Studies on Borate Esters. Part 5.[1,2] The System Glucarate–Borate–Calcium(II) as studied by ^1H, ^{11}B, and ^{13}C Nuclear Magnetic Resonance Spectroscopy

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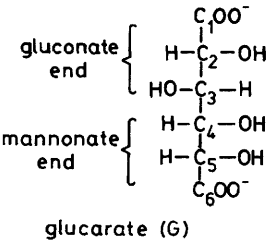
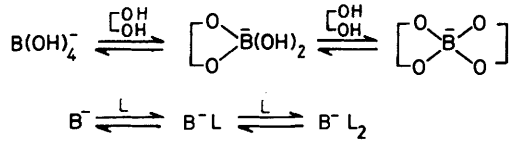
A combination of ^1H, ^{11}B, and ^{13}C n.m.r. spectroscopy is used to determine the identity, structure, and stability of compounds present in the aqueous glucarate–borate–calcium(II) system. Borate ester formation was found to occur preferably at the *threo*-3,4-position of glucarate. Two diastereoisomeric borate diesters of glucarate are the major calcium(II) co-ordinating species. Each borate diester contains two calcium(II) co-ordinating sites consisting of two carboxylate groups, two borate ester ring oxygens, and, depending on the α-CHOH configurations, up to two α-hydroxy groups. The overall calcium(II) co-ordinating strength of both borate diester diastereoisomers of glucarate is about equal, whereas this is not the case for the arabinonate diastereoisomers.

The cation-sequestering capacities of aqueous solutions of polyhydroxycarboxylic acids are known to increase substantially upon the addition of (per)boric acid at pH > 9.5. Mixtures of borate and glucarate (G), for example, are disclosed in the patent literature as potential sodium triphosphate substitutes in detergent formulations.[3,4]



Scheme 1.

This prompted us to study the structure and stability of both boric acid esters and borate esters of polyhydroxycarboxylic acids in aqueous medium with n.m.r. techniques.[2,5,6] Formation of borate esters takes place instantaneously in water at room temperature, but the exchange on the n.m.r. time scale generally is slow. Although both the carboxylic acid and hydroxy functions may be involved in ester formation, above pH 9 borate mono- and di-esters of diol functions are predominant.[5] *threo*-Diol



Scheme 2.

functions are preferred as borate binding sites while Coulomb repulsion between the carboxylate group(s) and the borate anion may be a secondary directing effect, with respect to the stability of the borate esters.[2,6]

The aim of the present investigation is to elucidate the structural origin of the pronounced calcium(II) sequestering properties of the glucarate–borate system with the use of a combination of ^1H, ^{11}B, and ^{13}C n.m.r. Concentration, pH, and temperature effects are included.

Results and Discussion

The System Glucarate–Borate.—Previous ^{11}B n.m.r. experiments[6] have shown that upon addition of boric acid to a solution of glucarate in D_2O at pD 11 borate mono- and di-esters of *threo*-diol functions are formed preferentially. Borate esters of the *erythro*-4,5- and *syn*-2,4-diol functions are less stable (Table 1). In the present study, ^{13}C (Table 2) and ^1H n.m.r. (Table 3) are used to obtain more detailed structural information on these borate esters, particularly to determine whether the main borate binding site is the *threo*-2,3- or *threo*-3,4-diol position.

The ^{13}C n.m.r. signals of free glucarate, with the exception of the carboxylate resonances, were assigned using two-dimensional heteronuclear shift correlation. Separate ^{13}C n.m.r. signals for the borate mono- and di-ester occurred, since the exchange between free glucarate and the borate monoester and between the borate monoester and the borate diester is slow on the ^{13}C n.m.r. time scale. The various carboxylate and hydroxymethylene ^{13}C signals of each ester could not be assigned unambiguously.

For the main borate mono- and di-ester 6 and 12 resonances were observed, respectively. The close resemblance of the spectra for these borate mono- and di-esters indicates that glucarate is bound to borate in a similar way in these esters. Upon borate ester formation, the carboxylate signals undergo small shifts ($-0.6 < \Delta\delta < 1.5$ p.p.m.). As such small shift differences are characteristic for ^{13}C atoms at the β- or γ-position with respect to the borate binding site,[2] the main

Table 1. ^{11}B N.m.r. data and association constants of borate esters of glucarate[a]

