VISUAL DEMONSTRATION OF THE IONIC STRENGTH EFFECT IN THE CLASSROOM. THE DEBYE-HÜCKEL LIMITING LAW

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Educação

The effects of ionic strength on ions in aqueous solutions are quite relevant, especially for biochemical systems, in which proteins and amino acids are involved. The teaching of this topic and more specifically, the Debye-Hückel limiting law, is central in chemistry undergraduate courses. In this work, we present a description of an experimental procedure based on the color change of aqueous solutions of bromocresol green (BCG), driven by addition of electrolyte. The contribution of charge product ($z_+|z_-|$) to the Debye-Hückel limiting law is demonstrated when the effects of NaCl and Na_2SO_4 on the color of BCG solutions are compared.

Keywords: color change; ionic strength effect; visualization of the Debye-Hückel law.

INTRODUCTION

There are numerous chemical systems that involve electrolytes and therefore depend on ionic strength of the medium. It is possible to highlight these biochemical systems, which involve electrolytes such as proteins and amino acids. For such systems, the control of ionic strength is essential, since the electrostatic interactions are the most intense interaction between the chemical species. For this reason, great deviations from ideality can be observed even when the species are in very dilute solutions. Ionic solutions are electrically neutral, but since ions with opposite charges are mutually attracted, the immediate vicinity of a given ion has an excess of counter ions. Therefore, an ionic surrounding is formed around the ion. As a result, the chemical potential of any ion decreases due to the interaction of the ion with its ionic surrounding. This lowering effect is due to the difference between the molar Gibbs energy (G_m) and the ideal value (G_m^{ideal}) of the solution, and hence can be identified with $RT \ln \gamma_\pm$, where R, T and $\gamma_\pm$, are the gas constant, temperature and mean ionic activity coefficient, respectively.[1]

According to the model developed by Debye-Hückel, $\gamma_\pm$ is related to the average interaction of the cation and anion with their respective ionic surroundings. At 25 °C and in a very dilute solution, the value of $\gamma_\pm$ can be estimated using the Debye-Hückel limiting law (Equation 1):[2]

$$\log \gamma_\pm = -0.5 z_+ |z_-| \sqrt{I} \qquad (1)$$

where i is the ion charge and I is the ionic strength defined by Equation 2:

$$I = \frac{1}{2} \sum_i z_i^2 \left(\frac{m_i}{m_0} \right) \qquad (2)$$

where m_i is the molality of the ion i and m^0 is defined by $m^0 \equiv 1 \, mol \, kg^{-1}$.

Equation 1 is called the *limiting law*, since it is valid only in the limit of infinite dilution (i.e. ionic solutions of very low molality). Equation 1 can be used to simulate how $\gamma_\pm$ varies with the ionic strength and electrical charge of the ions, as shown in Figure 1.

It can be observed that in all cases $\log \gamma_\pm < 0$ and therefore the values of $\gamma_\pm$ will always be smaller than 1. It is further noted
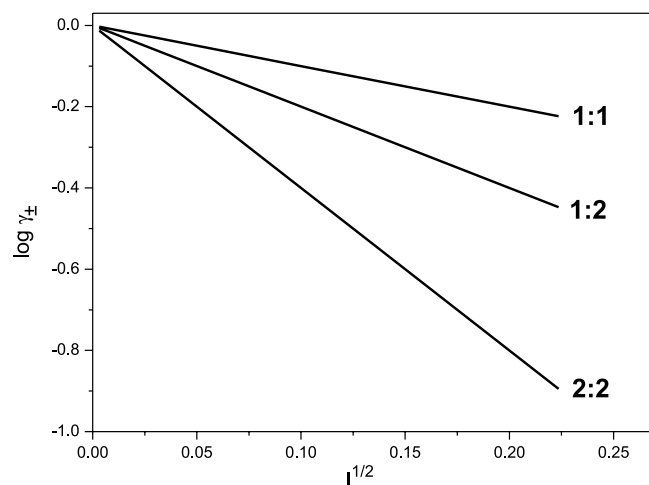

Figure 1. *Predictions of the Debye-Hückel limiting law: log $\gamma_\pm$ versus square root of ionic strength for dilute solutions of electrolyte of formula $M_{z_-}X_{z_+}$, where $z_+|z_-|= 1x1, 1x2$ and $2x2$*

that the slope of the lines, according to the model, is proportional to the product of the charge ($z_+|z_-|$) of the ions that compose the electrolyte. Thus, it is expected that for the same ionic strength, the value of $\gamma_\pm$ will always be higher for NaCl solution than for Na_2SO_4.

