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Determination of the acidity constants of neutral red and bromocresol green by solution scanometric method and comparison with spectrophotometric results

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ABSTRACT

In this study, we applied the solution scanometric method as a new, simple, fast and inexpensive method for estimating the acidity constants of neutral red (NR) and bromocresol green (BCG) indicators in pure water and an ionic strength of 0.1 mol L^{-1} (KNO_3).

The method is based on scanning cells containing the indicator solution with a scanner, and analyzing the color of each cell with a software written in visual basic (VB 6) media to red, green and blue values. The cells were made by making holes in the Plexiglas® sheet. Also, the acidity constants of the neutral red and bromocresol green indicators were studied with spectrophotometrically. HypSpec program has been applied for the estimation of pK_a values based on spectrophotometric data. The agreement between obtained pK_a values by solution scanometric, spectrophotometric method and values reported in the literature demonstrates the utility of the method here used. Also the HySS 2009 program was applied for drawing of the corresponding distribution diagrams.

1. Introduction

Dissociation constants are important parameters to indicate the extent of ionization of molecules in solution at different pH values. The acidity constants of organic reagents play a fundamental role in many analytical procedures such as acid–base titration, solvent extraction, complex formation, and ion transport. It has been shown that the acid–base properties affect the toxicity, chromatographic retention behavior (Roses and Bosch, 2002), and pharmaceutical properties of organic acids and bases (Gilli et al., 2009). Much of the theoretical foundation of modern organic chemistry is based on the observation of the effects on the acid–base equilibrium of changing molecular structure.

Different methods exist to measure pK_a values as [e.g., Fourier transform IR (FT-IR) spectrometry, UV-vis absorption and fluorescence spectrophotometry, and 1H NMR spectroscopy],

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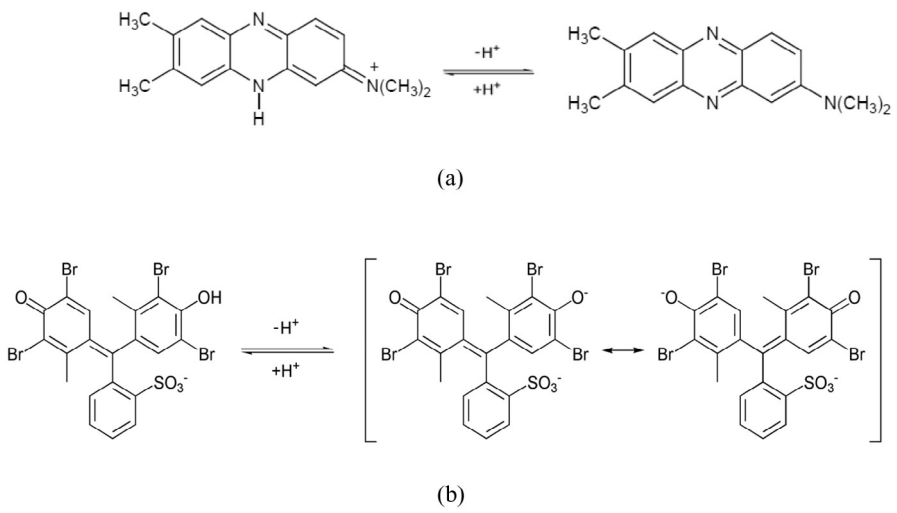

Fig. 1 – Structure of NR (a) and BCG (b) indicators.

potentiometric, chromatographic, capillary electrophoresis, calorimetric and conductometry methods (Bombara and Troyli, 1963; Cabot et al., 2010; Gervasini and Auroux, 2013; Hemmateenejad et al., 2008), and recently, solution scanometric method (Abbaspour et al., 2009, 2011a, 2011b, 2012; Shokrollahi and Davoodi Kashkoli, 2016; Shokrollahi and Roozestan, 2013; Shokrollahi and Shokrollahi, 2014), were developed to determine the stability constants of indicators by Shokrollahi et al. (Shokrollahi and Zare, 2016; Shokrollahi et al., 2015).