	δ (p.p.m.)		$\Delta\nu_{\frac{1}{2}}$/Hz		$K_{B^-L_n}$/l mol^{-1}[b]	
Borate binding site	B^-L	B^-L_2	B^-L	B^-L_2	B^-L	B^-L_2
threo-2,3/3,4-Diol	−13.4	−9.5	45	110	180	30
erythro-4,5-Diol	−14.0		30		20	
syn-2,4-Diol	−17.9				10	
threo-2,3/3,4-Diol (+phenylboronate[c])	−12.3		305		240	
α-Hydroxycarboxylic acid	−12.7	−9.4	170	210		

[a] C_G 0—0.2M; C_B 0—0.1M; D_2O; 25 °C; 64.12 MHz; 0.1M-boric acid as external reference. [b] Association constant for B^-L_n defined as $K_{B^-L_n} = [B^-L_n]/([B^-L_{n-1}][L])$. [c] Phenylboronate (δ −16.2 p.p.m.; $\Delta\nu_{\frac{1}{2}}$ 100 Hz).

binding site of borate in glucarate is the *threo*-3,4-position. The observation of 12 ^{13}C resonances for the borate diester of glucarate is due to the occurrence of a pair of diastereoisomers.[2] *threo*-2,3-Borate esters of glucarate could not be excluded using ^{11}B n.m.r. but since in the ^{13}C n.m.r. spectra no extra signals were observed besides those of the *threo*-3,4-borate esters, the stability of the *threo*-2,3-borate esters appears to be substantially lower than that of the *threo*-3,4-borate esters.

The ^1H n.m.r. spectrum of glucarate was assigned using selective labelling of the 2-position with deuterium. The results confirm that H_2 is the most deshielded α-proton.[7,8] Addition of boric acid to a solution of glucarate at pD 11.0 (C_B:C_G < 1) resulted in two additional sets of signals, besides the signals of free glucarate. This indicates slow exchange on the ^1H n.m.r. time scale between glucarate and its borate esters of the preferred *threo*-3,4-diol function. The two sets of signals were quite similar and their intensity (0.9:1.0) was independent of the molar ratio of borate and glucarate (C_B:C_G). This phenomenon again demonstrates the occurrence of two diastereoisomeric borate diesters of glucarate. This was further confirmed using phenylboronate and diphenylborinate as the esterifying agents (Table 3). In the case of phenylboronate a boronate monoester (Table 1) with a chiral centre atom is formed and the two diastereoisomers gave rise to two sets of ^1H signals. In contrast, the boron centre of the borinate monoester of diphenylborinate is achiral and no peak doubling was observed.

^{11}B (Table 1) and ^{13}C n.m.r. (Table 2) spectra demonstrated the presence of appreciable amounts of borate monoester of the *threo*-3,4-diol function. Since for this species no separate ^1H n.m.r. signals were observed, the exchange between these borate mono- and di-ester nuclei is probably fast on the ^1H n.m.r. time scale. This might be supported by the small upfield shifts (< 0.01 p.p.m.) observed upon increasing C_B:C_G.

For $C_B > C_G$ only a few broad ^1H resonances were observed probably due to a change in chemical exchange rates. Broad signals were also obtained for samples with lower C_B upon increasing the temperature.

Conformational changes of glucarate upon borate ester formation were studied with the use of vicinal ^1H coupling constants (Table 3). Torsion angles HCCH were estimated using the semi-empirical relation of Haasnoot *et al.*[9] For free glucarate, equilibria between two or three linear and bent conformations have been suggested.[7,8] Upon borate ester formation a decrease of ^3J[H(3),H(4)] was observed, which is in agreement with the formation of a borate ester ring including O(3) and O(4). The torsion angle C(1)C(2)C(3)C(4) of glucarate in the borate esters is *ca.* 170° which demonstrates that the C(1)C(5) part is in the planar zig-zag conformation. The torsion angle C(3)C(4)C(5)C(6) is estimated to be either −60 or 50°, the former value being more likely for steric reasons. The resulting solution structures of the diastereoisomeric (*R*)- and (*S*)-borate diesters of glucarate with borate bound at the *threo*-3,4-position are given in Figure 1. Here *R*- and *S*- represent the configuration at the central boron atom.[10]

The System Glucarate–Borate–Calcium(II).—The effects of stepwise addition of calcium(II) chloride to a solution of borate (0.1M) and glucarate (0.1M) at pD 10.5 up to C_{Ca} 0.08M, where precipitation occurred, were studied with ^{11}B n.m.r. The exchange of borate remained slow on the ^{11}B n.m.r. time scale,

