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SHORT COMMUNICATION

A TRIAZOLE DERIVATIVE AS A NEW ACID-BASE INDICATOR

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ABSTRACT. In this study a new pH indicator, 3-benzyl-4-*p*-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-on (BPNBAT), soluble in acetonitrile:water (1:4), was developed. The estimation of pH is possible either from the position of the absorption maxima or from the absorbance intensity at a constant wavelength. This feature allowed us to determine the basic transition range of the medium because BPNBAT is colorless at pH lower than 8.5 and showed strong yellow-green color with high extinction coefficient in the pH range of 8.5–10.1. pK_a, pH at equivalent point and the molar absorptivity (in the aqueous medium at 380 nm) of BPNBAT are determined as 9.3, 8.3 and 8.8 x 10^3 $L.mol^{-1}.cm^{-1}$, respectively. The color change at the transition range can be attributed to the resonance structures of BPNBAT. The triazole compound was compared with thymolphthalein for accuracy test.

KEY WORDS: Acid-base indicator, 3-Benzyl-4-*p*-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-on, UV-Vis spectrometry, Resonance, Transition point, Titrimetry

INTRODUCTION

Many substances, both naturally occurring and synthetic, display colors that depend on the pH of the solutions in which they are dissolved. Some of these substances, which have been used for centuries to indicate the acidity or alkalinity of water, are still employed as acid/base indicators [1]. Consider an indicator which is a weak acid, with the formula HIn. At equilibrium, the following equilibrium equation is established with its conjugate base:

$$\underset{\text{Acid (color A)}}{H_{in(aq)}} \quad + \quad H_2O \quad \leftrightarrows \quad H_3O^+_{(aq)} \quad + \quad \underset{\text{Conjugate base (color B)}}{In^-_{(aq)}} \qquad (1)$$

The acid and its conjugate base have different colors. At low pH values the concentration of H_3O^+ is high and so the equilibrium position lies to the left. The equilibrium solution has color A. At high pH values, the concentration of H_3O^+ is low, so the equilibrium position thus lies to the right and the equilibrium solution has color B [2–7]. Because many dyes and pigments, based on donor-acceptor chromogens, have this feature, they have been used as pH indicators by the reversible action of acid and base forms, and this behavior led to the concept of acid-base indicators.

In this study, 3-benzyl-4-*p*-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-on (BPNBAT), synthesized by Ikizler *et al.* [8], acts as an electron donor, and was tested as an acid-base indicator in the pH range of 8.5–10.1 with change in color. pK_a, pH at end point and the molar absorptivity (in the aqueous medium at 380 nm) of BPNBAT were determined as 9.3, 8.3 and 8.8 x 10^3 $L.mol^{-1}.cm^{-1}$, respectively. During the acid/base titration, this indicator provides a sharp end point like other universal indicators, such as phenolphthalein and thymolphthalein,

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which have nearly the same working pH range. For this compound, color change in the pH range 8.5–10.1 was investigated. Commonly used pH indicators and the proposed compound were compared in the same pH range. Possible usage of BPNBAT, which is soluble in organic solvent, acetonitrile, as a new pH indicator is discussed in terms of transition range and color change.

EXPERIMENTAL

Chemicals and instrumentations. A Dr. Lange CADAS-200 model spectrophotometer (Germany) with 10 mm quartz cells were employed for the UV absorption measurements between 300 and 550 nm. A Hanna 211 pH meter (Hanna Instruments®, USA) with a glass electrode was used for the pH adjustments. The electrode system was calibrated using Merck standard buffer solutions of pH 4.0, 7.0 and 10.0. NaOH, HCl and thymolphthalein were obtained from Merck (Merck, Germany) and acetonitrile and ethanol were obtained from Fluka (Sigma-Aldrich Chemie, Switzerland). Distilled-deionized water was used to prepare all solutions. All reagents, obtained from Merck were of analytical reagent grade.

Methods. The indicator solution (BPNBAT) was prepared as 0.2%, w/v 50 mL in acetonitrile:water (1:4). The maximum absorption wavelength (λ) was 380 nm in water (Figure 1). In order to determine the transition range for the corresponding color change of the indicator, the absorption was measured at 380 nm, and pH of the solution was adjusted by 0.1 M NaOH solution. A 0.5 mL aliquot of BPNBAT solution was added to 10 mL of 0.1 M HCl solution. Then, the mixture was titrated with 0.1 M NaOH solution. After adding each 50 µL NaOH portion, pH, mV and absorbance (at 380 nm) of the resulting solution were measured. From the data obtained, absorbance vs pH curve was plotted (Figure 2). Also values of $pH_{end\ point}$, pK_a and pH working range were determined using mL vs pH and mL vs $\Delta E/\Delta V$ graphs [9].

Accuracy test. The BPNBAT (endpoint range pH = 8.5–10.1) was compared with thymolphthalein (TMP) (endpoint range pH = 8.8–10.5), which is widely used as an acid-base indicator in titrimetry. Ten solutions containing 10.00 mL of 0.1 M HCl were prepared. The TMP solution in ethanol (0.1%, w/v, 0.5 mL) was added to the first five samples of these solutions, while the BPNBAT solution in acetonitrile:water (1:4) (0.2%, w/v, 0.5 mL) was added to the last five and all were titrated to the end point with 0.1 M NaOH. The average NaOH consumptions when TMP and BPNBAT were used as indicator compared and found to be 10.6 and 10.4 mL, respectively. The relative standard deviation percentage (% RSD) was found to be 2.8% for TMP and 3.1% for BPNBAT. The relative error percentage (% RE), which was predicated on the average consumption for TMP, was calculated as 1.4%.