The aim of this article is to present a visual demonstration of the limiting law, which can be easily run in a classroom. It is based on the color change of a bromocresol green (BCG) solution. Recently, an author of this article *et al.*,[3] demonstrated that the color of an aqueous BCG solution can change (from reddish to blue) simply by addition of water. This intriguing and, in principle, unexpected phenomenon, has been successfully used in an experiment developed in the undergraduate physical chemistry laboratory course for chemistry students at IQ-UNICAMP. The effect of ions to illustrate the Debye-Hückel limiting law complements the experiment.

SUGGESTION OF THE EXPERIMENTAL PROCEDURE TO BE USED IN CLASS

The demonstration of the ionic strength effect can be easily run

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in class. In the ensuing text, we present an experimental description that produces an excellent visual result (similar to the photograph shown in Figure 2).

A 1×10^{-3} mol L^{-1} stock solution of BCG is prepared by solving ≈ 70 mg of solid BCG (M = 698.02 g mol^{-1}) in a 100 mL volumetric flask with ethanol, since BCG has low solubility in pure water. In order to accelerate dissolution, the solution must be sonicated for 5 to 10 min (Thorton T-14 at 40 kHz and 50 W). Subsequently, an aliquot of 6.3 mL of stock solution is diluted in a 500 mL volumetric flask with water up to the 500 mL mark, obtaining a 1.3×10^{-5} mol L^{-1} aqueous BCG solution. At this concentration, both BCG species are present in representative quantities, allowing good change of color by addition of the electrolyte. Next, 100 mL of aqueous BCG solution are transferred to three separate glass vials, and at the time of the demonstration solid electrolytes are added, 0.58 g of NaCl to one vial, and 0.57 g of Na$_2$SO$_4$ to another vial. The mixtures are then agitated until complete dissolution of the solids. The addition of the electrolytes at the indicated ratio produces solutions with the same ionic strength ($I = 0.1$ mol L^{-1}).

PRINCIPLES AND DISCUSSION

Figure 2 shows a photograph of the three glass vials containing aqueous BCG solutions at the same concentration, and two of them containing NaCl and Na$_2$SO$_4$ in order to generate the same ionic strength, $I = 0.1$ mol L^{-1}. The color changes are clearly observed. Addition of electrolyte induces a color change to blue. Surprisingly, this effect is more intense for Na$_2$SO$_4$.
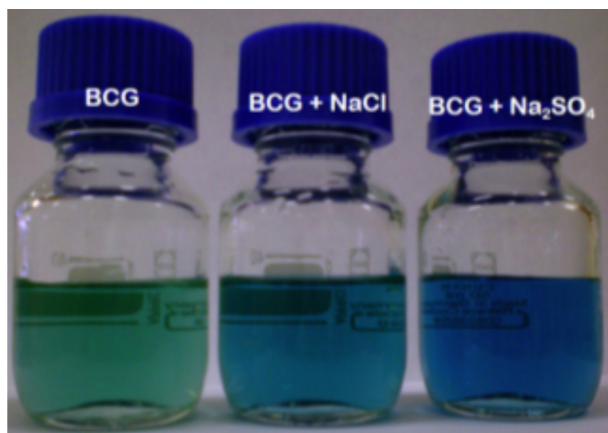

Figure 2. *Photograph of glass vials containing aqueous BCG solutions (1.3 x 10^{-5} mol L^{-1}) with: only water (left-hand side); NaCl, I = 0.1 mol L^{-1} (middle); Na$_2$SO$_4$, I = 0.1 mol L^{-1} (right-hand side)*

To explain the color change of the solutions, it must first be considered that BCG is an acid-base indicator, in which the protonated (BCG-H) and non-protonated (BCG$^-$) species can interconvert one to another according to the chemical equation (Figure 3):
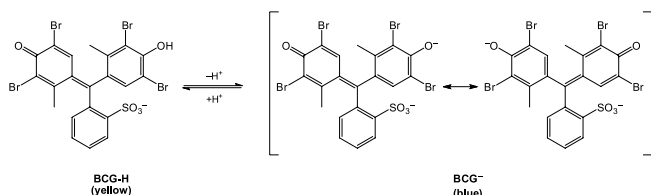

Figure 3. *Schematic representation of aqueous equilibrium of BCG*

The green color presented by the aqueous BCG solution is due

to the fact that both species are present in such quantities that the observed color is produced from the combination of the colors yellow and blue. Therefore, it can be inferred that the addition of electrolytes shifts the equilibrium towards the dissociated species (BCG$^-$). It is also noteworthy that, although the two electrolyte solutions present the same ionic strength, the BCG equilibrium shifts more intensively toward Na$_2$SO$_4$. Obviously for this comparison, the pH needs to be close. The pH of the BCG solutions were measured and the values were practically the same, at 5.2.