Table 2. ^{13}C chemical shifts (p.p.m.) for glucarate and its borate esters[a]

Compound	C(1)/C(6)		C(2)	C(3)	C(4)	C(5)
Glucarate	178.5	178.4	73.7	71.7	73.7	73.6
Borate monoester[b]	179.6	178.2	76.1	74.6	74.4	74.0
Borate diester[b]	179.7[c]	178.1	75.7[c]	74.2	73.9	73.7
	179.7[c]	177.9	75.7[c]	74.1	73.7	73.6

[a] C_G 0—0.2M; C_B 0—0.5M; D_2O; pD 11.0; 25 °C; 50.31 MHz; *p*-dioxane as internal standard (δ 66.6 p.p.m.). [b] The assignments of C(1),(6) and of C(2),(3),(4),(5) may be interchanged. [c] Broad signals.

Table 3. ^1H N.m.r. data for glucarate and its borate esters[a]

Compound	δ (p.p.m.) H(2)	H(3)	H(4)	H(5)	^3J(H,H)/Hz H(2)H(3)	H(3)H(4)	H(4)H(5)
Glucarate[b]	4.073	3.998	3.876	4.061	2.7	4.6	4.6
Borate diester[b]	3.623	4.077	4.099	4.146	1.3	<1.2	3.1
	3.594	4.061	4.060	4.112	1.4	<1.2	3.2
Phenylboronate monoester[c]	3.63	4.25	4.17	4.28	0.8	<1	2.8
	3.70	4.25	4.27	4.31	0.9	<1	3.2
Diphenylborinate monoester[c]	3.64				<3		

[a] C_G 0—0.2M; C_B 0—0.5M; D_2O; 25 °C; t-butyl alcohol as internal standard (δ 1.200 p.p.m.). [b] pD 9.0; 500 MHz; $\Delta\nu_{\frac{1}{2}}$ 1.2 Hz for all signals. [c] pD 11.0; 200 MHz; $\Delta\nu_{\frac{1}{2}}$ 0.8 Hz for the free glucarate signals and *ca.* 3 Hz for those of the esters.

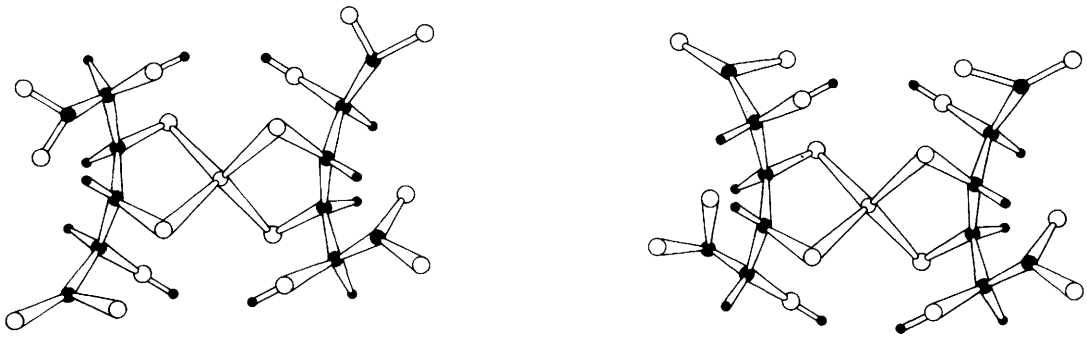


Figure 1. Diastereoisomeric (*R*)- and (*S*)-borate diesters of glucarate (symbols as in Figure 3)

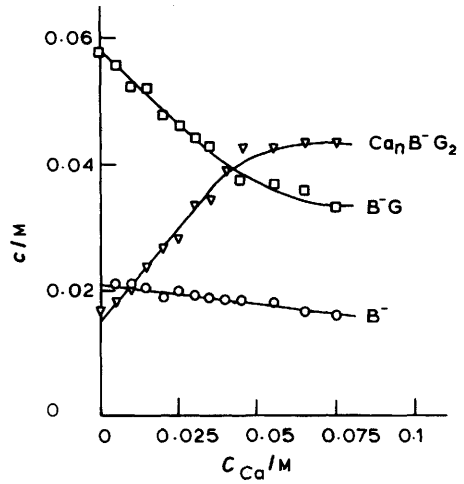


Figure 2. Effect of calcium(II) upon the concentration of boron-containing species for a solution of borate (0.1M) and glucarate (0.1M) at pD 10.5 and 25 °C as determined with ^{11}B n.m.r.

to an increase of the electric field asymmetry upon calcium(II) co-ordination.

