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New pH indicator based on 1,3-bisdicyanovinylindane

Young-A. Son[a], Sung-Hoon Kim[b,*]

[a]Department of Textile Engineering, Chungnam National University, Daejeon 305-764, South Korea
[b]Department of Dyeing and Finishing, Kyungpook National University, Daegu 702-701, South Korea

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Abstract

1,3-Bisdicyanovinylindane showed the application feasibility as a new pH indicator. In terms of absorption intensity occurring from the acid–base reactions, 1,3-bisdicyanovinylindane displayed strong blue colour with high extinction coefficient in the pH range 3.8–5.2. In addition, this corresponding colour development at the transition point was attributable to the resonance structures of 1,3-bisdicyanovinylindane which were caused by the hydrogen ion dissociation from the acidic form of the indicator in the presence of alkali.

Keywords: pH indicator; 1,3-Bisdicyanovinylindane; Transition point; Resonance

1. Introduction

Many chemical analyses are performed by titration, a procedure in which a reagent in a solution of known concentration, called the standard solution, is allowed to react with a sample containing an unknown quantity of substance to be analyzed. The point at which equivalent quantities of the reactants are present, exactly the equivalent point, is usually detected through the addition of an indicator to the solution being titrated. Indicator reagents are substances that enable the course of a chemical reaction to be followed or the state of a chemical system to be characterized. The term ''indicator'' is often employed without further explanation to refer to pH indicators [1,2]. For example, the dye phenolphthalein is colourless in the presence of excess hydrogen ion but turns red in the presence of excess hydroxide; hence it can be used as an indicator in an acid–base titration. The most commonly used pH indicators include azo dyes, nitrophenols, phthaleins and sulfonphthaleins [3].

The majority of dyes and pigments are based on donor–acceptor chromogens, i.e. the system consists of a substituent that readily releases electrons (the donor group) and is linked to an electron accepting substituent (the acceptor group) by an unsaturated bridge. 1,3-Bisdicyanovinylindane is a powerful electron acceptor and has been used as a starting material for the preparation of near infrared absorbing methine dyes [4,5].

The work herein comprises an investigation of 1,3-bisdicyanovinylindane which can be considered as a new pH indicator (Scheme 1). The absorption spectra in the range of colour transition point were examined.

2. Experimental

Melting points were determined using an Electrothermal IA 900 and were uncorrected. Visible spectra were recorded on Shimadzu UV 2100 spectrophotometer. Elemental analyses were recorded on a Carlo

* Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

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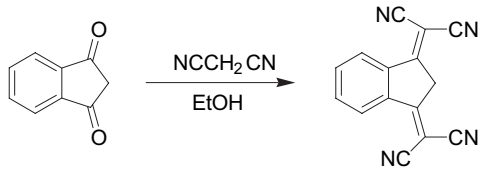


Scheme 1.

Elba Model 1106 analyzer. Mass analysis was recorded using a Shimadzu QP-1000 spectrometer with an electron energy of 70 eV and direct sample introduction.

2.1. Preparation of sodium 1,3-bisdicyanovinylindane

A mixture of 1,3-indandion (14.9 mmol, 2.18 g) and malononitrile (44.7 mmol, 2.95 g) in ethanol (50 ml) was prepared and stirred at room temperature for 15 min and sodium acetate (3.05 g) was then added. The reaction mixture was refluxed for 3 h. After the reaction was complete, the mixture was allowed to cool to room temperature. The blue solution was then filtered to remove monocondensation product such as 3-dicyanovinylindan-1-one. The filtrates were diluted with water (100 ml) and acidified using hydrochloric acid to give a white solid precipitate. The precipitate was filtered off, washed thoroughly and dried [4]. Yield: 55.59% (2.01 g); m.p. 263–266 °C; calculated for $C_{15}H_6N_4$: C, 74.37; H, 2.50; N, 23.13. Found: C, 74.78; H, 2.49; N, 23.48; m/z (M^+): 242; λ_{max} (nm) (H_2O), ($\varepsilon \times 10^5$); 580, (8.79).

1,3-Bisdicyanovinylindane (1.59 mmol, 0.385 g) was dissolved in water (40 ml) containing NaOH (0.006 g) and the sodium salt of 1,3-bisdicyanovinylindane was precipitated by adding 20 ml of saturated aqueous NaCl solution. The precipitate was collected by filtration, washed with dilute NaCl solution and dried. The colour changing phenomena were observed in response to a change in pH with alkali addition. M.p. > 300; calculated for $C_{15}H_5N_4Na$: C, 65.65; H, 2.37; N, 19.86. Found: C, 65.21; H, 1.98; N, 19.24.

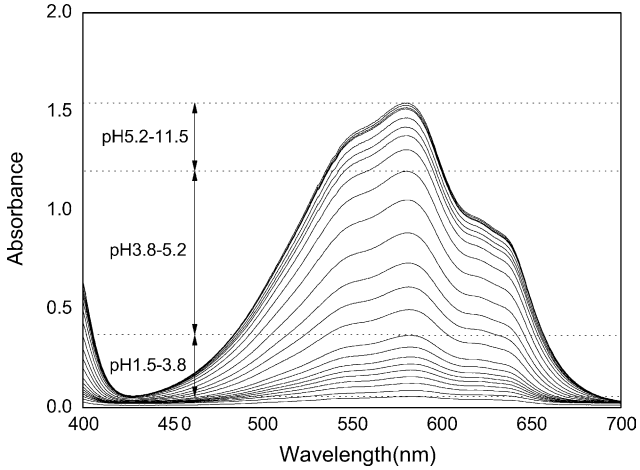


Fig. 1. Spectral changes of 1,3-bisdicyanovinylindane at different pH values.