The equilibrium shift can be noted in the electronic absorption spectra as shown in Figure 4 (obtained on a Shimadzu UV-Vis, spectrophotometer).
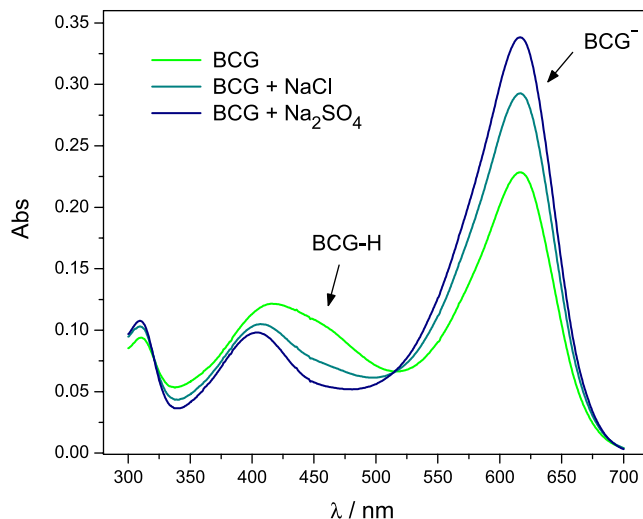

Figure 4. *Electronic spectra of BCG solutions (1.3 x 10^{-5} mol L^{-1}) in water and with NaCl and Na$_2$SO$_4$ (I = 0.1 mol L^{-1})*

As can be observed, the interconversion is well characterized by the decreased intensity of the band at approximately 440 nm and the increased band at 620 nm. The isosbestic point, around 520 nm, clearly indicates the direct interconversion of one specie into the other.

Students have good knowledge about chemical equilibrium shifts, caused by the addition of a common ion. However, in the BCG case, the equilibrium shift cannot be explained by this effect. The approach should involve the effect of the increasing ionic strength of the solution leading to the stabilization of the ionic species (BCG$^-$ and H$^+$). The equilibrium constant for the reaction is written according to Equation 3:

$$K = \frac{a_{H^+} a_{BCG^-}}{a_{BCG-H}} \qquad (3)$$

where a is the activity of the species involved in the equilibrium.

For dilute solutions, the equilibrium constant can be approximated as shown in Equation 4:

$$K \approx \frac{\gamma_{\pm}^2 \, [H^+][BCG^-]}{[BCG-H]} \qquad (4)$$

The activity coefficient for BCG-H is ≈ 1, since its concentration is relatively small and because it is a neutral molecule, it is not highly influenced by ionic strength. We can rearrange the Equation 4 to:

$$[H^+][BCG^-] = K \frac{[BCG-H]}{\gamma_{\pm}^2} \qquad (5)$$

According to the Debye-Hückel limiting law (Figure 1), $\gamma_{\pm}$ is less than 1 in dilute solutions of electrolyte. Thus, from Equation 5

we note that the analytical concentrations of H^+ and BCG^-, $[H^+]$ and $[BCG^-]$, should be greater when the value of $\gamma_\pm \approx 1$, i.e., when the ionic strength tends to zero. Thus, it is demonstrated that the increase of ionic strength shifts the chemical equilibrium due to the stabilization of the ionic species, lowering the difference of free energy ($RT \ln \gamma_\pm$).

Clearly, the relative shift in the equilibrium of BCG solutions containing NaCl and Na_2SO_4 cannot be explained by differences in ionic strength. However, according to the Debye-Hückel limiting law, $\gamma_\pm$ is proportional to the charge product $z_+|z_-|$ (Equation 1). Hence, in the case of both electrolytes, even though the ionic strength is the same, the charge products are: 1 x 1 and 1 x 2, for NaCl and Na_2SO_4, respectively. Therefore, even at the same ionic strength, the effect of the SO_4^{2-} anion is two-fold greater than that of the Cl^- counterpart, and consequently, the energy stabilization is greater.

CONCLUSION

By means of a simple experiment, it is possible to perform a visual demonstration of the effect of ionic strength on chemical electrolyte equilibrium. The clear change in the color of the BCG solution is associated with the equilibrium shift of the indicator due to the stabilization of the ionic species present. Moreover, the importance of the product of ionic charges ($z_+|z_-|$) in the Debye-Hückel limiting law is demonstrated in a visual and colorful way.

ACKNOWLEDGMENTS

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