Carbohydrate Research, 163 (1987) 127–131
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Complexation of calcium ions by complexes of glucaric acid and boric acid

PAUL J. M. DIJKGRAAF*, MATTY E. C. G. VERKUYLEN, AND KEES VAN DER WIELE
Department of Chemical Technology, University of Technology, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

(Received August 21st, 1986; accepted for publication, December 18th, 1986)

Sugars and sugar derivatives are well-known complexing agents. Ekstrom and Olin[1] studied the interaction of Pb(II) and pentoses. The complexation of sugars and metal ions[2] and with ions of alkali and alkaline-earth metals[3] has been reviewed. The interaction of sugar alcohols and metallic ions has been studied[4–6].

Sugar acids are well-known complexing agents. Mehltretter *et al.*[7] investigated the interaction of calcium, iron, and copper ions with sugar acids by precipitation methods. The complexation of metallic ions by glucaric acid has been studied by Velasco *et al.*[8,9]. Wilham and Mehltretter[10] have investigated glucaric acid as a builder, but found that it does not meet the requirements for application in detergents.

Several authors mention an improvement of the complexation of metal ions by sugar derivatives by the addition of borate. A remarkably high complexing capacity for calcium ions by glucarate/boric acid mixtures has been reported[11], although there are contradictory results[12].

The system glucarate/boric acid may be used in detergents to replace polyphosphates which cause environmental problems (eutrophication processes), and accurate knowledge of the complexing capacity relative to that of polyphosphate is necessary for an evaluation of its applicability. Therefore, the complexation capacity of this system for calcium ions has been reinvestigated by means of a calcium ion selective electrode.

Fig. 1 shows a typical titration curve for glucaric acid and boric acid in a molar ratio of 1:1 at pH 9. The complexing capacity of a certain system is defined as the amount of calcium ions (g) complexed by 100 g of the agent used, when only 10% of the total calcium ions remain uncomplexed.

Table I summarises the results for glucaric acid, glucaric acid/boric acid (1:1 and 1:2), and sodium tripolyphosphate. The complexing capacity of boric acid ap-

*Author for correspondence.

0008-6215/87/$ 03.50

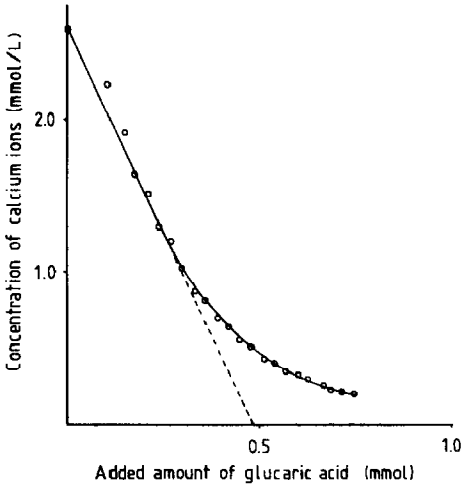


Fig. 1. Typical titration curve for glucaric acid and boric acid (1:1, pH 9).

TABLE I

COMPLEXING ABILITY[a] FOR CALCIUM IONS AS A FUNCTION OF pH

Complexing agent	*pH*			
	7	*9*	*11*	*12.5*
Glucaric acid	0.5	0.5	0.5	0.5
Glucaric acid/boric acid (1:1)	2.6	4.6	5.2	5.4
Glucaric acid/boric acid (1:2)	2.3	5.3	5.7	5.3
Sodium tripolyphosphate	5.1	14.9	17.8	19.8

[a]The amount of calcium ions complexed by 100 g of the agent used, when only 10% of the total calcium ions remain uncomplexed.

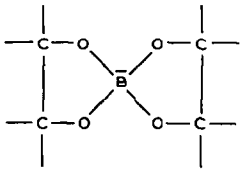
peared to be negligible. The results show that there is no significant effect on increasing the proportion of boric acid to >50%. The complexing capacity of glucaric acid/boric acid is low compared to that of sodium tripolyphosphate. When sodium or lithium chloride was used instead of potassium chloride as a buffer for the ionic strength, the same results were obtained.

