A PGSE NMR Methodology to Characterize Multi-Site Halogen-Bonded Adducts in Solution

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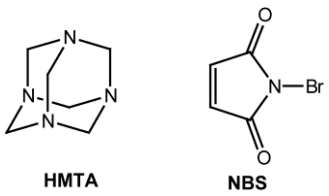
Abstract

Here, a NMR method to characterize halogen-bonded adducts is presented, giving information otherwise inaccessible.

Introdução

Halogen bonding (XB) is nowadays a powerful tool for the synthesis of advanced materials,[1] and, in the recent years, several applications in solution have been explored, as catalysis and anion recognition.[2] The characterization of XB systems in solution is often limited to titrations, through NMR (^{1}H and ^{19}F) or UV-Vis measurements.[3] Recently, ^{19}F, ^{1}H HOESY NMR experiments have been used to characterize the structure of the XB adducts.[4]
Here, we propose the diffusion NMR Pulsed field Gradient Spin Echo (PGSE)[5] technique as a simple and reliable tool to characterize multi-site halogen bonding systems (Scheme 1).



Scheme 1.

As known, PGSE NMR measurements give information about the hydrodynamic volume of the molecular species.[5] In case of an aggregation process, the measure of the hydrodynamic volume allows the quantification of the equilibrium constants involved in the process.

Resultados e Discussão

PGSE NMR measurements on solutions containing **HMTA** (2.1 mM) and increasing concentrations of **NBS** showed that the hydrodynamic volume (V_H) of **HMTA** increases from 217 to 438 Å^3. The trend of the experimental data reveals that there is a *plateau* at high concentration of **NBS**, and V_H(**HMTA**) tends to 450 Å^3. Such a value is very similar to the hydrodynamic volume of the 1:2 adduct. Therefore, despite **HMTA** has four different nitrogen atoms and can establish an interaction with four different molecules of **NBS**, experimental data demonstrate that the **HMTA** cannot be fully saturated and only two aggregation steps are active in solution. Fitting the experimental data considering only K_{a1} and K_{a2}, leads to K_{a1} = 90 and K_{a2} = 60 M^{-1} (Figure 1).

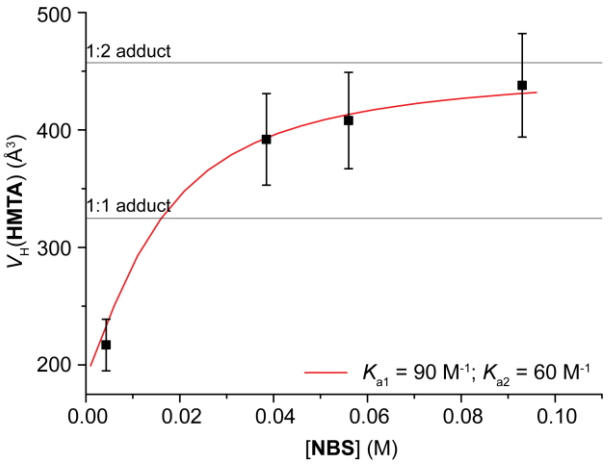


Figure 1. Experimental hydrodynamic volume of **HMTA** (c = 2.1 mM) at different concentrations of **NBS**. The red line represents the best fit.

Conclusões

In conclusion, PGSE NMR resulted to be a powerful technique to characterize multi-site XB adducts in solution, providing information about the nuclearity of the system that are very difficult to obtain with other techniques.

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