RESULTS AND DISCUSSION

Effect of pH on the absorption intensity. The absorption intensity during the acid-base reactions of BPNBAT exhibited quite strong color change in the alkali pH range. Figure 1 shows that the absorption intensity of the compound increases with increasing pH and reaches to approximately 3.5 times higher absorption value.

To determine the transition range for color change of the compound, the measurement of absorption was carried out at 380 nm with addition of dilute alkali solution (NaOH). With the addition of 0.1 M NaOH, the compound showed strong yellow-green color at λ_{max} (H_2O) 380 nm in the pH range 8.5–10.1 (at room temperature) (Figure 2).

Effect of the resonance structures on the color development. The corresponding color development at the transition point can be explained by the resonance structures of the compound (BPNBAT).

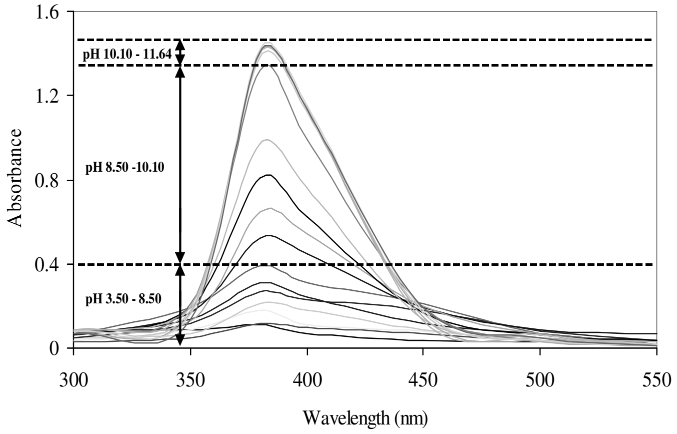


Figure 1. Spectral changes of the BPNBAT (0.2%, w/v in acetonitrile:water (1:4)) at different pH values.

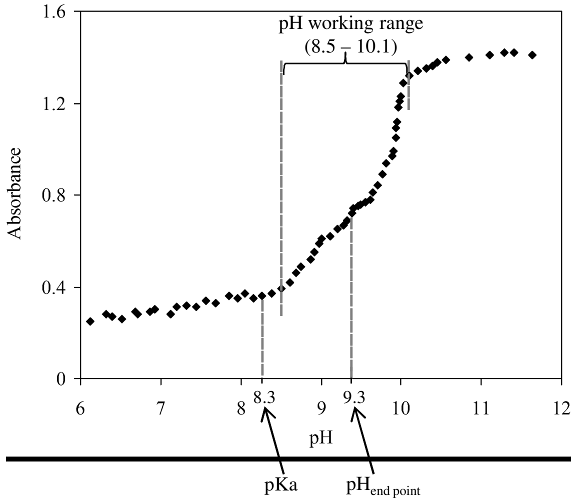
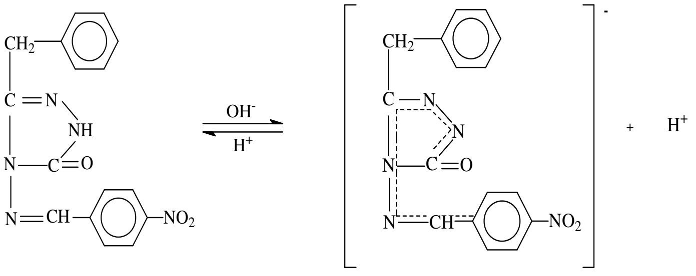


Figure 2. Effect of pH on the maximum absorption intensity of the BPNBAT (0.2%, w/v in acetonitrile:water (1:4)) (λ_{max} (H_2O) 380 nm).

The geometrical and electronic structures of the molecule (BPNBAT) had been previously investigated by an Austin Model 1 (AM1) lower case semiempirical method [10, 11]. The full geometric optimization of the molecule was performed by the method with Fletcher-Reeves algorithm and the most stable configuration of the molecule was determined. The bond degree, length and the charge distribution of the anion were investigated, and the negative charge was found to be delocalized (Figure 3). Sensitive acid-base reaction property of the compound can be explained by the formation of a π system within the dye structure. From the UV-Vis absorption spectra based on the varying basicity, a pH-dependent equilibrium between BPNBAT (HIn, acidic medium) and its deprotonated form was established in a mixture of sodium hydroxide and CH_3CN/H_2O system. BPNBAT was colorless in the acidic medium (0.1 M HCl). However, when alkali was added to the colorless state, the color of the medium was dramatically changed to yellow-green in the pH range 8.5–10.1. Color changes were reversible and the compound was stable in acidic and alkali conditions.



Colorless (HIn) Yellow-Green (In^-)

Figure 3. Resonance structure of 3-benzyl-4-*p*-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-on.

BPNBAT (0.2%, w/v in acetonitrile:water (1:4)), thus, can be considered as a new pH indicator since a considerable increase of the absorption intensity was observed by addition of alkali in the pH range of 8.5–10.1.

CONCLUSIONS

The results reveal that BPNBAT can be effectively used as an acid-base indicator because it shows reversible, sharp, clear color change and low RE (1.4%) in the pH range 8.5–10.1. When approximately 0.5 mL of BPNBAT is added to 50 mL of an aqueous solution, the color will turn from colorless to strong yellow-green in the pH range mentioned.

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