Color Changes in Indicator Solutions

An Intriguing and Elucidative General Chemistry Experiment

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Can an indicator solution change color upon dilution? Our usual experience in chemistry suggests to us that such behavior is impossible. Generally, dilution only decreases the intensity of the color but does not change the wavelength of absorbing light. This is the answer most frequently given when either students or professors of chemistry are asked. However, the answer to the question is affirmative, as shown in this paper. A simple experiment involving the dilution of an aqueous bromocresol green (BCG) solution is proposed, wherein the color of the solution changes from reddish to blue simply by addition of water.

Personal experiences in science have often shown that we learn more about a subject when our observations contradict our intuitions. This experiment allows students to investigate this phenomenon and learn more about acid–base indicators. A more detailed investigation, using pH measurements and analyzing the electronic spectra of the indicator solution, can prove that such behavior is in agreement with equilibrium concepts. Following this, a general discussion can be proposed by the instructor about the main characteristics that any system must have to show a similar phenomenon.

Experimental Section[W]

Glassware and Reagents

BCG was used as received (Merck, Darmstadt, Germany). The glassware, including the volumetric flasks, was not calibrated. Aliquots were taken using a calibrated adjustable pipet.

Observing the Phenomenon

First, the students should prepare some solutions by diluting portions of 0.50, 1.00, 1.50, 2.50, 3.90, 4.50, 5.10, 6.00, 6.30, and 7.50 mL of a 1.8×10^{-4} mol L^{-1} stock solution of BCG to the mark in 10-mL volumetric flasks. At this point, the instructor should call the students' attention to the striking color differences among the various diluted solutions. The instructor should also ask the students about the reasons for the color changes, if only a dilution was performed. After a brief discussion about the possible reasons for the observed phenomenon, a further investigation should be done through pH measurements and observation of the electronic spectrum of each diluted solution. From these experiments it is possible to verify that the pH values increase upon dilution and that changes in the electronic spectra are clearly observed.

Determination of pK_{In} of the Indicator Using the Henderson–Hasselbalch Equation

Using the pH value of each solution and the concentration of all the species involved, students can calculate the pK_{In} through the Henderson–Hasselbalch equation.

According to the Henderson–Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_{In} + \log([In^-]/[HIn]) \quad (1)$$

the pK_{In} can be determined by plotting the pH value of each solution as a function of log($[In^-]/[HIn]$) (*1–3*). The concentration of HIn can be determined from a calibration curve, and the $[In^-]$ can be calculated from the expression

$$[In^-] = [HIn]_0 - [HIn] \quad (2)$$

where $[HIn]_0$ is the total analytical concentration of the indicator added, as described in the supplemental material.[W]

Hazards

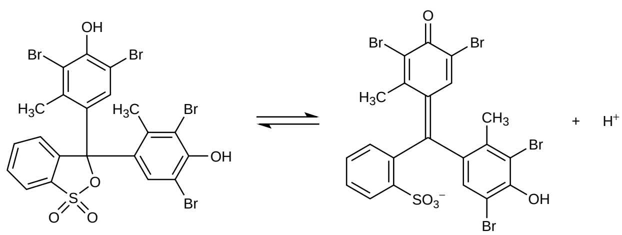
This experiment presents no significant hazards.

Results and Discussion

Dilution of the BCG Aqueous Solution

After preparing the diluted BCG solutions, students can observe the color changes pictured in the supplemental material.[W] The most concentrated solution of BCG shows a reddish color, which changes to green and then to pale blue as the dilution proceeds.

BCG is a well-known acid–base indicator, which is yellow (HIn) in acid medium and blue (In^-) in a basic medium. This process is represented by the following equilibrium:



HIn In⁻

The relationship between the pH and the concentration of both species (HIn and In^-) is described by the Henderson–Hasselbalch equation.

The addition of water to the stock solution of BCG could shift the equilibrium in the direction of the dissociated species (In^-). The electronic spectra of the diluted solutions[W] show bands at 440 and 628 nm. A decrease is observed in the intensity of the band at 440 nm as the dilution is carried out. However, the band at 628 nm does not change proportionally. It can be concluded that the degree of ionization (α) increases with dilution as the equilibrium shifts in the forward direction to In^-. If this equilibrium is described by the Henderson–Hasselbalch equation, we can determine the

pK_{In}, using the pH value for each diluted solution, to compare with the value found in the literature (*4*).

