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Short Communication

Calcium complexation by low molecular weight dicarboxycellulose in aqueous solution

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Abstract

Carbohydrate polymers having the ability to complex calcium ions are of commercial interest. The effects of molecular weight and neighbouring carboxylate functional groups on a cellulose chain have been reported in this paper. High molecular weight sodium carboxymethylcellulose (viscosity of 2% solution 12 cP) was found to be marginally superior to low molecular weight sodium dicarboxycellulose (viscosity of 2% solution 1.1 cP) in its calcium complexing ability. Thus the sterically favourable effects of the neighbouring carboxylate groups can be offset by viscosity effects; both these are therefore important parameters in deciding the calcium complexing ability of a polymer. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sodium dicarboxycellulose; Calcium complexing; Viscosity; Cellulose; Neighbouring groups

A number of ring-opened dicarboxylate polysaccharides like cellulose, starch, alginates, maltodextrins, etc. have been investigated for their calcium binding properties, as this property is a prerequisite for their application as a detergent builder. Therefore, a large number of research publications have appeared and patents taken on this important subject (Avebe, 1990; Bright, Lamberti & Powers, 1973; Casu et al., 1980, 1984; Creseenzi, Dentini, Meoli, Casu, Naggi & Torri, 1984; Crutchfield, 1978; Dannoue & Matsumara, 1993; Diamantoolou, Maegericin, Zielke & Cornelissens, 1976; Eldib, 1971; Emery & Ploumen, 1972; Floor, Kiegboom & van Bekkum, 1991; Floor, Petern, van Bekkum, Kiegboom & Koek, 1990; Kohn, 1975; Maekawa & Koshijima, 1984; Nieuwenhuizen, Kiegboom & van Bekkum, 1983, 1985, 1987). One group has reported that the calcium-complexing properties for dicarboxycellulose and dicarboxystarch are poor below M_w 10^4 (d.p. 50), increasing significantly from M_w 10^4 to 10^5 and reaching a constant level at $M_w > 10^5$ (Maekawa & Koshijima, 1984). A stoichiometry of one Ca^{2+} ion per two dicarboxy units has been proposed (Casu et al., 1980, 1984; Creseenzi et al., 1984; Nieuwenhuizen et al., 1985). A later publication has suggested that a monomeric unit that coordinates a calcium ion should be represented by a moiety containing four carboxylate groups (Nieuwenhuizen et al., 1987). Calcium sequestering ability has been reported to be in the range of 2.2–3.6 mmol/g (Avebe, 1990; Floor et al., 1990; Maekawa & Koshijima, 1984). However, these samples of dicarboxycellulose were not well characterised for their molecular weights and viscosity behaviour. Another recent report has stated that the molecular weight for optimum biodegradability and utility as a builder for detergents is between 1500–2000 (Dannoue & Matsumara, 1993). Chemical modification of cellulose is known to decrease its crystallinity. We have found 98% oxidised cellulose to be completely amorphous and also of very low molecular weight (Varma & Chavan, 1995a,b). In the study of structure–property relationships of polymers, it is known that amorphous polymers are much more likely to be biodegradable than crystalline polymers, and lower molecular weight polymers are more biodegradable than higher molecular weight polymers (Varma, 1999). A recent study has shown that oxidised polysaccharides are indeed biodegradable, though at a slower rate (van der Zee, Stoutjesdijk, van der Heihden & DeWit, 1995). However, entire ranges of well-characterised oxidised polysaccharides have to be investigated to arrive at more accurate predictions.

Therefore, it is very important to report results of calcium complexation with well-characterised polysaccharides. We now report our results of the calcium complexing ability of a well-characterised sodium dicarboxylate cellulose, having a degree of polymerisation of 8–14. Its rheological properties and characterisation are reported elsewhere (Varma & Chavan, 1995a,b). While the effect of molecular weight

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Table 1
Calcium ion bound gram/gram to NaDCC and NaCMC (with 1×10^{-3} M KCl added for adjusting the ionic strength of the medium), final pH of solution 8.2

