Proton Magnetic Resonance Study of Solute-Solvent Interactions of Sucrose with Calcium Ions in Aqueous Solution

LAURENCE PONCINI
Department of Chemistry & Biochemistry, James Cook University, Queensland 4811, Australia

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PMR spectroscopy has been employed to study solute-solvent interaction between sucrose (solute) and the hydrated calcium ion (solvent). No evidence for complexation in this system is found. Instead, the proton shifts (H-1, H-1', H-6-H-6') are indicative of a rapidly exchanging bulk solute-solvent effect. All the proton signals followed are found to move approximately by equivalent amounts as the metal ion is progressively added.

During the last decade there has been a renewed interest in the study of interaction of metal ions with sucrose. This field has been the subject of a recent review by the author. During the compilation of this review it became evident that no work has been carried out, using PMR spectroscopy, to investigate the solute-solvent interactions that are known to occur between sucrose and multivalent ions. The technique most commonly used to study such interactions has been conductance.

It was anticipated that PMR spectroscopy would provide a direct method for the study of such interactions in an aqueous solution of sucrose and divalent metal ion. Any relative downfield proton shift would indicate the presence of interaction occurring between the solute (sucrose) molecules and solvent (hydrated metal ion). The extent of such shifts would indicate the strength of these interactions as well as the possible site or sites of attack. The divalent calcium ion was chosen in this study because of its extensive use in sugar industry.

Sucrose (AR, 143 mg, 4.18 x 10^-4 M) was accurately weighed into the outer tube of a coaxial PMR tube. Deuterium oxide (99.99% pure, 0.5 ml) was added with the help of a graduated syringe to this tube. The tube was capped and sonicated until sucrose totally dissolved. Both the outer tube and coaxial inner cell (reference, t-butanol) were capped in common. The PMR spectrum (chemical shift in ppm) was recorded on a 100 MHz Jeol JHN-MH-100 spectrometer operating on internal lock with a normal probe temperature of 32°. This spectrum corresponded to a zero ligand [L] : substrate [S] ratio. The peak frequencies (ppm) were measured using an 80 MHz Hewlett digital frequency counter.

An aliquot (0.1 ml) of a 2% stock solution of CaCl₂ in D₂O was added to the outer coaxial tube. The spectrum was recorded as previously. CaCl₂ stock solution was added progressively (0.1 ml each time) until a [L] : [S] ratio of 2.58 was reached. Beyond this value precipitation occurred in the tube.

The progressive addition of divalent calcium ion to sucrose in deuterium oxide results in the various proton peaks moving approximately equivalent amounts (Fig. 1). To best follow this movement only clearly resolvable peaks were selected. These were the anomeric protons H-1 (4.54) and H-1' (2.79); and a broad based singlet H-6-H-6' (2.93). These peaks were assigned according to Bruyn and workers.

The plots of change in chemical shifts (Δ, ppm) as a function of molar ratio of calcium (L) to sucrose (S) (Fig. 1) afford a series of parallel lines. Inspection of Table 1 indicates that all these peaks shift relative to each other by the same amount. Such a behaviour seems best interpreted in terms of a non-specific interaction of Ca²⁺ with sucrose, i.e. the progressive addition of CaCl₂ results in a progressive bulk solvent effect which causes an approximately similar variation of the chemical shifts of the sucrose resonances that are being followed. It is evident that such a behaviour is not in accord with the interaction of calcium chloride with a single binding site (or adjacent sites) on sucrose. Angyal and coworkers have shown that the addition of calcium chloride to solutions of cyclitols in deuterium oxide causes downfield shifts of some protons because of complex formation. It has been established that the extent of this shift results from the cation binding to three oxygen atoms which have an axial-equatorial-axial sequence. McGavin et al. have also reported a downfield shift for proton resonances on complexation of metal ions with sugars in aqueous solution. They concluded that two neighbouring oxygen atoms were involved in the formation of the complex. Assuming 1:1 complex formation...
Table I—Shift in Peak Position on Gradual Addition of Calcium Chloride to Sucrose in Deuterium Oxide

<table>
<thead>
<tr>
<th>f [L]:[S] molar ratio</th>
<th>Peak position (ppm) relative to t-ButOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-1</td>
</tr>
<tr>
<td>0.00</td>
<td>4.54</td>
</tr>
<tr>
<td>0.32</td>
<td>4.57</td>
</tr>
<tr>
<td>0.48</td>
<td>4.58</td>
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<tr>
<td>0.64</td>
<td>4.60</td>
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<td>0.97</td>
<td>4.62</td>
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<tr>
<td>1.29</td>
<td>4.65</td>
</tr>
<tr>
<td>1.94</td>
<td>4.70</td>
</tr>
<tr>
<td>2.58</td>
<td>4.76</td>
</tr>
</tbody>
</table>

(with calcium) the stability constant was calculated and found to be small \( (K = 0.11-0.01 \text{ M}^{-1}) \).

