

# STANDARIZATION OF BOEHM TITRATION ANALYSIS OF SURFACE FUNCTIONALITIES OF CNTS AS REINFORCEMENTS FOR COMPOSITES

Y. S. Kim, S. J. Yang, S. W. Kim, H. J. Lim, T. Kim, and C. R. Park\*

Carbon Nanomaterials Design Laboratory, Global Research Laboratory, Research Institute of Advanced Materials, and Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

\*Corresponding author ([crpark@snu.ac.kr](mailto:crpark@snu.ac.kr))

**Keywords:** *Boehm titration, Carbon nanotube, Acidic Carbon Fragment, Carbon Dioxide*

## 1. Introduction

Carbon nanotubes (CNTs) have been actively applied as reinforcing fillers of various polymer composites due to their exceptionally high Young's modulus and tensile strength [1]. One of the issues for improving the mechanical properties of CNT composites is to improve the interfacial interaction of CNTs and a given matrix. In this case, it is important to measure the number and reactivity of surface functional groups of CNTs which is directly related with the covalent or non-covalent bonds with CNTs and the matrix.

Boehm titration [2] has been adopted as one of usual methods to characterize surface functionality of CNTs [3-5]. To characterize the representative functionalities such as carboxylic, lactonic and phenolic hydroxyl group, Boehm suggested selective neutralization of each functionality using different strength of base solutions called reaction bases; ie, sodium hydroxide (NaOH) neutralize all of three functionalities while sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) neutralize carboxylic and phenolic groups, and sodium bicarbonate ( $\text{NaHCO}_3$ ) only neutralize phenolic groups [6]. However, there are a few sophisticated issues involved in Boehm's titration of CNTs. When CNTs are acid-oxidized, the side wall of CNTs concurrently disintegrates to some extent to yield acidic carbon fragments (ACFs) with phenolic and/or carboxylic functional groups on the periphery of aromatic core [7]. Under this circumstance, it becomes very important to discern the functionalities of CNTs themselves from those of ACFs. This is because the functional groups of the ACFs can also influence the interfacial interaction between CNTs and matrices [8], and hence the mechanical performance of the given composite, although it is not clear at this stage whether it would be positive or negative. However, to discern the functionalities of ACFs by Boehm titration is not easy because ACFs dissolve into the basic solution such as reaction bases for Boehm titration to make

conjugated bases [4]. Furthermore, dissolution of atmospheric carbon dioxide ( $\text{CO}_2$ ) into the reaction base makes the situation more complicated; therefore thought to be avoided by additional operations [5]. The titration behaviors of the reaction bases are significantly affected by these acidic components, therefore these effects must be analyzed quantitatively.

Herein, we suggest a standard for the analysis of Boehm titration results, with which it would be possible to quantify the amount and reactivity (related with  $\text{pK}_a$ ) not only of surface functional groups of CNTs themselves, but also of functional groups of ACFs and contribution of the dissolved  $\text{CO}_2$ . For this purpose, 5-hydroxyisophthalic acid (HPA) was chosen as the model ACF as the molecule contains both carboxylic and phenolic group like ACF. Therefore, the titration behaviors of the reaction bases, ie. NaOH solution, with HPA dissolved would suggest the principles of titration behaviors of the reaction bases with ACF dissolved. And the titration curves of mixtures of the reaction bases and HPA along with the influence of atmospheric  $\text{CO}_2$  were analyzed based on revised Henderson-Hasselbalch equation.

## 2. Experimental

### 2.1. Chemicals and materials

HPA were purchased from Sigma-Aldrich and used without further treatment as model organic acids for ACFs. The other chemicals for titration were purchased from Daejung (Korea).

