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PHYSICO-CHEMICAL STUDY OF SUCROSE AND CALCIUM IONS INTERACTIONS IN ALKALINE AQUEOUS SOLUTIONS

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Abstract: Interactions between sucrose and calcium hydoxide have been the subject of our work. They were studied in dilute solutions (sucrose concentration < 40% w/w, with a molar stoichiometric ratio $Ca(OH)_2$ / sucrose < 2) by several physico-chemical methods, titration of free and bound calcium ions, ^{13}C NMR spectroscopy, static light scattering and low shear viscosimetry. From these analyses we propose a polymer-like complex formation with calcium ions bound to at least two sucrose molecules. Moreover, this polymer-like aggregate can be described as a linear short chain at low $Ca(OH)_2$ and sucrose concentrations and as dense fractal particles at higher concentrations.

Introduction

Interactions between sugars and cationic species have been the subject of many studies. Sugar/cation complexes have been described either in the crystalline state or in dilute solutions [1-3]. Co-ordination bonds have been established between sugar hydroxyl groups and cations. Generally, sugar/ion interactions have been studied at neutral pH. Thus, the bonds are believed to be only of a co-ordination type and possible deprotonation of hydroxyl groups can be neglected. Calcium, which is of interest in biological mechanism and industrial process, generally has a total co-ordination number of 8 [4-6]. The calcium ions are co-ordinated with either three oxygen atoms of the same sugar molecule or with oxygen atoms belonging to two or more sugar molecules. All these complexes are hydrated. However, nothing is known about the aggregation number of these complexes. If dimerization of sugar by co-ordination to calcium/ion is often described, the formation of oligomer-like or polymer-like aggregates is generally not considered.

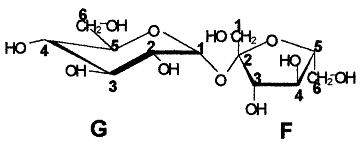

Figure 1 : Sucrose molecule

There is little reliable information on the behaviour of sucrose, α D Glucopyranosylβ D Fructofuranosyl, (given in figure 1) with hydroxide calcium [7]. To our knowledge, no characterisation of this latter system has been considered.

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So we have undertaken a physico-chemical study of sucrose/calcium hydroxide/water system in diluted solutions. We present some experimental results from different physico-chemical studies: titration of free and bound calcium and ^{13}C NMRs to confirm the existence of sucrose/calcium interactions and complex formations; light scattering and viscosity measurements to indicate complexation effects. Finally we propose a model for this polymer-like complex.

Physico-chemical studies

Experimental part

Samples : Sucrose (99 %) and $Ca(OH)_2$ (95 %) (both Aldrich) were used without further purification. Experiments was performed under air.

$Ca(OH)_2$ was added to vigorously stirred sucrose solution. Composition of the different series of mixture sucrose/$Ca(OH)_2$/water prepared was given in Table 1. Each mixture was characterised by the parameter **n**, the molar ratio $[Ca(OH)_2]$ / [sucrose]. After 12 hours of stirring, we observed two kind of mixtures: the homogeneous solutions and biphasic systems with supernatant liquids and dense phases. The solutions and supernatants were characterised by i) Elemental analysis (EA) ii) potentiometry (calcium selective electrodes), iii) titration against EDTA, iv) ^{13} C NMR, v) light scattering, vi) viscosimetry.

Table 1: Composition of various series of sucrose/$Ca(OH)_2$/water mixtures

Series S	concentration in % of the initial sucrose solution	molar concentration of sucrose	concentration (g ml^{-1})	Molar ratios n $Ca(OH)_2$ / sucrose
1	5	0.14	0.05	0.25;0.5;0.75;1;1.5;2;4;10;20
2	10	0.30	0.10	0.25;0.5;1;1.5;2;3
3	20	0.61	0.21	0.25;0.5;0.75;1;1.5;2;3;4;5
4	30	0.99	0.34	0.5;1;1.5;2;3
5	37	1.22	0.42	0.5;1;1.5;2

Elemental analyses and titration

Elemental analysis of the lower powdered phase showed that it is exclusively $Ca(OH)_2$. EA, titration against EDTA and potentiometry of the homogeneous solutions and supernatant indicated the presence of both free and bound calcium. Thus sucrose interacts with calcium to form soluble complexes. To follow the variations in the solubility of $Ca(OH)_2$ as a function of sucrose concentration we determined **s** as molar ratio calcium / sucrose in solution which

