

Short communication

# Role of the anion in the alkali halides interaction with D-ribose: a $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy study

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## Abstract

The alkali halides interaction with D-ribose in D<sub>2</sub>O solutions was studied by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The observed changes in the NMR spectra are interpreted according to a model in which the hydroxyls rich region, from C<sub>1</sub> to C<sub>4</sub>, interacts with the cation while the CH<sub>2</sub> group at C<sub>5</sub> on the opposite side of the sugar interacts with the anion. It seems, during the salt–sugar interaction, cation and anion preserve, at least partially, their ion-pair character. The cooperative interaction of the sugar hydroxyl groups with the cation leads to a polarization within the sugar molecule, which favors the anion interaction with its most positive region. A correlation between the chemical shift of C<sub>5</sub> atom and the atomic number of the anion was observed, which is discussed as a neighboring paramagnetic effect; as higher is the halogen atom more pronounced is the resulting shift of the C<sub>5</sub> signal. The anion effect is weak but also observed in the  $^{13}\text{C}$  signals of those carbon atoms bound to hydroxyl groups where the interaction is predominant with the cation. The  $^1\text{H}$  signal of the anomeric protons and the relative population of isomers in the alkali halide solution also show an anion dependence.

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## 1. Introduction

The interactions of carbohydrates with inorganic salts are a subject of current interest due to the importance of carbohydrate–metal complexes in chemistry and biology [1–7]. The formation of sugar–salt complexes is attributed to the interactions of the cations with the oxygen atoms of the sugar [5–7]. The binding force is dependent on the nature of the cation, increasing with the charge ( $Z$ ) and decreasing with the atomic radii ( $r$ ), therefore increasing with the cation polarizing power ( $Z/r$ ). The stability of the complexes also depends on the structure and conformation of the sugar, being most favorable the axial–equatorial–axial disposition (in the following *ax.–eq.–ax.*) of three vicinal OH groups in pyranose forms [7–11] (see Fig. 1). For this reason, D-ribose forms the strongest complexes with cations, due to its *ax.–eq.–ax.*

disposition of the OH groups in  $\alpha$ -D-pyranose in  $^4\text{C}_1$  and  $^1\text{C}_4$  conformations and  $^1\text{C}_4$  conformation in  $\beta$ -D-pyranose forms (see Fig. 1).

Ribose interaction and complex formation with metals in neutral solutions have been studied for a large number of ions, e.g. La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> mainly using NMR spectroscopy [12–14]. NMR probably is the most sensitive and informative technique to study these interactions [5–7]. The results have been interpreted exclusively on the basis of cation–sugar interactions with total disregard on the anion effect, which could be minor for the case of these large cations, but not when the cation–sugar interaction is weak as in the cases of Na<sup>+</sup> and K<sup>+</sup> salts. Another important factor in the stability of the complex is the nature of the solvents. Strong hydrogen bonding solvents such as water and methanol or very polar solvents as DMSO, tend to interact strongly with both, the cations and the hydroxyl sugar groups, interfering with the complex formation. However, non-polar solvents

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