### 2.2. Boehm titration

Potentiometric titrations were carried out by 888 Titrando (Metrohm, Swiss), and stable pH (stable for maximum 150 s with drift of no more than  $\text{pH } 0.12 / \text{min}$ ) was measured by glass electrode (Metrohm, Swiss) and recorded according to dosed volume of 0.01 M HCl titrant. Breakpoints of each curve were

determined by containing program to detect end points. 0.01 M of NaOH solutions were prepared as reaction bases, and 0.01 M of HCl solution was used as titrant. Different amount (0, 0.003, 0.015, and 0.03 meq) of HPA was dissolved in 5 mL of NaOH solution and titrated with HCl titrant to elucidate the effect of phenolic and carboxylic groups on the titration curve.

### 3. Results and discussion

#### 3.1 Effects of acidic functional groups

Theoretically, Assuming all of the protons ( $H^+$ ) in the titrant is transferred to each base ( $A_i^-$ , the conjugated base of  $HA_i$ ) in the titrand, the relation between concentration of hydroxide ions ( $OH^-$ ) and added HCl titrant ( $Q_{H^+}$ ) in mmol is obtained by the following modified Henderson-Hasselbalch (H-H) equation [8] as

$$Q_{H^+} = \sum \frac{Q_{A_i^-}}{1 + [OH^-]/K_{b,A_i^-}} \quad , (1)$$

where  $Q_{A_i^-}$  is the quantity of a specific base component  $A_i^-$  in mmol. However, equation (1) matched up well with the real titration curves only in the middle range of the titration, because the effects of water solvents in either titrants or titrands as the other proton binding sites were not considered. Herein, we revised equation (1) to apply these effects, and the theoretical titration curves from revised H-H equation also matched up well around the region of the initial and final states of the titrations.

Fig.1 clearly shows two representative end points (EPs), viz. the ones ( $EP_a$ ) at around pH 8 (black circles in Fig.1a) and the other ones ( $EP_b$ ) at around pH 5 (black crosses in Fig.1a). In Fig.1a, both EPs move to the left as the HPA concentration increases. These titration behaviors can be easily analyzed by revised H-H equation considering the sorts of functional groups in HPA.

HPA molecule has three representative acidic functional groups, ie. two carboxylic groups and one phenolic hydroxyl group. The  $pK_a$  of each proton binding site is not the same but different. When they are dissolved in the excess of strong base such as NaOH solution, each functional group would produce sodium carboxylate and phenolate with average  $pK_b$  10~11 and 4~5, respectively [9]. Fig.1 shows the proton dissociation behavior of HPA step by step. As shown in the illustration, there are three

conjugated bases of HPA denoted as  $HPA^-$ ,  $HPA^{2-}$ , and  $HPA^{3-}$ . Because carboxylic acid is the strongest acid among the three acidic functional groups in HPA, the proton bound on the first carboxylic acid would dissociate first when they are dissolved in the aqueous solvent and provide the conjugated base  $HPA^-$ . And the dissociations of the rest of protons would be followed as shown in Fig.2.