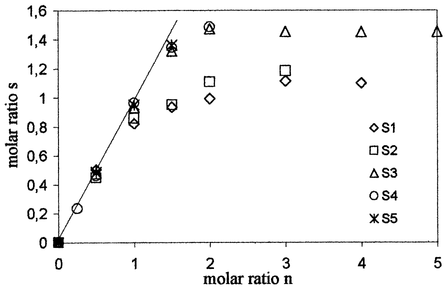

Figure 2: variation in s versus n

differs from n when phase separation occurs. Figure 2 reports variation in s versus n indicated by titration for each series of mixtures. Two behaviours are observed. When n<1 the ratio s is directly proportional to n with a slope close to 1, *i.e.* $Ca(OH)_2$ introduced into these mixtures is completely dissolved. When n>1 plateaux are observed which correspond to the appearance of $Ca(OH)_2$ precipitates. Shifting of these different plateau heights towards higher values of s reaching 1.5 for series 5 indicate an increasing of the complex stoichiometry sucrose / calcium . We can deduce from these titration experiments that soluble sucrose / calcium complexes are formed with stoichiometries varying from 1/1 at lower $Ca(OH)_2$ and sucrose concentrations to 1/1.5 at higher concentrations.

^{13}C NMR spectroscopic characterization

From ^{13}C NMR study we determined the different calcium ion co-ordination sites on sucrose hydroxyl. When $Ca(OH)_2$ is added to sucrose solutions, no development of new peaks is observed but changes in chemical shifts and broadening of the NMR peaks of the sucrose carbons are observed, as shown in Figure 3. These effects vary with each sucrose carbon. these effects have been used to estimate the complex co-ordination site [8]. We reported in Figure 4 some variations in the increment of different chemical shifts (Δδ) of sucrose solutions in the presence of $Ca(OH)_2$ versus s. Curve A shows changes in chemical shifts for carbons F_6, F_5, G_4, G_5 and G_6 (only F_6 is shown

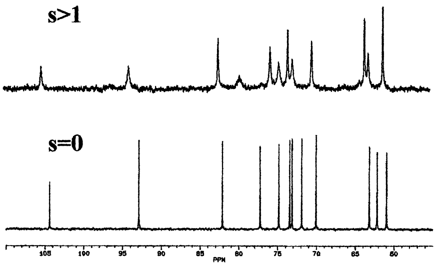

Figure 3: ^{13}C NMR spectrum of sucrose for different values of molar ratio s

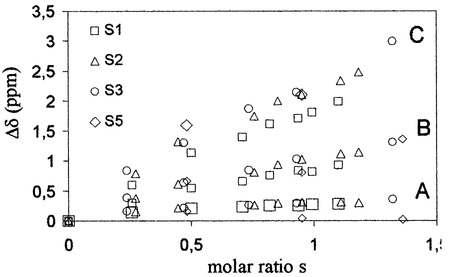

Figure 4: Variation in Δδ of carbone F_6 (A), G_3 (B) and F_3 (C) versus s

for simplicity) and corresponds to values of $\Delta\delta$ which do not exceed 0.5 ppm. We assume that hydroxyl groups associated with these carbons are not involved in complex formation. Curve B is representative for carbons G_1, G_2, G3, F_1, F_4, and F_2 (and only G_3 is shown) and corresponds to significant changes in $\Delta\delta$ up to 1.25 ppm. We assume that hydroxyl groups associated with these carbons are involved in complex formation from co-ordination bonds. Curve C correspond to the chemical shifts of carbon F_3, and changes in $\Delta\delta$ are greater than that seen for other carbons. The hydroxyl associated with this carbon is assumed to be deprotonated at high pHs and is considered to be the dominant complexation site for calcium ions. We show in Figure 5 several possible calcium ion co-ordination sites inferred by changes in $\Delta\delta$.

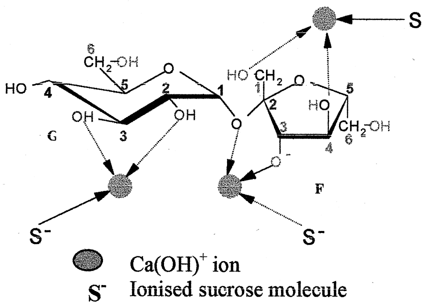

Figure 5 : Varying co-ordinations of calcium with sucrose molecules

Light scattering and viscosity measurements

Light scattering and viscosity experiments were performed in order to confirm aggregate formation. Figure 6 shows variations in apparent weight average molecular weights, $\overline{M_{wapp}}$, against s for the five series. $\overline{M_{wapp}}$ is equal to the reciprocal value of KC/ΔI and is called "apparent" *(by using refractive index increment (dn/dc) of sucrose in water and we verified that particles present in these solutions have negligible sizes with respect to the wavelength of light in water)*. We observed for s<1, $\overline{M_{wapp}}$ varies linearly with s and attains values of about 2000, corresponding to an aggregation of 4-5 "monomer units", where a monomer-like unit is