Mol/l	(Ca^{2+}), mol/l	Free (Ca^{2+}), mol/l	Bound (Ca^{2+}), mol/l	Bound (Ca^{2+}), g/g
NaDCC				
4.2×10^{-4}	6.25×10^{-5}	3.75×10^{-5}	2.5×10^{-5}	0.010
4.2×10^{-4}	1.25×10^{-4}	6.25×10^{-5}	6.25×10^{-5}	0.025
4.2×10^{-4}	2.5×10^{-4}	1.20×10^{-4}	1.38×10^{-4}	0.055
NaCMC				
4.2×10^{-4}	6.25×10^{-5}	2.5×10^{-5}	3.755×10^{-5}	0.015
4.2×10^{-4}	1.25×10^{-4}	4.75×10^{-5}	7.75×10^{-5}	0.031
4.2×10^{-4}	2.5×10^{-4}	8.75×10^{-5}	1.60×10^{-4}	0.065

has been dwelt with at length in publications so far, the effects of rheological properties of the solution have not been addressed as yet. Further, in order to elucidate the effect of two neighbouring carboxylate groups on the polysaccharide chain, we have also compared the results obtained for sodium 2,3-dicarboxylate cellulose with the complexing ability of sodium carboxymethyl cellulose, which has only one carboxy group on the C-6 carbon atom. The experimental conditions chosen were such that the complexed calcium ion and the free calcium ion were both in solution.

Preparation of sodium dicarboxylate cellulose (NaDCC). Sodium dicarboxylate cellulose having 98% of the glucose monomer units ring opened with carboxylate functional groups at the C-2 and C-3 positions was prepared by earlier reported procedures (Maekawa & Koshijima, 1984; Varma & Chavan, 1995a). The sodium ion content, as measured by use of Atomic Absorption Spectrophotometer model Z-8000 (Hitachi) was 19.65%, showing complete agreement with the theoretical value. The degree of polymerisation was estimated to be 8–14 (Varma & Chavan, 1995a).

Equipment. Calcium ion selective electrode along with Ag/AgCl type double junction reference electrode (Orion Research Inc., USA) was used for measurement of calcium ion concentrations. Potential measurements were made with a pH/ion meter (EILUK).

Preparation of standard solution of 1000 ppm Ca^{2+}. of $CaCO_3$ (0.25 g) was dissolved in 10 ml of 4 N hydrochloric acid solution. After diluting to 30 ml, the solution was adjusted to pH 5 using 0.5 N KOH solution in a 100 ml volumetric flask to give 100 ml solution.

Ionic strength adjuster. KCl (2 M) was prepared by dissolving the required amount of KCl in water. One millilitre of this solution was added to 50 ml of the sample or standard solution before taking readings with the Ion Selective Electrode.

Preparation of standard solution (1000 ppm) of 98% sodium 2,3-dicarboxycellulose (NaDCC) and sodium carboxymethylcellulose (NaCMC). Each polymer (0.1 g) was dissolved in 40 ml distilled water and then diluted to 100 ml in a volumetric flask.

Calibration curve of Ca^{2+} ion concentration using ion selective electrode. The 1000 ppm Ca^{2+} solution was used for preparing 1, 10 and 100 ppm solutions by appropriate dilutions in 100 ml volumetric flasks. A calcium ion selective electrode and a reference electrode type were introduced in these solutions and millivolt readings recorded.

Calcium binding for 98% sodium 2,3-dicarboxycellulose (NADCC) and sodium carboxymethyl cellulose (NACMC). NaDCC solution (1000 ppm) was taken with 1 ml ion strength adjuster solution and standard 2.5 ml Ca^{2+} ion solution (containing 1000 ppm Ca^{2+}) so that the final concentration of Ca^{2+} in the solution was 2.5 ppm. Using a Ca^{2+} ion selective electrode and the reference electrode millivolt readings were taken on the ionmeter. Other solution mixtures were studied in a similar fashion, such as

1. 100 ppm NaDCC containing 5 ppm Ca^{2+} ion;
2. 100 ppm NaDCC containing 10 ppm Ca^{2+} ion;
3. 100 pm NaDCC containing 20 ppm Ca^{2+} ion.

The results are presented in Table 1. Free Ca^{2+} ions were read off from the calibration curve.

The binding experiments were so designed that the bound as well as complexed Ca^{2+} remained in solution. It can be seen that under identical conditions of ppm concentration NaCMC and NaDCC have comparable calcium complexing abilities. The slightly superior calcium complexation by NaCMC could be attributed to its higher molecular weight. The Brookfield viscosity of a 2% NaCMC was 12 cP and that of a 2% NaDCC was 1.1 cP. We are currently synthesising a series of soluble polysaccharide derivatives so that their cation complexation behaviour can be studied as a function of viscosity of the medium. From our results it is clear that the favourable effect of the oxydiacetate moiety in NaDCC can be offset by viscosity effects as seen from the results of NaCMC. The effect of viscosity is much more pronounced when the cation has a valency higher than two, such as Al. Our studies on flocculation of $Al_2(SO_4)_3$ using the same samples of NaDCC and NaCMC have shown that the NaCMC used was twice as effective as the NaDCC due to its higher viscosity under identical concentrations (Varma & Chavan, 1995a). We expect to publish our work on the effects of solution rheology on cation complexing efficiencies in a future publication.

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