The pK_{In} was calculated from the graph of pH versus $\log([In^-]/[HIn])$.[W] The value obtained was 5, which is in good agreement with the literature value (*4*) of 4.7. However, the pK_{In}, found in the literature was calculated using the same equation but a different experimental procedure, involving varying the pH value at a fixed concentration of the indicator. A good review of the procedures for determining the p*K* of indicators can be found in the work of Patterson (*3*).

The pK_{In} value of BCG is very close to the p*K* value of acetic acid (4.75). Acetic acid is probably the most widely used example to illustrate changes in the α value with dilution. In this way, a simple comparison of the equilibrium of BCG and the equilibrium of acetic acid can be very useful.

Why Does Dilution Change the Color of an Indicator Solution?

A discussion can be proposed to show that the color change phenomenon would be observed with any indicator upon dilution. Nevertheless, the phenomenon depends on the pK_{In} value, as shown.

The equilibrium for a general acid–base indicator can be described as

$$HIn \rightleftharpoons In^- + H^+ \tag{3}$$

$$K_{In} = [In^-][H^+]/[HIn] \tag{4}$$

The relative concentration of the three species involved are summarized in the following table:

Concentration	Species		
	HIn	In^-	H^+
Initial	$[HIn]_0$	0	0
Change	$-\alpha[HIn]_0$	$+\alpha[HIn]_0$	$+\alpha[HIn]_0$
Equilibrium	$(1-\alpha)[HIn]_0$	$\alpha[HIn]_0$	$\alpha[HIn]_0$

where α is the degree of ionization ($\alpha = [In^-]/[HIn]_0$) and $[HIn]_0$ is the total analytical concentration of the indicator. Expressing the K_{In} in terms of α we obtain:

$$K_{In} = \alpha^2[HIn]_0/(1-\alpha) \tag{5}$$

The color change will be clearly observed when α is about 0.5. Therefore, using eq 5 and α = 0.5 we can estimate that a color change will be observed when $K_{In} \cong 0.5[HIn]_0$; that is, the analytical concentration of the indicator is of the same order of magnitude as the K_{In} value.

It can then be explained that changes in the color of a solution by a simple dilution are observed if certain conditions are involved:

1. The protonated and non-protonated species must have different colors (or must absorb light at different wavelengths).
2. In solution, the concentration of an indicator must be in the same range as the pK_{In} value.
3. The presence of an acid or basic substance in the solvent medium should be in the same concentration range as the pK_{In} value.

It is possible to discuss other examples of indicators whose solutions can change color by dilution. A list of some acid–base indicators is presented in the supplemental material.[W] Some extreme cases were chosen to encourage discussion.

If the indicator has a low pK_{In} value, the color change would be observed only at high concentrations in water. However, many indicators are organic substances that are only slightly soluble in water. For example, the color change for thymol blue (pK_{In} = 1.7) in water could only be observed in the concentration range around 10^{-1} mol L^{-1}. Other indicators have pK_{In} values higher than 9; here the color change will never occur because the indicator is still un-ionized even at infinite dilution, where the hydrogen ion concentration is nearly 10^{-7} mol L^{-1}, as shown by Stock (*5*).

Conclusion

The success of the experiment is related to the fact that the students should reflect about the changes in color brought on by the dilution. First it is interesting that they propose possible effects, which are discussed using experimental data obtained in the laboratory. Usually, the students first answer that the phenomenon is due to the contamination of the water or the presence of impurities already in the volumetric flask. With this simple way to observe and understand the intriguing behavior of indicators, students easily learn the concepts of chemical equilibrium and the chemistry of acid–base indicators. The simple dilution of the BCG can also be made in the classroom, allowing students to understand the changes in α by looking at the color change phenomenon.

Acknowledgments

We are thankful to Carol H. Collins for useful comments and suggestions. We also thank Rita C. R. Figueredo and Priscilla M. Freitas for valuable help.

[W]Supplemental Material

A detailed description of the experimental procedure and results is available in this issue of *JCE Online*.

Literature Cited

1. Lai, S. T. F.; Burkhart, R. D. *J. Chem. Educ.* **1976,** *53*, 500.
2. Sallzberg, H. W.; Morrow, J. I.; Cohen, S. R.; Green, N. E. *Physical Chemistry Laboratory: Principles and Experiments*; Macmillan: New York, 1978; pp 402–405.
3. Patterson, G. S. A. *J. Chem. Educ.* **1999,** *76*, 395.
4. Bishop E., *Indicators*, Pergamon: Oxford, UK, 1972; pp 65–137.
5. Stock, D. I. *J. Chem. Educ.* **1967,** *44*, 764.