High degrees of complexation of calcium and glucarate ions in the presence of borate ions have been reported[11]. Complexation abilities of 1:1 glucaric acid with boric acid are reported which are equal to those of sodium nitrilotriacetic acid (NTA) and sodium tripolyphosphate. These results were obtained by using a precipitation method. Thus, a solution of sodium oxalate and the complexing agent was titrated with a solution of calcium salt until calcium oxalate precipitates. From the known concentration and the titrated amount of the calcium salt, the complexing capacity of the complexing agent can be calculated.

For the systems glucaric acid/sodium tetraborate/sodium oxalate/calcium

chloride, however, not only does the complex of glucarate and borate interact with the calcium ions, but also the free borate ions interact with the oxalate ions[13]. In spite of this, the equivalence point is also partly determined by the interaction of borate and oxalate ions, resulting in improbable values for the complexing capacity of the system glucarate/boric acid.

Gorin and Mazurek[14] investigated the interaction of linear 1,2-diols and sodium tetraborate by ^{13}C-n.m.r. spectroscopy. When sodium tetraborate is added to a solution of 1,2:5,6-di-*O*-isopropylidene-D-mannitol in the ratio 1:2, a 1:2 spiran complex (**1**) is formed. Similar structures are given by Böeseken[15], who used boric acid for the determination of the configuration of carbohydrates. Glucarate and borate ions probably interact in the same way and the carboxyl groups of glucarate are probably pulled together, creating a structure similar to that in ethylenediaminetetra-acetic acid (EDTA). Therefore, these carboxyl groups are probably involved in the complexation of the calcium ions. This view has been confirmed by Van Duin *et al.*[16–18], who investigated the structure and stability of boric esters of polyhydroxycarboxylates and related polyols by ^{11}B-, ^{1}H-, and ^{13}C-n.m.r. spectroscopy.



1

A high complexing ability is expected when the concentration of $B(OH)_4^-$ ions is high. Ingri[19] showed that the conversion of boric acid into $B(OH)_4^-$ increases with increase in the pH, which explains the increased complexation of calcium ions at higher pH (compare the results for pH 7 and 9 in Table I). The complexation of metal ions by polyhydroxy compounds which occurs at high pH has been attributed[7] also to the ionisation of the hydroxyl groups[7].

From the slope of the tangent shown in Fig. 1, the amount of calcium which is complexed can be calculated. This ratio (at a concentration of complexing agent extrapolated to zero), when plotted as a function of the pH, increases with increase of pH (Fig. 2) of the solution and accords with the observed increase of complexing ability on increasing the pH.

EXPERIMENTAL

Determination of complexation capacity. — To 2.5mM calcium chloride (100 mL) at 20° were added solutions of the complexing agent (0.1M) and borate. The pH of the solution was kept constant by the addition of 0.1M potassium hydroxide. The concentration of calcium ions in this solution which were not complexed was measured by using a calcium ion selective electrode (Radiometer F2112Ca K401 Selectrode).

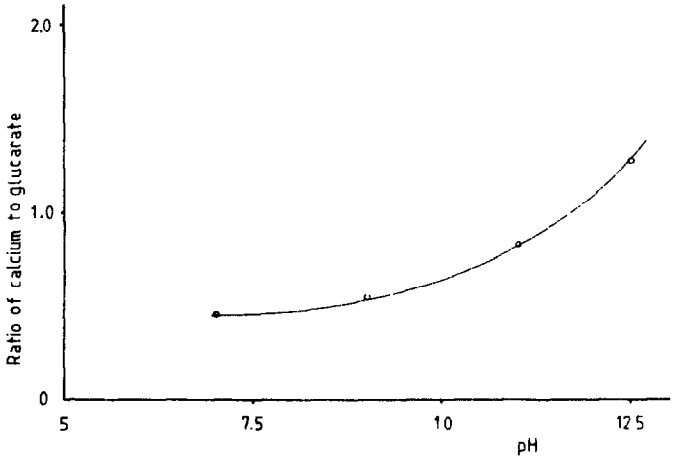


Fig. 2. Number of calcium ions complexed per molecule of glucarate as a function of the pH.