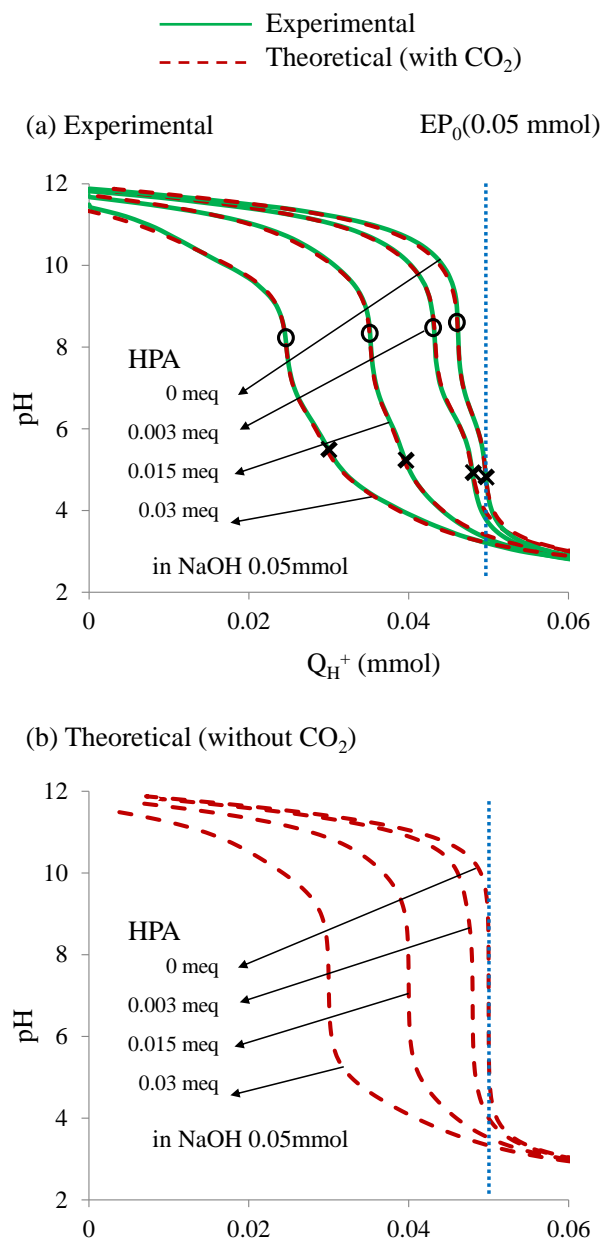


Fig.1. (a) Experimental (green solid lines) and theoretical (red dashed lines) titration curves of 5 mL of 0.01 M NaOH with no air exposure containing different amount of HPA. (b) Theoretical titration curves of the same titrands as (a) with the assumption that no  $CO_2$  is dissolved.

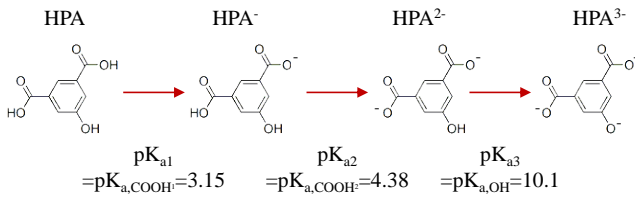


Fig.2. Proton dissociation behaviors of HPA (Each average  $\text{pK}_a$  value was calculated via revised H-H equation analysis.).

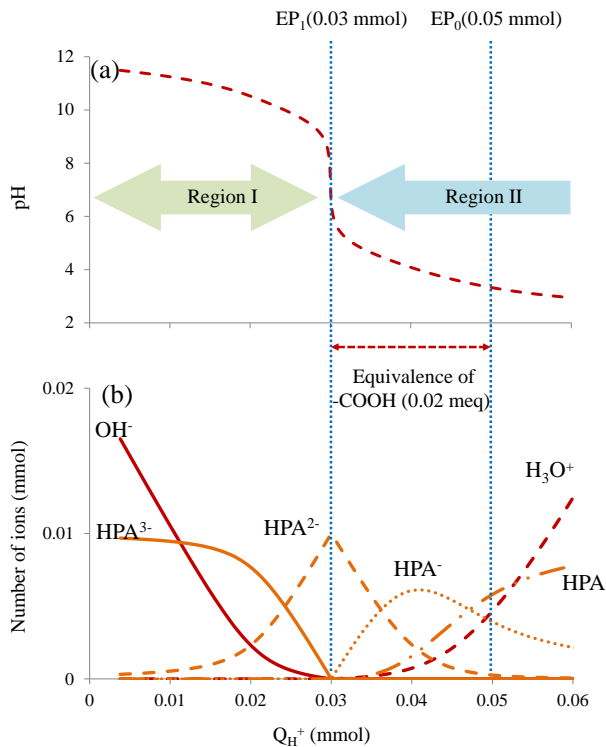


Fig.3. (a) Theoretical titration curve of NaOH with 0.03 meq of HPA dissolved shown in Fig.1(b), and (b) concentrations of the various base components in the titrand.

