

## **DETERMINATION OF PROTONATION CONSTANTS FOR 2-HYDROXY-1-(2-HYDROXY-4-SULPHO-1-NAPHTHYLAZO)-3-NAPHTHOIC ACID**

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### **ABSTRACT**

Chemical speciation modelling in combination with potentiometric titration method was used to determine the protonation constants for 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid, the Patton and Reeder's reagent, at 25° C in three ionic strengths of 0.1 mol dm<sup>-3</sup>, 0.01 mol dm<sup>-3</sup> and 0.001 mol dm<sup>-3</sup> NaNO<sub>3</sub>. Potentiometric titrations were performed and pH, titrant volume, temperature and free and total proton concentrations at each titration point were measured. Constants were determined for three of the four protonated sites and the fourth one being a very low value as this site is always in the ionic form and is readily ionized in aqueous solutions.

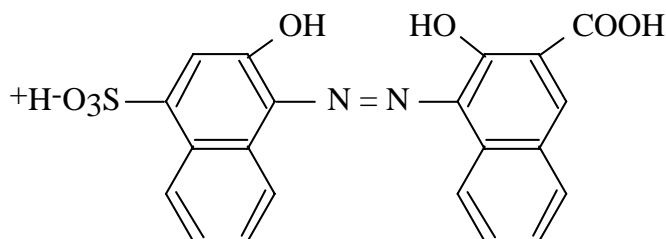
**Keywords:** Patton and Reeder, Protonation constants, Potentiometric titrations, Chemical speciation modelling

### **INTRODUCTION**

Chemical speciation modelling has developed in recent years as an important tool for analytical chemists. It has been widely used to explain the behavior of metal ions in solutions (Duffield & Williams, 1989, Liyanage & Janaratna, 2002, Liyanage & Allas, 1999). In a similar fashion chemical speciation has played a critical role in the determination, correction and confirmation of thermodynamic formation constants

(Jackson & Seymour 1995; Jackson & Seymour 1995; De Robertis & *et al.*, 1995, L-Gonzalez and *et al.*, 1997).

2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (Figure 1) which is named as Patton and Reeder's reagent and abbreviated as HHSNNA ( $H_4L$ ) is mainly used as the indicator in the direct titration of calcium, particularly in the presence of magnesium, with ethylenediaminetetraacetic acid (EDTA).



**Figure 1. 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (Patton and Reeder's Reagent)**

The protonation constants of this compound are needed when these titrations are modeled to study the underlying chemical principles. However, protonation constants of the Patton and Reeder's reagent were not determined previously and were not found in well-established databases (Smith & Martell, 1989). Hence the overall aim of this investigation was to determine these constants using a potentiometric titration method in combination with chemical speciation modelling.

## EXPERIMENTAL

### *Materials*

Patton and Reeder's reagent used for the study was obtained from Loba chemie (India) and unless otherwise mentioned, all other chemicals were from BDH (UK) and Sigma (USA). Prior to distillation, water was passed through a mixed bed ion exchange resin to remove any ionic contaminants. Distilled water thus prepared was boiled for two hours to minimize atmospheric carbon dioxide contamination; there after it was cooled to ambient room temperature, 25° C, in a closed vessel leaving no headspace.

All titrations were conducted at 25° C under high purity (99.996%) nitrogen or argon-purged conditions.

### **Methods**

Potentiometric titrations were performed to quantify protonation binding of Patton and Reeder's reagent using an auto-titrator/IBM PC data collection system (Orion Research Institute, USA, 960 auto chemistry analyzer) at 25° C in a glove box under nitrogen atmosphere. The glove box was constructed to minimize CO<sub>2</sub> contamination from atmospheric environments. The reaction vessel was placed in the glove box that is connected to the auto-titrator to monitor pH, titrant volume and temperature at each titration point. Free and total proton concentrations measured at 50 µl volume increments were captured by an IBM PC linked via RS232C interface (the minimum dispensing volume of the Orion 960 auto chemistry analyzer was 50 µl). Titration experiments were performed in three ionic strengths that are 0.1 mol dm<sup>-3</sup>, 0.01 mol dm<sup>-3</sup> and 0.001 mol dm<sup>-3</sup> NaNO<sub>3</sub> concentrations. Reagent interferences were minimized by performing blank titrations in all three ionic strengths. The volume versus pH data was interpolated by cubic spline technique to subtract the effects caused by the solution matrix. 10 ml aliquots of the titrant were placed in the glove box in tightly capped 25 ml polypropylene centrifuge tubes that were filled with N<sub>2</sub> previously. All samples were equilibrated in a water bath shaker at regulated temperature conditions at 25° C.

