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## THERMODYNAMIC STUDY FOR THE PROTONATION OF HALLOYSITE

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The Halloysite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ) is an abundant and cheap clay and is considered one of the most promising nano structured and naturally occurring clay mineral. Large deposits of this material are present in France, Belgium, China, New Zealand and USA [1,2]. Among the spheroidal, tubular or platy morphologies, the tubular is the most common and abundant one. Typically, halloysite nanotubes (HNTs) are formed by 15 – 20 aluminosilicate layers, having a length of  $1 \pm 0.5 \mu\text{m}$ , and inner and outer diameters of 10 – 15 nm and 50 -70 nm, respectively [1]. In each layer, the SiOH and the AlOH groups are disposed on the external and the internal surfaces, respectively. As consequence, in each nanotube and in a large pH range, there is a charge separation between the inner and the outer surfaces. In particular, the inner surface is positively charged because of protonation of AlOH groups and the outer surface is negatively charged because of the gradual deprotonation of SiOH groups at pH higher than 2.

This charge separation is one of the most important features for the HNTs versatility and is strictly dependent on the acid – base properties of their functional groups. In this work, the protonation / deprotonation of SiOH and AlOH groups of HNTs is evaluated by ISE- $\text{H}^+$  potentiometric titrations of HNTs aqueous suspensions in different ionic media and ionic strengths ( $0.025 \leq I / \text{mol L}^{-1} \leq 0.750$ ) and in a wide pH range (2 – 11), at  $T = 25^\circ\text{C}$ . ISE- $\text{H}^+$  potentiometric titration data have been processed by using the same models successfully used in a previous work for carboxylic and phenol groups of humic and fulvic substances [3]. Moreover, the change of superficial charge with the changing of pH was also evaluated by  $\zeta$  potential measurements. Correlations between the  $\zeta$  potential trend and the distribution of protonated and deprotonated species of HNTs were found.

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