The synergic calcium(II) sequestration in solutions of borate and glucarate thus finds its origin in the good calcium(II) co-ordination by the borate diesters of glucarate. The borate anion brings two glucarates, each of which co-ordinates calcium(II) only moderately, together and thus creates two new calcium(II) co-ordinating sites. Each site consists of two carboxylate oxygens (each of a different glucarate molecule), two oxygens of the five-membered borate ester rings, and up to two non-esterified α-hydroxy groups, depending on the α-CHOH configuration (Figure 3).

In the solid state some related structures are known, *viz.* the borate diesters of malic acid[11] and (±)-tartrate,[12] KB^-(malic acid)$_2$·H_2O, and Na_5B^-[(±)-tartrate]$_2$·$8H_2O$, respectively (Figure 4). Here the co-ordination polyhedron of the alkali ions consists of two carboxylic acid or carboxylate oxygens, each belonging to a different polyhydroxycarboxylic acid of the borate diester, one oxygen of the borate ester ring, and two other oxygen atoms. In the natural borate esters boromycine[13] and aplasmomycine,[14] two oxygen atoms (each of a different five-membered borate ester ring) contribute to the co-ordin-

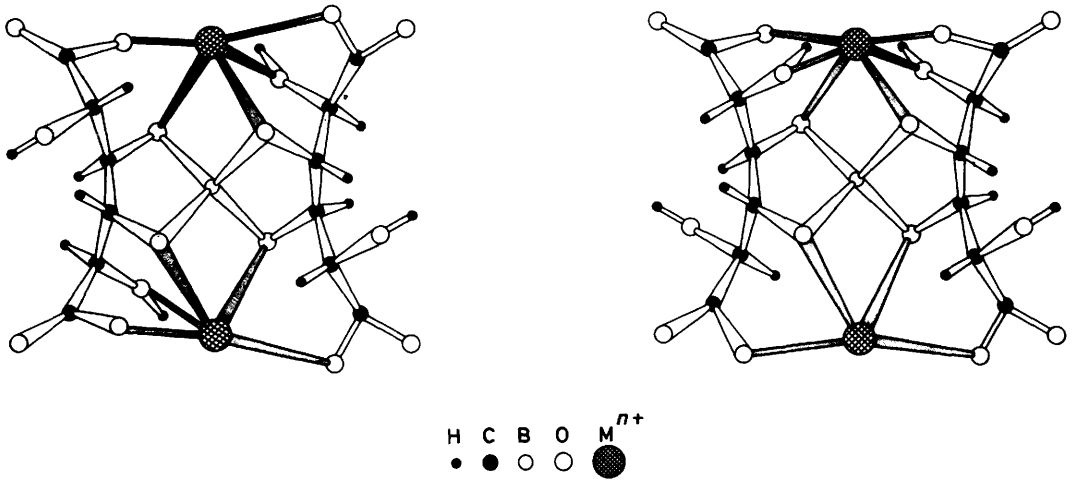


Figure 3. Calcium(II) co-ordination in the diastereoisomeric (*R*)- and (*S*)-borate diesters of glucarate in water

whereas the exchange between the various borate esters and the corresponding calcium(II) complexes is fast on the ^{11}B n.m.r. time scale as no separate ^{11}B signals were observed for the calcium(II) complexes. Upon calcium(II) chloride addition up to C_{Ca} 0.04M the total amount of the borate diester-containing species [borate diesters and their calcium(II) complexes] increased about one mol per two mol of calcium(II), whereas the concentrations of the borate monoester and of free borate decreased (Figure 2). The total concentration of the *erythro*-4,5 and *syn*-2,4 borate ester remained <0.01M. So the borate diesters are the predominant calcium(II) co-ordinating species, which is supported by a small calcium(II) induced shift (CaIS) of the ^{11}B resonance of the borate diesters (0.5 p.p.m.). Furthermore, each borate diester contains two calcium(II) co-ordinating sites. The linewidths of the borate mono- and di-ester signals increased,* from 60 to 100 and from 170 and 250 Hz, respectively, which may be ascribed to exchange phenomena or ation of the monovalent cations. Co-operation of two or more carboxylate groups is known to result in relatively good calcium(II) co-ordinating sites, as was shown for relatively small ligands such as oxalate, oxydiacetate, citrate, and carboxymethyloxysuccinate,[15] but is even more evident for larger molecules such as calcium binding proteins[16] and oxidized polysaccharides.[17]