Advantages of solution scanometry include simplicity (handheld scanner and PC), high scanning speed, inexpensive, portable systems and easy immobilizing of reactants, no need to find the λ_{max}, intensive archive of experiences, short response time, limiting the interferences, capability of various simultaneous tests and using non-transparent solution and investigation of the reflective properties of the surface. However, there are disadvantages such as the lack of uniformity in the membrane that causes serious effects on the relative standard deviation percent and precision of analysis.

Neutral red (NR) (3-amino-*m*-dimethylamino-2-methylphenazine hydrochloride) (Fig. 1a) is a weak cationic azine dye. It is a pH indicator as well, with a transition range of 6.8 (bluish-red) and 8 (orange-yellow), pK_a value of this reaction is 6.7 in water and 8.2 in methanol and ethanol. It is widely used for the colorimetric measurement of pH with buffer solution, liquid crystal displays (Klein and Geisonw, 2006), solar cells (Chane et al., 2005), thermochromics materials (Zhang, 2005), coloring wood (Leach and Zhang, 2005), detergents (Macdonald et al., 2005), assessment of tobacco smoke (Bombick, 2002), cosmetics (Maillefer et al., 2005), detection of bacterial infection (Stickler and Waters, 2006), endodontics, diabetes, obesity, cancer, age-related macular degeneration, viral diseases (Hofmann, 2005a, 2005b, 2005c, 2005d, 2006) and as an assay of viability in cultured fish cells (Kado, 1993).

Bromocresol green (BCG) (3', 3", 5', 5"-tetrabromo-m-cresolsulfonphthalein) (Fig. 1b) is a sulfonphthalein dye, with a transition range of pH 3.8 to 5.4. In the acidic form, it appears yellow, and in the basic form, it is blue. It is used as a pH indicator and as a tracking dye for DNA agarose gel electrophoresis. It can be used in its free acid form (light brown solid), or as a sodium salt (dark green solid). In aqueous solution, BCG will ionize to give the monoanionic form (yellow), that further deprotonates at higher pH to give the dianionic form (blue), which is stabilized by resonance. It is widely used in Sol-gel matrix (Kowada et al., 2005; Zaggout, 2005), fuel cells (Yamamoto and Harada, 2006), sensors (Nakamura, 2006), display devices (Liu, 2005), one-step testers for ammonia (Hrboticka, 2005), cleansing products (Krzysik et al., 2005), for carbohydrates detection (Kobayashi et al., 2005), lactic acid bacteria (Horikoshi et al., 2006), and for neoplasma treatment (Yu, 2005). Also, it is suitable for visualizing the compounds with functional groups whose pK_a is below 5.0 (carboxylic acids, sulfonic acids, etc.). These appear as yellow spots on a light or dark blue background; no heating is necessary (Diamond et al., 2008; Senese, 2001).

In this work, the acidity constants of the cited i.e. indicators including NR and BCG indicators were determined by solution scanometric method (Fig. 2), and the results were compared with the spectrophotometry results obtained by HypSpec program, a new version of the pHab program (Gans et al., 1996, 1999), and from literature (Christopher and Dennis, 1983; Diamond et al., 2008; Jansen, 2008; Nemocova et al., 1996; Nikitina et al., 2011). HypSpec is a program for calculating the pK_a of ligands (Pithadia et al., 2012; Sharma et al., 2012; Shokrollahi et al., 2015) and the stability of constants of complexes in aqueous and nonaqueous solution, using spectrophotometric data (Santos-Figueroa et al., 2012; Shokrollahi and Roozestan, 2013; Shokrollahi et al., 2011, 2013).

2. Experimental section

2.1. *Apparatus*

The cells (with 1000 μL volume for each of them) were made by using a sheet of Plexiglas® (Abbaspour et al., 2009). A Canoscan LiDE 200 flatbed scanner was used to scan the Plexiglas® sheet. The resolution of the scanner was regulated at