All pH measurements were made using Ross combination pH electrode and auto chemistry analyzer in well-stirred solutions.

The proton binding data was modeled using 1-pK basic Stern layer model (BSM). All calculations were carried out using FITEQL (Herbeli & Westll, 1994) and ECOSAT-FIT (Keizer & van Riemsdijk, 1999, Kinnburgh, 1993) algorithms.

## **RESULTS**

Titrations for determination of protonation constants at three different ionic strengths, at 0.1 mol dm<sup>-3</sup>, 0.01 mol dm<sup>-3</sup> and 0.001 mol dm<sup>-3</sup> NaNO<sub>3</sub> were carried out

and the results are shown in the Table 1. The total concentration of the legend ( $H_4L$ ) used was  $0.01 \text{ mol dm}^{-3}$ .

**Table 1. Protonation Constants of the Legend**

Protonation Constant		Ionic Strength $\pm$ SD (n=10)		
		$0.1 \text{ mol dm}^{-3}$	$0.01 \text{ mol dm}^{-3}$	$0.001 \text{ mol dm}^{-3}$
$\text{Log } \beta_{HL}$	$H + L^{4-} = HL^{3-}$	$10.550 \pm 0.006$	$10.500 \pm 0.004$	$10.600 \pm 0.005$
$\text{Log } \beta_{H_2L}$	$2H + L^{4-} = H_2L^{2-}$	$14.911 \pm 0.005$	$15.352 \pm 0.003$	$15.149 \pm 0.003$
$\text{Log } \beta_{H_3L}$	$3H + L^{4-} = H_3L^{-}$	$17.298 \pm 0.003$	$18.119 \pm 0.004$	$17.895 \pm 0.002$

The  $\beta$  values for the protonation of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid correspond to the stepwise protonation constants in the Table 2.

**Table 2. Stepwise Protonation Constants**

Stepwise Protonation Constant			Ionic Strength		
			$0.1 \text{ mol dm}^{-3}$	$0.01 \text{ mol dm}^{-3}$	$0.001 \text{ mol dm}^{-3}$
$\text{Log } K_{HL}$	$H + L^{4-}$	$= HL^{3-}$	$10.550 \pm 0.006$	$10.500 \pm 0.004$	$10.600 \pm 0.005$
$\text{Log } K_{H_2L}$	$H + HL^{3-}$	$= H_2L^{2-}$	$4.361 \pm 0.005$	$4.852 \pm 0.003$	$4.549 \pm 0.003$
$\text{Log } K_{H_3L}$	$H + H_2L^{2-}$	$= H_3L^{-}$	$2.387 \pm 0.003$	$2.767 \pm 0.004$	$2.746 \pm 0.002$

## DISCUSSION

The  $pK$  of only three of the four protons could be determined for this compound and the  $pK$  of the other proton being very low.

The high value of  $\text{Log } K_{\text{HL}}$  and the large difference between  $\text{Log } K_{\text{HL}}$  and  $\text{Log } K_{\text{H}_2\text{L}}$  may be indicative of the intramolecular hydrogen bonding between the protonated and deprotonated hydroxyl groups.

Three proton constants for 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid could be determined in three different ionic strengths at  $0.1 \text{ mol dm}^{-3}$ ,  $0.01 \text{ mol dm}^{-3}$  and  $0.001 \text{ mol dm}^{-3}$   $\text{NaNO}_3$  media. This forth site is always in the ionic form and this site is readily ionized in aqueous solutions.

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