To elaborate the structural changes of the borate diesters upon calcium(II) co-ordination, calcium(II) chloride was added to solutions containing borate and glucarate until precipitation occurred. The exchange between the various free compounds and the corresponding calcium(II) complexes is fast on the ^1H and ^{13}C n.m.r. time scales, as for ^{11}B n.m.r. The ^{13}C and ^1H n.m.r. chemical shifts (Figures 5 and 6) confirm that the borate diesters are the main calcium(II) co-ordinating species, since only the borate diester signals showed a significant CaIS. After addition of calcium(II) chloride all diastereoisomeric borate diester ^{13}C signals were separated.

Comparison of the conformations of the two diastereoisomeric borate diesters of glucarate (Figure 1) with the corresponding calcium(II) co-ordination compounds (Figure 3) shows that upon co-ordination of the 6-carboxylate, a rotation

* The free borate signal shifted from −17.1 to −17.6 p.p.m. and its line width decreased from 40 to 25 Hz. This can be explained by a small increase in the borate:boric acid ratio due to some calcium(II) co-ordination by borate.

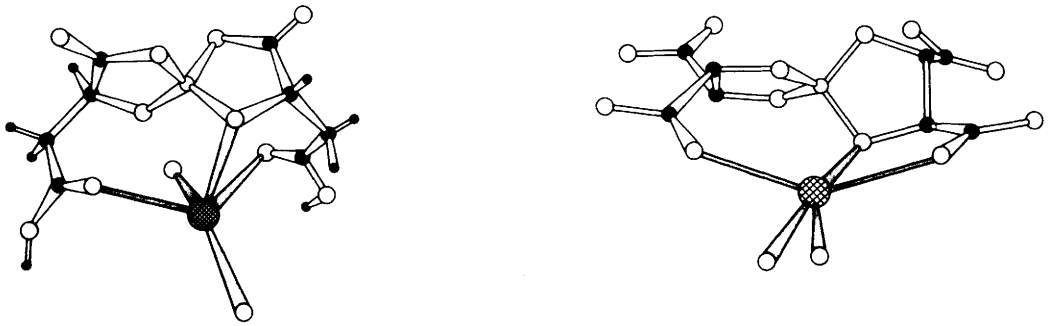


Figure 4. Solid-state co-ordination sites in borate diesters of malic acid (K^+)[11] and (±)-tartrate (Na^+)[12] (symbols as in Figure 3)

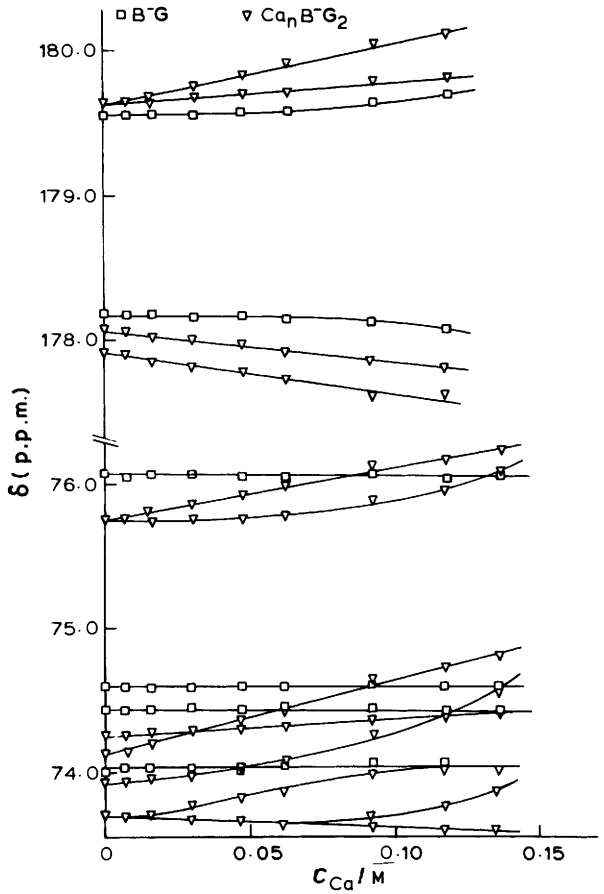


Figure 5. Calcium(II)-induced ^{13}C n.m.r. shifts for a solution of borate (0.15M) and glucarate (0.2M) at pD 10.5 and 25 °C