3. Results and discussion

Many dyes have been used as pH indicators by the reversible action of acid and base and this behavior led to the concept of acid–base indicators. In this work, 1,3-bisdicyanovinylindane for pH indicator displayed its colour change in the pH range 3.8–5.2. To compare the transition ranges with other dyes or compounds, the commonly used pH indicators in the pH range 3–5 are listed in Table 1 in order of their increasing transition points.

In terms of transition ranges and colour changes, 1,3-bisdicyanovinylindane exhibited quite acceptable properties to be used as an indicator. With alkali addition, 1,3-bisdicyanovinylindane showed strong blue colour at λ_{max} (H_2O) 580 nm in the pH range 3.8–5.2.

Fig. 1 shows that the absorption intensity of the indicator increased with increasing pH and that the remarkable absorption increase was observed in the pH range of around 3.8–5.2. Above pH 5.2, the extent of absorption increase gradually decreased. Further investigation was considered to support the finding from Fig. 1.

Table 1
Commonly used pH indicators

pH (transition range)	Indicators	Colour change	Composition of indicator solution (%)
3.0–4.5	Bromochlorophenol blue	Yellow–blue violet	0.1 (in 20% ethanol)
3.0–4.6	Bromophenol blue	Yellow–blue violet	0.1 (in 20% ethanol)
3.0–5.2	Congo red	Violet–orange red	0.2 (in water)
3.1–4.4	Methyl orange	Pink–yellow orange	0.04 (in 20% ethanol)
3.5–5.8	2,5-Dinitrophenol	Colourless–yellow	0.1 (in 70% ethanol)
3.7–5.0	1-Naphthyl red	Red–yellow	0.1 (in 70% ethanol)
3.8–5.2	1,3-Bisdicyanovinylindane[a]	Colourless–blue	In water
3.8–5.4	Bromocresol green	Yellow–blue	0.1 (in 20% ethanol)

[a] The prepared dye used as a pH indicator in this study.

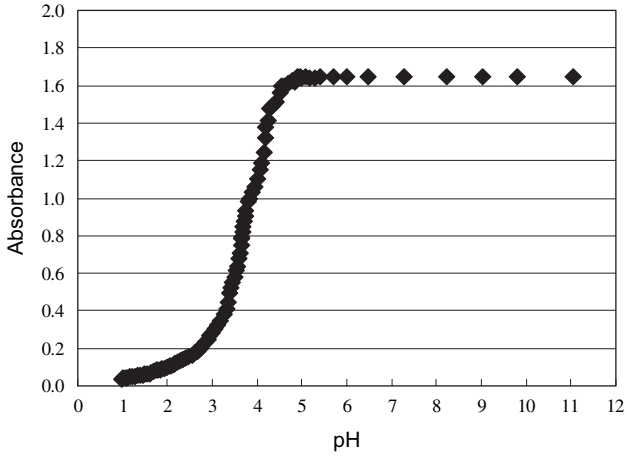
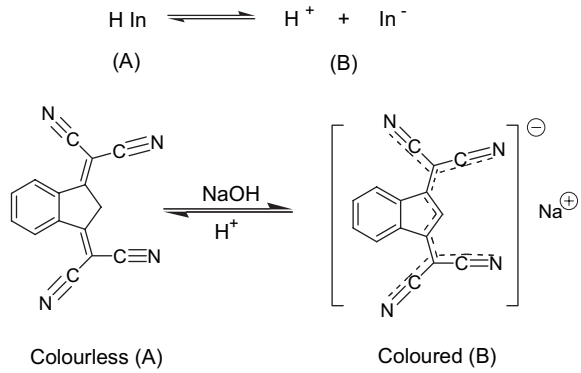


Fig. 2. Effect of pH on the absorption intensity transition: λ_{max} (H_2O) 580 nm.

To determine the transition range for colour change of the indicator, the measurement of absorption was carried out at 580 nm with addition of dilute alkali solution (NaOH). The result is shown in Fig. 2. As a result of the reaction between acid and base, a considerable increase of the absorption intensity was observed by addition of alkali in the pH range 3.8–5.2, in which 1,3-bisdicyanovinylindane showed the colour transition property to be acceptable as a pH indicator.

This corresponding feasibility of using 1,3-bisdicyanovinylindane as a pH indicator can be explained by the sensitive acid–base reaction property which occurred by the formation of π system within the dye structure (Scheme 2).

1,3-Bisdicyanovinylindane was colourless in the acidic condition. However, when alkali was added to the colourless state, it slowly converted to the coloured base form in the pH range 1.5–3.8 and then dramatically changed its absorption spectra in the pH range 3.8–5.2. The coloured form showed very strong blue colour with high extinction coefficient. Scheme 2 displays the colour changing behaviors of 1,3-bisdicyanovinylindane; the indicator of weakly acidic form usually shows the colour change by the dissociation of H^+ and In^- (Indicator$^-$) in alkaline condition from the acidic form of HIn. As shown in Scheme 2, with alkali addition its corresponding resonance structures are attributed to the sharply increased colour absorption intensity. In this context, 1,3-bisdicyanovinylindane could be considered to be used as a new pH indicator.



Scheme 2.

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