Form these respects, the theoretical titration curves of the reaction bases with HPA dissolved were calculated and plotted in Fig.1b, on the simple assumption that  $\text{pK}_{a1}=3.5$ ,  $\text{pK}_{a2}=4.5$  and  $\text{pK}_{a3}=10$ . The resultant titration curves (Fig.1b) were similar with those from experimental titrations (Fig.1a). However different from experimental results (Fig.1a) and general respect that the number of EPs is directly related with the sorts of bases, there exist only single EP in each theoretical titration curves. The existence of single EP of which the number is more than the sorts of acids (ie. OH<sup>-</sup>, carboxylate

and phenolate ions) is related with concurrent neutralization of bases in the titrands. When the titrand is titrated with HCl titrant, firstly OH<sup>-</sup> ions ( $\text{pK}_b=0$ ) originally existed in the titrand and HPA<sup>3-</sup> ( $\text{pK}_b=4$ ) might bind with protons from titrant simultaneously because their  $\text{pK}_b$  is not large enough. As a result, no individual EPs from OH<sup>-</sup> and HPA<sup>3-</sup> ions arise in the theoretical titration curve. Secondly, the EPs at  $Q_H^+=0.05$  mmol, the initial EP (EP<sub>0</sub>) of NaOH solution, disappear. It seems that EP<sub>0</sub> moves to the left as more amount of HPA was added in the NaOH solution. The disappearance of EP<sub>0</sub> might be arose from the concurrent neutralization of HPA<sup>-</sup> ( $\text{pK}_b=10.5$ ) and water ( $\text{pK}_b=14$ ) from the titrant or titrand.

To prove that these assumptions state, the concentrations of various bases in the titrands during the titration were calculated from adopting the relation between the concentration of base components and pH [10] into the revised H-H equation. Fig.3 shows the concentrations of the various base components in the NaOH solution with 0.03 meq of HPA dissolved during the titration. As expected, OH<sup>-</sup> and HPA<sup>3-</sup> ions (or phenolate ions) neutralized concurrently at region I (the region from initial state of the titration to EP 1). At the end of region I, only HPA<sup>2-</sup> ions remained in the titrand with negligible amount of the other ions to made single EP (EP<sub>1</sub>). In region II (the region from EP<sub>1</sub>), HPA<sup>1-</sup> ions began to neutralize. However the existence of HPA molecules at the initial state of region II (around  $Q_H^+=0.035$  mmol in Fig.3b) implies that some of HPA<sup>2-</sup> ions received two protons at once to make HPA directly without forming of HPA<sup>-</sup> ions. However, the majority of HPA<sup>2-</sup> ions received only one proton to make HPA<sup>-</sup> ions. The concurrent neutralization of HPA<sup>2-</sup> and HPA<sup>-</sup> ions also appeared because they have similar  $\text{pK}_b$  values. Besides, it was also possible to confirm the concurrent neutralization of H<sub>2</sub>O water molecules to form H<sub>3</sub>O<sup>+</sup> ions and HPA<sup>2-</sup> and HPA<sup>-</sup> ions, or carboxylate ions, as previously mentioned.

In short, OH<sup>-</sup> and phenolate ions (from HPA<sup>3-</sup> ions) neutralized at region I, and H<sub>2</sub>O molecules and carboxylate ions (form HPA<sup>2-</sup> and HPA<sup>1-</sup> ions) neutralized at region II. Because of the large gap of  $\text{pK}_b$  between carboxylate and phenolate ions, single EP appeared between region I and II (EP<sub>1</sub>). Furthermore, the difference between EP<sub>0</sub> and EP<sub>1</sub> directly gave the equivalence of carboxyl groups (0.02 meq in the case of Fig.3) in HPA. It will be possible to apply this to elucidate the quantity of

carboxyl groups in organic acids with arbitrary structures such as ACFs from CNTs. However, the quantity of phenolic groups might be related with the shape of region I in Fig.3a. Therefore, more generalized fitting method is required to obtain the quantity of phenolic groups in ACFs.