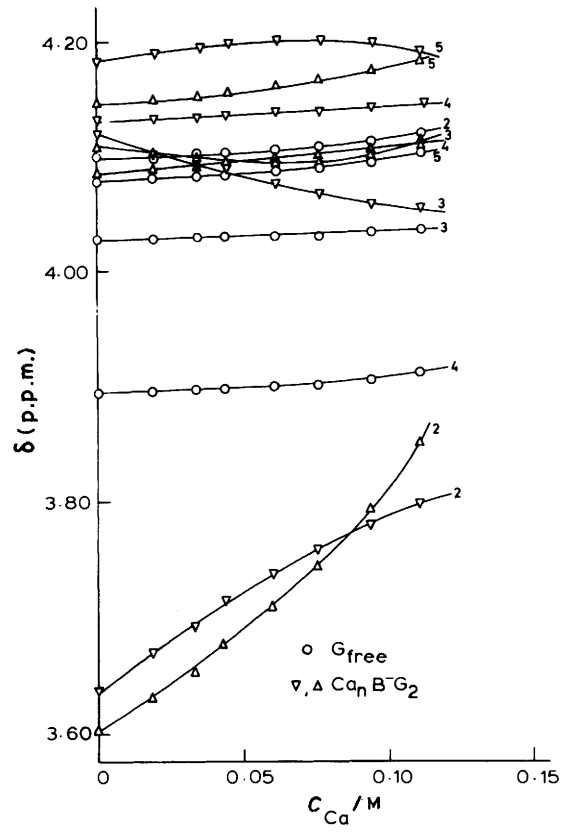


Figure 6. Calcium(II) induced ^1H n.m.r. shifts for a solution of borate (0.1M) and glucarate (0.2M) at pD 9.0 and 25 °C

of the torsion angle C(3)C(4)C(5)C(6) from 60 to 180° is required. Accordingly ^3J[H(4),H(5)] increased upon calcium(II) chloride addition, whereas the other vicinal coupling constants remained constant. Thus both glucarates probably are in a planar zig-zag conformation in the dicalcium(II) complexes of the borate diesters (Figure 3).

Molecular models show that α-hydroxy groups belonging to the gluconate ends (C_2) are able to participate in the calcium(II) co-ordination, contrary to those of the mannonate ends (C_5). This contribution was reflected by the relatively large CaIS of the H_2 signals of glucarate in the borate diesters, *viz.* 0.17 and 0.10 p.p.m. at C_{Ca} 0.11M (Figure 6).

As a consequence three different calcium(II) co-ordinating sites exist in the borate diesters. Because of the required C(4)C(5) rotation upon calcium(II) co-ordination and the lack of co-ordination of the 5-hydroxy in the case of a mannonate end, the calcium(II) co-ordination strength is assumed to decrease in the order of sites composed of two gluconate ends, of one gluconate and one mannonate end, and of two mannonate ends.

Distinction between the two sets of four ^1H signals for each of the diastereoisomeric borate diesters was possible, because the CaIS curves of one set of signals were concave *versus* C_{Ca}, whereas those of the other set were convex (Figure 6). The intensity ratio of both the ^1H and the ^{13}C signals of the two diastereoisomeric diesters was *ca.* 1:1 and was independent of the amount of calcium(II) present. Thus the overall calcium(II) co-ordinating strengths of the (*R*)- and (*S*)-borate diesters of glucarate are comparable. This is probably due to the fact that the (*R*)-borate diester contains two equal pentadentate co-

