

# Potentiometric studies of the acid–base properties of tropical humic acids



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## ABSTRACT

The key to understanding cation binding to humic acids rests in the ability to quantify the acidic groups in the humic acids. Potentiometric titration has been effectively used in these quantitation and the results are very good. Also, potentiometric titration offers access to other behavioral information that may not be accessible when other methods (Baryta and acetate method) are used for the acidity estimations. The total acidities obtained ranged from 4.5 to 13.0 mmol/g. Although there were differences in the shape of the titration curves, the normalized curves showed that humic acids of different sources can exhibit common similarities. The charge density curves were found generally to diverge with increasing pH, with the difference in charge density ranging from 0.01 to 0.43 meq/g at pH 5.0 for 2-fold increase in ionic strength. The experimental data when model with Stockholm humic model yielded a reasonably good fit with maximum root mean square error of 0.25. The humic acids generally exhibited a hydrophobic and rigid character. Also humic acids of tropical origin were observed to have high acidity.

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## 1. Introduction

The ubiquitous nature of humic substances (HS) in the terrestrial and aquatic environments tends to have a significant influence on the heavy metals in these environments. These natural organic matters have the ability to bind the metal ions and after binding, determine the fate of the heavy metals in the environments. Humic moieties are weak acid polyelectrolytes and as such information from their acid–base equilibria becomes substantial when rationalizing their environmental behavior (Ephraim et al., 1986; Fukushima et al., 1995; Marinsky and Ephraim, 1986; Tipping, 2002). Two acidic groups (carboxylic and phenolic) have been identified as the major protonated sites on a humic moiety; with the carboxylic groups considered as the most predominant group (Ephraim et al., 1986; Kinniburgh et al., 1999; Ritchie and Perdue, 2003; Tipping, 2002). Besides the acidic content and buffer capacity estimates (Campitelli et al., 2003; Janoš et al., 2008; Perdue, 1985; Tipping, 2002), information from acid–base titration has come in handy in estimations of the salt permeability and rigidity of these polyelectrolytes (Ephraim et al., 1986; Marinsky and Ephraim, 1986). Also potentiometric data have given support to structural assumptions such as the  $\alpha$ -helical structure by Ephraim et al. (1986), cylindrical structure by Barak and Chen (1992) and the spherical structure (Kinniburgh et al., 1999; Tipping, 1998).

Numerous methods have been used to estimate the functionality of HS with the direct and indirect titration methods been the most commonly used (Janoš et al., 2008; Perdue, 1985). The potentiometric method employed in this work is operationally defined, considering the carboxylic acidity as the amount of base consumed up to pH 8 and the phenolic group as half the amount of the carboxylic acid measured. This way of estimating the phenolic content is based on the assumption used in Model V/VI and SHM (Gustafsson, 2001; Tipping, 2002). This assumption is also corroborated by the strong correlation that existed between the 1:2 line and the phenolic-to-carboxylic acid plot for the indirect titration method. Thus instead of using the operational estimation which had its inherent problems, a theoretical estimate of the phenolic group was used. This yielded a good agreement between the estimated total acidity of both model and experimental results.

This work sought to find out how protonation behavior of tropical and high molecular weight humic acids (HA) differs from humic moieties of other origin. The permeability and flexibility of these molecules are also ascertained to aid in addressing how they will react with metal ions.

### 1.1. Modeling

Only a brief discussion of the Stockholm humic model (SHM) used is presented here and for detailed discussion of the model, refer to Gustafsson (2001). The SHM employs the discrete binding model to describe the dissociation character of the HS and this was chosen because of availability and ease of use. The model approach is the same as the Model V/VI with just slight differences. The model considers 8 binding

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sites with the first 4 attributed to carboxylic acid type groups and the last 4 related to phenolic acid type groups. The dissociation of HS is represented as



$$i = 1-4 \quad \text{Log}K_i = \text{Log}K_A \frac{(2i-5)}{6} \Delta pK_A \quad (2)$$

$$i = 5-8 \quad \text{Log}K_i = \text{Log}K_B \frac{2i-13}{6} \Delta pK_B \quad (3)$$

$K_i$  is intrinsic dissociation constant. R represents humic molecule.

The model treats electrostatic effects by assuming the humic moiety as impermeable sphere with a surface where interactions occur. The Basic Stern Model (BSM) is used to treat the electrostatic effects. Unless otherwise stated all model parameters are treated as in Gustafsson (2001).

## 2. Materials and methods

### 2.1. Extraction of humic acids

Twelve different humic acids (HA) were studied. The HA were isolated according to the method proposed by the International Humic Substance Society (Swift, 1996). The samples were as follows; 5 farm samples were taken from different locations within 200 m of the active gold mining site (Bibiani and Obuasi). The samples I and III were from farms around the Bibiani gold mines while VII, X and XI were from different farms around the Obuasi gold mines. KI, KIII and KIV are samples from different farms on Kwame Nkrumah University of Science and Technology (KNUST). PTRII and STRRTDII are samples taken from sites around the Pompora Treatment Plant (PTP) and Southern Treatment Plant (STP) tailing dams respectively. STPPD3 II is sediment sample taken from STP wastewater pond 3 all within Obuasi gold mines. HA were extracted according to the IHSS method (Swift, 1996) with slightly modification as shown in Fig. 1.