### 3.2. Effects of atmospheric CO<sub>2</sub>

Even though the effects acidic functional groups of HPA, the model compound of ACF, were analyzed, there still remained unsolved problems. The shapes of the theoretical titration curves (Fig.1b) were somehow different from the experimental ones (green solid lines in Fig.1a) in that the additional EPs appeared in the experimental ones. It was found that the dissolution of atmospheric CO<sub>2</sub> into the reaction base slightly deformed the titration curve because of the formation of the additional base components, CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ions in the reaction base as a result of reaction between CO<sub>2</sub> and the reaction base [5]. Even though as prepared NaOH solutions were used for the titration, CO<sub>2</sub> might be dissolved into the solutions during sample preparation processes

The effects of CO<sub>2</sub> were added in revised H-H equation and the experimental titration curves were analyzed based on the revised H-H equation. The theoretical titration curves (red dashed lines in Fig.1a) matched up better with experimental ones (green solid lines in Fig.1a), which implied the analysis was valid. The average pK<sub>a</sub> of each conjugated form of HPA was obtained from the analysis and expressed in Fig.2.

### 4. Conclusion

It was shown that ACFs and atmospheric CO<sub>2</sub> significantly influences on the Boehm titration results when they are dissolved in the reaction base. However with the revised H-H equation and EPs determinations, the exact quantity of each component can be determined with ease from Boehm titration curves. Based on our work, it will become possible to discern the quantity or reactivity of functional groups between CNT surface and ACFs by analyzing Boehm titration curve, regardless of the influence of atmospheric CO<sub>2</sub>. Furthermore, it will support the systemic study related with interfacial interaction between CNTs and polymer matrix in the CNT composites.

### 5. References

- [1] F. H. Gojny, J. Nastalczyk, Z. Roslaniec and K. Schulte "Surface modified multi-walled carbon nanotubes in CNT/epoxy-composites". *Chemical Physics Letters*, Vol. 370, No. 5-6, pp 820-824, 2003.
- [2] H. P. Boehm. "Some Aspects of the Surface-Chemistry of Carbon-Blacks and Other Carbons". *Carbon*, Vol. 32, 5, pp 759-769, 1994.
- [3] H. Hu, P. Bhowmik, B. Zhao, M. A. Hamon, M. E. Itkis and R. C. Haddon "Determination of the acidic sites of purified single-walled carbon nanotubes by acid-base titration". *Chemical Physics Letters*, Vol. 345, No. 1-2, pp 25-28, 2001.
- [4] Z. W. Wang, M. D. Shirley, S. T. Meikle, R. L. D. Whitby and S. V. Mikhalovsky "The surface acidity of acid oxidised multi-walled carbon nanotubes and the influence of in-situ generated fulvic acids on their stability in aqueous dispersions". *Carbon*, Vol. 47, No. 1, pp 73-79, 2009.
- [5] S. L. Goertzen, K. D. Thériault, A. M. Oickle, a. C. Tarasuk and H. A. Andreas "Standardization of the Boehm titration. Part I. CO<sub>2</sub> expulsion" *Carbon*, Vol. 48, No.4, pp 1252-1261, 2010.
- [6] H. P. Boehm. "Surface oxides on carbon and their analysis: a critical assessment". *Carbon*, Vol. 40, No. 2, pp 145-149, 2002.
- [7] K. A. Worsley, I. Kalinina, E. Bekyarova and R. C. Haddon "Functionalization and Dissolution of Nitric Acid Treated Single-Walled Carbon Nanotubes" *Journal of American Chemical Society*, Vol. 131, No. 50, pp 18153-18158, 2009.
- [8] A. Katchalsky and P. Spitnik "Potentiometric Titrations of Polymethacrylic Acid" *Journal of Polymer Science*, Vol. 2, No. 4, pp 432-442, 1947.
- [9] X. Zhang and R. B. Bai "Mechanisms and kinetics of humic acid adsorption onto chitosan-coated granules". *Journal of Colloid and Interface Science*. Vol. 264, No. 1, pp 30-38, 2003.
- [10] D. W. Oxtoby, H. P. Gillis and N. H. Nachtrieb "Principles of Modern Chemistry". 5th edition, Thomson Learning, Inc., 2002.