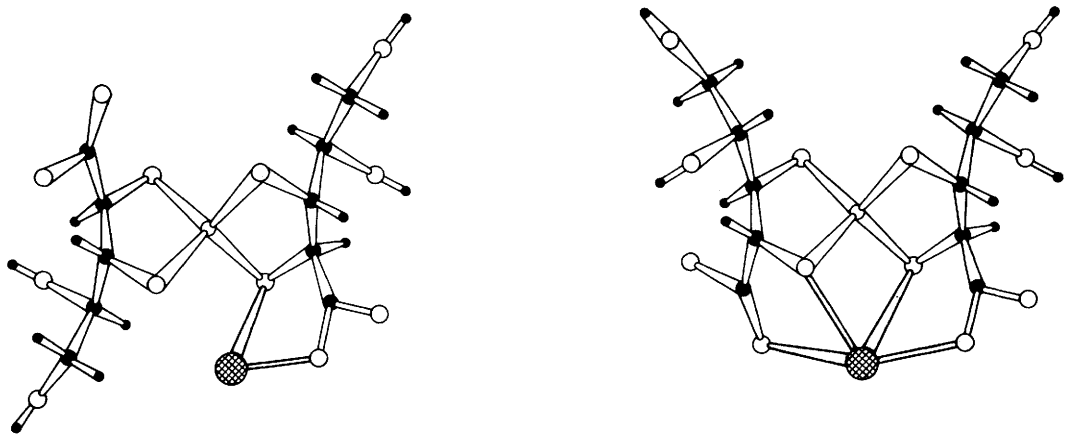


Figure 7. Calcium(II) co-ordination in the diastereisomeric (*R*)- and (*S*)-borate diesters of arabinonate in water (symbols as in Figure 3)

ordination sites, while the (*S*)-borate diester contains one tetra- and one hexa-dentate co-ordination site.

Additional evidence for the co-operation of two carboxylate groups upon borate diester formation was obtained from arabinonate. Borate ester formation occurs at the *threo*-2,3-position,[6] which for the borate diester results in two diastereoisomers as depicted in Figure 7. Upon addition of calcium(II) chloride considerable CaIS for one set of borate diester ^{13}C resonances was observed, whereas the other signals did not shift at all. Furthermore the intensity ratio between the shifted and non-shifted borate diester signals increased from 0.6 (C_{Ca} 0) to 4 (C_{Ca} 0.1M) and the signals of free arabinonate and its borate monoester almost disappeared. Obviously, preferential calcium(II) co-ordination by the (*R*)-borate diester, acting as a tetradentate ligand, is favourable (Figure 7).

For free glucarate the CaIS of H(2) and H(5) were larger than those of H(3) and H(4), *viz.* 0.025 and 0.024 p.p.m. *versus* 0.018 and 0.011 p.p.m. (C_{Ca} 0.11M). This agrees with the general observation that in calcium(II) co-ordination compounds of polyhydroxycarboxylates the carboxylate and the α-hydroxy oxygens form the calcium(II) co-ordinating site.[18,19] Plotting the CaIS of H(2)–H(4) as a function of the CaIS of H(5) for free glucarate gave straight lines whereas plots of the CaIS *versus* C_{Ca} (Figure 6) were convex. These results suggest that glucarate as such binds just one calcium(II) ion, only when the relatively strongly co-ordinating sites in the borate diesters are fully occupied.

Effect of Concentration, pH, and Temperature on the Glucarate–Borate–Calcium(II) System.—Upon dilution of a sample with $C_B = C_G = 0.1$M at pD 11.0, ^{11}B n.m.r. spectra demonstrated that the concentrations of the borate mono- and di-ester of glucarate have decreased as should be expected. When $C_B = C_G < 0.025$M the borate diester signal was no longer observed. The association constants in Table 1 did not change significantly upon dilution. In the presence of calcium(II) (0.05M) dilution also resulted in dissociation of the borate esters, but a remaining concentration of the borate diester species of *ca.* 0.5 C_{Ca} was observed, even in the mM-range. Once more this shows that the borate diesters strongly co-ordinate two calcium(II) ions, which has been quantified by calcium(II) ion selective electrode measurements.[20]

The effect of pH was studied using ^{11}B n.m.r. for the system borate–glucarate in the absence and presence of calcium(II) (Figure 8). The curves for the borate esters include both esters of α-hydroxycarboxylic acid and diol functions (Table 1). The pD optima for the borate mono- and di-esters of the α-hydroxycarboxylic acid functions without calcium were at pD