The measured potential of the electrode is correlated to the activity of the calcium ions by the Nernst equation.

$$E = E_0 + RT/z_iF \times \ln(a_i),$$

where E is the potential of the electrode (mV), E_0 the standard potential (mV), R the gas constant (J/mol.K), T the temperature (K), F the Faraday constant (C/eq), z_i the valence of ion i, and a_i the activity of ion i.

The activity (a_i) of ion i is related to the concentration of ion i by the activity coefficient. According to the Debye–Hückel theory, the activity coefficient depends on the ion strength, which depends on the concentration and valence of all ions in the solution. In order to determine the calcium ion concentration, potassium chloride was added to the solution up to 0.1 M as a buffer for the ionic strength. In this way, a constant activity coefficient was obtained over a wide range of calcium ion concentrations. The calcium ion concentration can be calculated by means of a calibration line.

Measurements were made at different pH values and molar ratios of the complexing agent and boric acid.

ACKNOWLEDGMENT

We thank the Dutch Foundation for Technological Research (STW) for financial support.

REFERENCES

1 L. G. Ekstrom and A. Olin, *Acta Chem. Scand., Ser. A*, 31 (1977) 838–844.
2 S. J. Angyal, *Pure Appl. Chem.*, 35 (1977) 131–146.

3 J. A. RENDLEMANN, JR., *Adv. Carbohydr. Chem.*, 21 (1966) 209–271.
4 A. P. G. KIEBOOM, T. SPOORMAKER, A. SINNEMA, J. M. VAN DER TOORN, AND H. VAN BEKKUM, *Recl. Trav. Chim. Pays-Bas*, 94 (1975) 53–59.
5 A. P. G. KIEBOOM, A. SINNEMA, J. M. VAN DER TOORN, AND H. VAN BEKKUM, *Recl. Trav. Chim. Pays-Bas*, 98 (1979) 393–394.
6 A. P. G. KIEBOOM, A. SINNEMA, J. M. VAN DER TOORN, AND H. VAN BEKKUM, *Recl. Trav. Chim. Pays-Bas*, 96 (1977) 35–37.
7 C. L. MEHLTRETTER, B. H. ALEXANDER, AND C. E. RIST, *Ind. Eng. Chem.*, 45 (1953) 2782–2784.
8 J. G. VELASCO, J. ORTEGA, AND J. SANCHO, *J. Inorg. Nucl. Chem.*, 38 (1976) 889–895.
9 J. G. VELASCO, S. ALLYON, AND J. SANCHO, *J. Inorg. Nucl. Chem.*, 41 (1979) 1075–1078.
10 C. A. WILHAM AND C. L. MEHLTRETTER, *J. Am. Oil Chem. Soc.*, 48 (1971) 682–683.
11 J. G. HEESEN, Neth. Appl. NL 7,215,180 (1974); *Chem. Abstr.*, 81 (1974) 176040z.
12 W. P. FERGUSON, personal communication.
13 M. J. PLOQUIN, *Bull. Soc. Pharm. Bordeaux,* 95 (1956) 13–20.
14 P. A. J. GORIN AND M. MAZUREK, *Carbohydr. Res.* 27 (1973) 325–339.
15 J. BÖESEKEN, *Adv. Carbohydr. Chem.*, 4 (1949) 189.
16 M. VAN DUIN, J. A. PETERS, A. P. G. KIEBOOM, AND H. VAN BEKKUM, *Tetrahedron*, 40 (1984) 2901–2911.
17 M. VAN DUIN, J. A. PETERS, A. P. G. KIEBOOM, AND H. VAN BEKKUM, *Tetrahedron*, 41 (1985) 3411–3421.
18 M. VAN DUIN, J. A. PETERS, A. P. G. KIEBOOM, AND H. VAN BEKKUM, *J. Chem.* Soc., *Perkin Trans. 2,* in press.
19 N. INGRI, *Acta Chem. Scand., Ser. A,* 16 (1962) 439–448.