO\textsubscript{2}\textsuperscript{-} ($K_a = 8x10\textsuperscript{-13}$), were found to have $K_b$ values greater than or equal to 10\textsuperscript{-11}.

**CONCLUSION**

A universal pH indicator solution was used to differentiate inorganic anions. The indicator was able to differentiate F\textsuperscript{-} from the other halides. Protonated anions (HSO\textsubscript{4}\textsuperscript{2-}, HSO\textsubscript{3}\textsuperscript{-} and H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}) were
also differentiated from its conjugate base pairs (SO$_4^{2-}$, SO$_3^{2-}$, HPO$_4^{2-}$, and PO$_4^{3-}$). Oxyanions SO$_3^{2-}$, HSO$_3^-$, NO$_3^-$, ClO$_2^-$ and ClO$_3^-$ were differentiated from oxyanions with more oxygen atoms attached, namely SO$_4^{2-}$, HSO$_4^-$, NO$_2^-$ and ClO$_2^-$). The color produced can be correlated with the pH of the solution and corresponding acid ionization constant $K_a$ and/or base hydrolysis constant $K_b$ of the anion.

This approach is simple and can be used as a demonstration or laboratory experiment in high school or freshmen college chemistry to help learners understand the acidic or basic nature of anions. It also applies principles of chemical equilibrium, ionization constants, and nature of amphiprotic anions through visual observation.

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Conflict of interest
No conflict of interest.

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