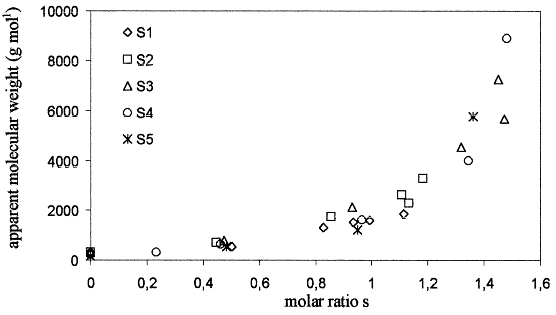

Figure 6: variation in apparent molecular weights versus s

constituted of one sucrose molecule and one calcium atom. When s > 1, apparent aggregation of 20 monomer-like units is attained.

Low shear viscosity measurements have shown that the relative viscosity η of sucrose/$Ca(OH)_2$ solutions does not increase much with s for series 1 and 2, while a very high divergence is observed for the three other series. Qualitatively, this is consistent with the light scattering results, since an increase of $\overline{M_{wapp}}$ is expected to induce an increase in viscosity.

Light scattering and viscosity experiments indicate formations of aggregates or polymer-like complexes with linear chains of about 4-5 monomer units at low total concentrations which also confirm 1/1 stoichiometry. At higher concentrations, some cross-links are indicated with greater than 2 calcium atoms bound to each sucrose molecule giving rise to a branched architecture (fractal particles are expected) concentrations which confirm 1.5/1 stoichiometry. At very high concentrations, percolation of these particles induces a strong viscosity divergence.

Polymer-like complexation proposed

Formation of monomolecular complexes at low concentration

To define more precisely the nature of the calcium sucrose interactions we studied $Ca(OH)_2$ dissociation equilibrium and different sucrose ionisation ones by using equilibrium constant values given in literature [9, 10]. From equilibrium calculation we determined for s close to 1 (at low total concentration), that the main species into sucrose-$Ca(OH)_2$ solutions are $Ca(OH)^+$ and SH_2^- (first ionisation of sucrose) to form the dominant complex species $Ca(OH)SH_2$ (which corresponds well with the experimental stoichiometry 1/1). From these results it is indicated that the first step of calcium / sucrose complexation is the formation of this mono-molecular complex involving one of each ionic species $Ca(OH)^+$ and SH_2^-: it is due to an electrostatic attraction between two oppositely charged species. We assume this monomer-like unit is hydrated by at least 4 or 5 ligand water molecule to complete calcium co-ordination shell to 8. A dimer may be formed if a water molecule is replaced by an hydroxyl group of another sucrose/calcium mono-molecular complex yielding $Ca(OH)SH_2$ - $Ca(OH)SH_2$.

Possible model of association pseudo-polymer formation at high concentration

At higher concentrations (s>1), the complexes involve more than one calcium per sucrose molecule (1.5/1 stoichiometry). Figure 5 is an example of such stoichiometry where half of the sucrose molecules are associated to 2 calcium atoms and the other half to 3 calcium atoms. It shows that the aggregates or polymer-like complexes are necessarily branched systems.

The general scheme of complexation and the polymerisation-like reaction is given in Figure 7: mono-molecular complexes are formed and then linear oligomers form while the stoichiometry remains 1/1. In subsequent steps, branched or fractal polymer-like aggregates are formed.

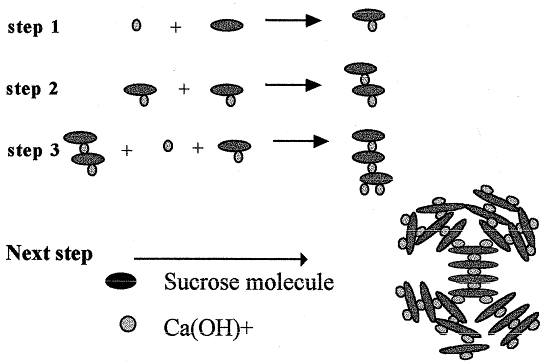

Figure 7 : Schematic representation of complexation and polymerisation of sucrose and calcium ions

Conclusion

These experiments give rise to a qualitative description of sucrose / $Ca(OH)_2$ interactions. We conclude that complexation phenomena are accompanied by a polymerisation-like reaction. Characterisation of concentrated sucrose / $Ca(OH)_2$ systems have been studied [11] and we have shown these systems exhibit rheological behaviours similar to those of entangled polymer solutions.

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