### 2.2. Potentiometric titration

HA stock solution (1 g/L) was prepared and the pH adjusted to 10 with NaOH to ensure total dissolution under a blanket of argon. To prevent oxidation of the HA, the pH of the solution was adjusted to less than pH 5 and kept in the dark. Fresh stock solution was prepared every other day. A specific volume of the stock solution necessary to attain a concentration of 300 mg/L was measured into a 50 ml volumetric flask. The amount of  $\text{NaNO}_3$  needed to attain the desired ionic strength was added from a 1 M  $\text{NaNO}_3$  stock solution. The ionic strength was varied from 0.001 to 0.100 M. The titration was performed in a beaker with an improvised rubber cover, with holes created in the cover to allow for the pH electrode, temperature probe, burette tip and an argon gas inlet/outlet. The pH of the solution was adjusted with 0.1 M HCl to pH of  $3.0 \pm 0.1$  and purged with argon gas for about 15 min while stirring. Purging with the Ar gas was continued throughout the entire titration. The temperature of the titration system was maintained at  $25 \pm 0.3$  °C by suspending the beaker in a bigger beaker containing water. The temperature was controlled by the addition of ice or warm water. The titration was performed from pH 3.0 to 11.0 with standard 0.097 M NaOH solution. The pH was measured only when the drift was less than 0.03 units per min. This was achieved within 2–3 min but a reaction time of 4 min was allowed before reading the pH. Blanks were prepared at various ionic strengths and also titrated. The addition of the base was done with an automatic burette and the pH was read with a combined ref-pH electrode connected through an interface to a computer. The whole titration was controlled automatically by Measure software from Phywe (Germany).

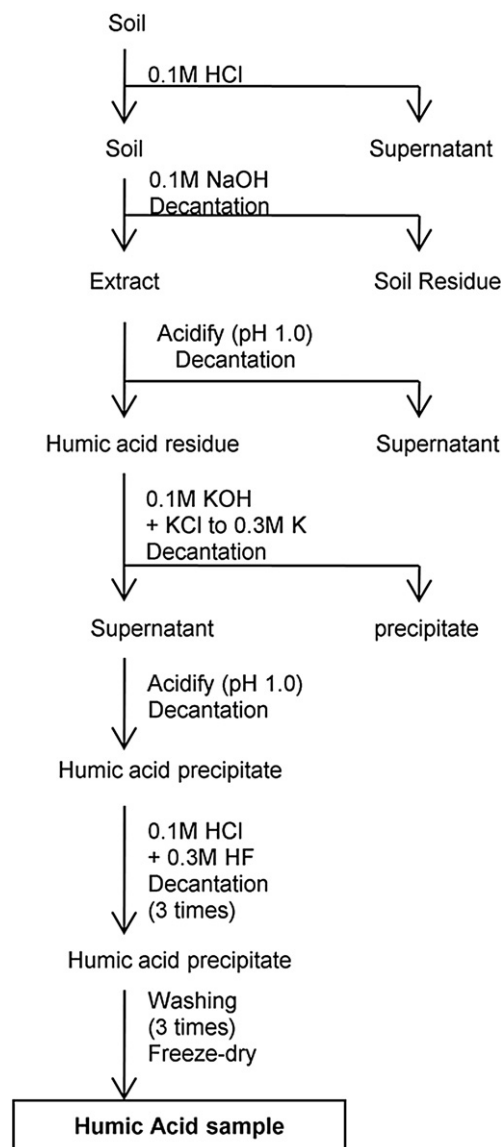


Fig. 1. Isolation procedure employed in the extraction of the HA.

The total acidity and carboxylic acidity of the HA were also determined by the conventional Baryta and the Calcium Acetate method respectively. The phenolic acidity was determined as the difference of the two acidities.

## 3. Results and discussions

### 3.1. Titration data

The dissociation of the functional groups in the humic moiety shows a strong dependence on both pH and ionic strength (Fig. 2). The screening effect posed by the inorganic salts demonstrates the highly sensitive nature of the potentiometric properties of these acidic macromolecules to the ionic strength of the medium. Due to the ionic strength influence, a defined ionic strength of 0.01 M  $\text{NaNO}_3$  is used in all calculations unless otherwise stated. The titration curve as obtained is used to estimate the content of acidic functional groups in the HA. The carboxylic acid is calculated as the amount of NaOH needed to titrate to a pH of 8 while the phenolic content was estimated as half the amount of carboxylic acid measured due to the inconsistencies in the pH values obtained above pH 8. This is just a theoretical definition for the acidity of humic

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