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Brief communication

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^-, ClO_2^- and NO_2^- can be differentiated from oxyanions with more oxygens attached, namely, SO_4^{2-}, HSO_4^-, ClO_3^-, 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,[2–7] 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_2SO_4, $NaHSO_4$, $NaHSO_3$, Na_2SO_3, NaClO, $NaClO_2$, $NaNO_3$, $NaNO_2$, Na_3PO_4, Na_2HPO_4, NaH_2PO_4, KCl, KBr, $KHSO_4$, 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.

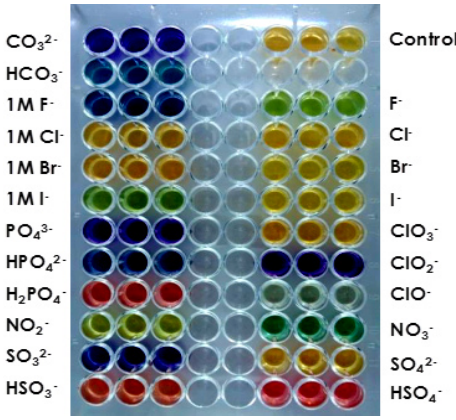

Fig. 1. Microplate wells containing 0.1 M anion solutions (unless otherwise indicated) in distilled water with a universal pH indicator solution. Tests were done in triplicates

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 $H_2PO_4^-$ 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^-, at the onset, is violet but eventually turns to light green, then colorless. It should be noted that hypochlorite, ClO^-, is a widely-used bleach and a strong oxidant, and is known to degrade dyes.[17,18] Meanwhile, oxyanions with a higher number of oxygen atoms attached, SO_4^{2-} and ClO_3^-, result in a yellow solution. On the other hand, for oxyanions NO_3^- and NO_2^-, 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_2^-, ClO^-, CO_3^{2-} and PO_4^{3-} with pH of 10 or greater exhibited a violet color. SO_3^{2-} and HPO_4^{2-} with pH 9 to less than 10 imparted a blue solution. HCO_3^- with pH ranging from 8 to less than 9 yielded a blue-green color. On the other hand, NO_3^- and F^- with pH 7 to less than 8 presented a green color. Oxyanions SO_4^{2-}, ClO_3^- and NO_2^- with pH from 6.4 to less than 7 displayed a yellow-green solution. Meanwhile, halides I^-, Cl^-, and Br^- with pH from 6 to less than 6.4 imparted a yellow color. For protonated anions, $H_2PO_4^-$ (pH 4-5) gave off orange color, while HSO_3^- and HSO_4^- (pH < 4) yielded red-orange or red, respectively.

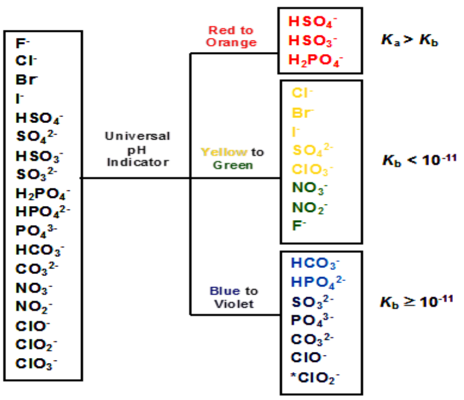

Fig. 2. Diagram for grouping anions based on the color of indicator and its ionization constants K_a, or K_b. *Chlorite is the only exception as its $K_b < 10^{-11}$

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).[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_4^-, HSO_3^- and $H_2PO_4^-$) 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_3O^+ in solution via acid ionization than OH^- ions produced via base hydrolysis, as exemplified by HSO_4^- in Figure 3.

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

Anion	Acid Ionization constant (K_a)[19]	Base Hydrolysis constant (K_b)*
HSO_4^-	$1.2x10^{-2}$	Very small
HSO_3^-	$6.3x10^{-8}$	$8.3x10^{-13}$
$H_2PO_4^-$	$6.2x10^{-8}$	$1.3x10^{-12}$

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

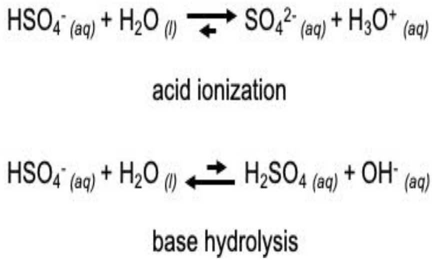

Fig. 3. Acid ionization and base hydrolysis reactions involving HSO_4^-

On the other hand, anions that turn the pH indicator to yellow or yellow-green (Cl^-, Br^-, I^-, SO_4^{2-}, NO_2^- and ClO_3^-) or green (F^- and NO_3^-) were found to have K_b values less than 10^{-11}. Finally, anions that turn the pH indicator to blue or violet (ClO_2^-, SO_3^{2-}, HPO_4^-, PO_4^{3-}, HCO_3^-, CO_3^{2-} and ClO^-) are relatively basic. These anions, except for ClO_2^- ($K_b = 8x10^{-13}$), were found to have K_b values greater than or equal to 10^{-11}.

CONCLUSION

A universal pH indicator solution was used to differentiate inorganic anions. The indicator was able to differentiate F^- from the other halides. Protonated anions (HSO_4^-, HSO_3^- and $H_2PO_4^-$) 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_2^-, ClO^- and ClO_2^- were differentiated from oxyanions with more oxygen atoms attached, namely SO_4^{2-}, HSO_4^-, NO_3^- and ClO_3^-. 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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