Bugg and Cook\textsuperscript{12} have pointed out that in the solid state calcium yields complexes with charged sugars in which the calcium ion is surrounded by a square-antiprism coordination shell composed of water molecules and sugar hydroxyl groups. These authors\textsuperscript{12} have demonstrated that many uncharged carbohydrates in the hydrated solid state often chelate calcium ions through pairs of hydroxyl groups. However Fig. 1 shows no evidence for any interaction involving specific hydroxyl groups, i.e. no proton peaks are found moving approximately parallel to each other and at approximately the same rate.

If the structural features of the solvent-water, hydrogen-bonding capabilities and hydration characteristics of the sucrose molecule and the structural behaviour of the ion in the aqueous solution are considered then these results are typical of a structure-making/breaking situation\textsuperscript{3}. Greyson and Snell\textsuperscript{14} have reported that entropies of transfer between heavy and normal water for alkaline-earth chlorides indicate these chlorides behave as structure-breaking salts. It is concluded that the sucrose-calcium ion interaction in Fig. 1 is suggestive of a bulk solvent effect where the calcium ion is rapidly exchanging with the solvent and solute in a typical solute-solvent interaction in which hydrogen-bonding and ion hydration\textsuperscript{5} may also be involved in such a system.

The presence of chloride ions in human bones\textsuperscript{11,12} and the existence of isomorphism\textsuperscript{22-24} between hydroxyapatite \( \text{CHAp, Ca}_{10}(PO_4)_{6}F_2 \) and chlorapatite \( \text{CHAp, Ca}_{10}(PO_4)_{6}Cl_2 \) suggest the possibility of Cl\textsuperscript{-}/OH\textsuperscript{-} exchange on OHAp leading to the formation of solid solutions of the latter with ClAp. In this investigation a series of solid solutions of ClAp and OHAp have been prepared and characterized on the basis of spectral (X-ray, electron microscopic and infrared analyses) data.

A sample of OHAp was prepared by a wet method based on Eq. (1); the rest of the details being the same as reported earlier\textsuperscript{4}:

\[
\text{2Ca} (\text{NO}_3)_2 + 6(\text{NH}_3)_2\text{HPO}_4 + 8\text{NH}_3\text{OH} = \text{Ca}_{10n}(\text{PO}_4)_{6n}\text{OH}_{2n} + 20\text{NH}_3\text{NO}_3 + 6\text{H}_2\text{O} \quad (1)
\]

The sample so prepared was subjected to the following solid state reaction:

\[
2\text{Ca}_{10n}(\text{PO}_4)_{6n}\text{OH}_{2n} + n\text{CaCl}_2 = 2\text{Ca}_{10n}(\text{PO}_4)_{6n}\text{OH}_{2n} + n\text{Ca}(\text{OH})_2 \quad (2)
\]

\[
\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O} \quad (3)
\]

where \( n = 2 \) for ClAp and varied between 0.2 and 1.8 for solid solutions. The optimum temperature and duration of heating, 900°C and 3 hr respectively required for the occurrence of reaction (2) were determined by studying the preparation of a representative sample, ClAp, which was obtained by a complete OH\textsuperscript{-}/Cl\textsuperscript{-} exchange in OHA. Further, one of the products underwent decomposition at 900° facilitating its progress from left to right.

An approximately 5% stock solution of anhyd. calcium chloride was prepared in doubly distilled and a dried sample of ethanol, its calcium\textsuperscript{5} and chloride\textsuperscript{7} contents being determined titrimetrically. Based on Eq. (2), to a calculated amount of OHA was added a calculated volume of calcium chloride solution, in which its amount was stoichiometric with that of OHA to form a paste. This was heated at 900° for 3 hr for the completion of the reaction (2). The extraneous phases like calcium chloride, triacetic