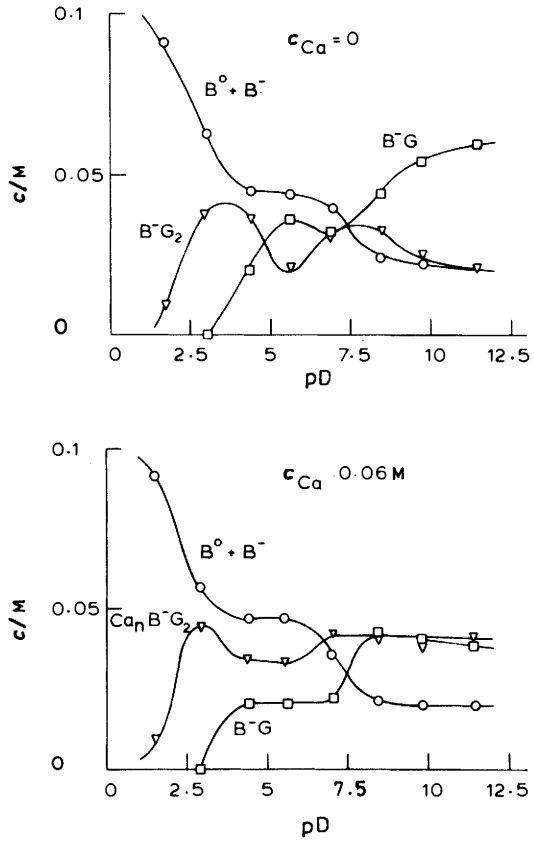


Figure 8. Distribution of boron-containing species as function of pD for a solution of borate (0.1M) and glucarate (0.1M) in the absence and presence of calcium(II) (0.06M) at 25 °C as determined with ^{11}B n.m.r.

5.5 and 3.5, respectively, which is in agreement with the pH rule of thumb postulated previously.[5] With calcium(II) these maxima were at pD 5.0 and 3.0, respectively, which demonstrates the decrease of pK_a upon cation co-ordination. The concentration of the borate esters of diol functions were independent of pD when pD > 11.5 and 9.0, in the absence and presence of calcium(II), respectively. The relatively high concentration of borate diester species in the presence of calcium(II) is due to the high calcium(II) co-ordinating strength of the borate diesters, as discussed before.

The temperature dependence of the borate ester equilibria as

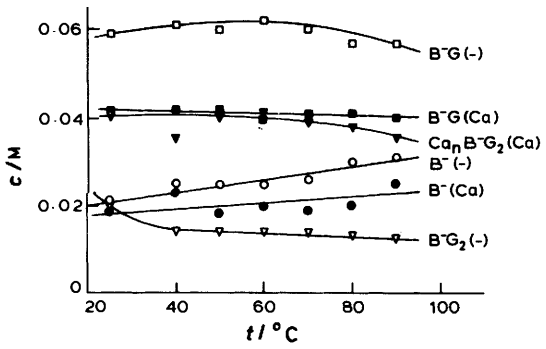


Figure 9. Distribution of boron-containing species as function of the temperature for a solution of borate (0.1M) and glucarate (0.1M) in the absence and presence of calcium(II) (0.06M) at pD 11.4 as determined with ^{11}B n.m.r.

studied with ^{11}B n.m.r. (Figure 9) was small, in particular when calcium(II) was present. This contrasts the destabilizing effect of temperature increase usually observed,[6] and favours the application of the present system as builder in detergent formulations.

Experimental

The n.m.r. spectra were measured for solutions of boric acid (0—0.2M), potassium hydrogen glucarate (0—0.2M), and calcium(II) chloride (0—0.12M) in D_2O at pD 9—11.5 and 25 °C unless stated otherwise. 200 MHz ^{1}H N.m.r. spectra were recorded with a Nicolet NT-200 WB spectrometer using t-butyl alcohol (δ 1.200 p.p.m.) as internal standard. The H_2 signals of glucarate and its borate esters were assigned using [2-^{2}H]-glucarate. The coupling between H(2) and H(3) and between H(4) and H(5) of the borate esters was established with the aid of ^{1}H homonuclear shift correlation (COSY)[21] of solutions of borate (0.1M), glucarate (0.2M), and calcium(II) (0 and 0.08M) at pD 9.0 with a 300 MHz spectrometer built at the Department of Applied Physics, Delft University of Technology.[22] The sample without calcium(II) was also recorded at 500 MHz on a Bruker WP 500 spectrometer. Since ^3J[H(3),H(4)] < 1 Hz, coupling between H(3) and H(4) in the borate diester manifested itself only as line broadening. ^{11}B and ^{13}C n.m.r. spectra were recorded on a Nicolet NT-200 WB spectrometer at 64.19 and 50.31 MHz, respectively. A 0.1M-boric acid solution (δ 0.0 p.p.m.) and *p*-dioxane (δ 66.6 p.p.m.) were used as external and internal reference, respectively. The reproducibility of the intensities of the ^{11}B signals was *ca.* 5%. A ^{1}H–^{13}C heteronuclear shift correlation spectrum[21] was recorded for a sample of glucarate in D_2O. Potassium hydrogen [2-^{2}H]glucarate was synthesized by oxidation of a mixture of [2-^{2}H]glucitol and [2-^{2}H]mannitol,[23] obtained by $NaBD_4$ reduction of fructose,[24] followed by selective precipitation using K_2CO_3.[25]

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