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SYNERGIC COORDINATION OF CALCIUM IN BORATE–POLYHYDROXYCARBOXYLATE SYSTEMS*

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ABSTRACT

The increased abilities of polyhydroxycarboxylates (L) to coordinate calcium in aqueous alkaline solution upon addition of borate (B^-) have been studied by ^{11}B-n.m.r. spectroscopy, determination of the capacity for sequestering calcium, and ion-selective electrode measurements of calcium. The synergic effect is caused by the formation of mono- and di-calcium complexes of the borate diesters of the polyhydroxycarboxylates (B^-L_2). The association constants ($\beta_{B^-L_2}$ and $\beta^{Ca}_{Ca_nB^-L_2}$ for the equilibria

$$B^- + 2\,L \rightleftharpoons B^-L_2 \overset{n\mathrm{Ca}}{\rightleftharpoons} Ca_nB^-L_2$$

determine the synergic effect quantitatively.

INTRODUCTION

The application of sodium triphosphate (STP) as a builder in synthetic detergent formulations[3,4] contributes to eutrophication in stagnant surface water[5]. In a search for STP substitutes, various inorganic and organic compounds have been screened, particularly with respect to their ability to sequester calcium[6–9]. We have synthesised polyhydroxycarboxylates[10,11] and have studied their formation of complexes with calcium, using calcium-ion-selective electrode measurements[11] and multinuclear n.m.r. techniques[12].

The coordination of calcium by polyhydroxycarboxylates can be improved sometimes by the addition of a second ligand. Such synergic effects can be attributed to interactions of the two different ligands[13,14], and mixed-ligand systems (MLS) with polyoxygen ligands have been studied[7,15–20]. Zeolites with carboxylates as co-builder might be regarded[21] as a special class of MLS. Mixtures of (per)boric acid and polyhydroxycarboxylic acids at pH >9.5 have been disclosed[22–24] in the

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*Studies on Borate Esters, Part VI. For Part V, see ref. 1.

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patent literature as promising systems for sequestering cations. Boro-gluconates and -glucoheptonates are commercially available sequestering agents.

In aqueous media at pH >9, borate forms[25] mono- and di-esters with the diol functions of polyhydroxycarboxylates (Fig. 1). The preferred borate-binding sites and the stability of the borate esters have been established for a series of polyhydroxycarboxylates, using ^{11}B- and ^{13}C-n.m.r. spectroscopy[2,26]. The presence of a chiral axis through the central boron atom in some borate diesters results in diastereomerism[2]. Also, it was demonstrated that the diastereomeric 3,4-borate diesters of D-glucarate form stable dicalcium complexes[1]. Sites for the coordination of calcium involve two carboxylate oxygens, two borate-ester ring oxygens, and, depending on the configuration, up to two α-hydroxyl oxygens (Fig. 2)[1].

We now report on the calcium-coordinating properties of mixtures of borate and various polyhydroxycarboxylates (**1–24**) in aqueous alkaline solution.

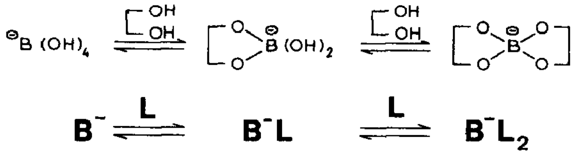


Fig. 1. Equilibria between borate (B^-) and a diol function of a polyhydroxycarboxylate (L) in water at pH >9.

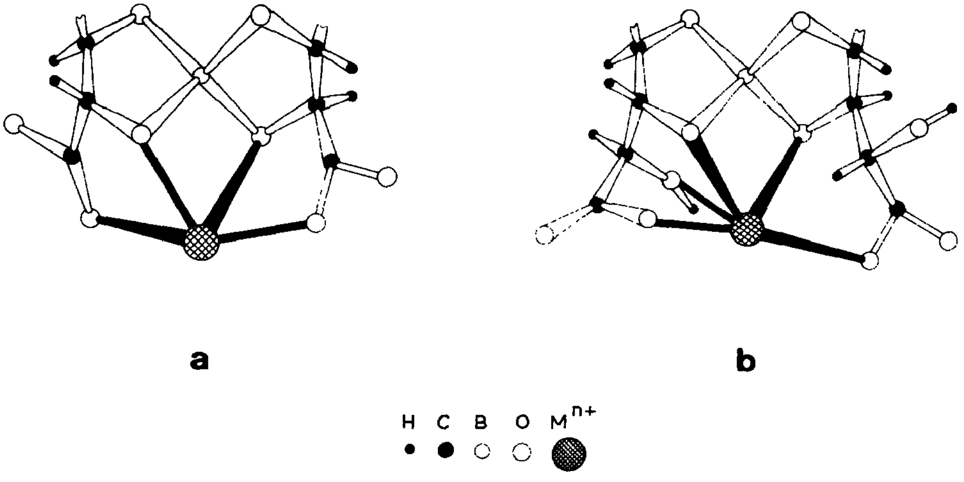
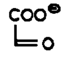


Fig. 2. Calcium-coordination sites in borate diesters of polyhydroxycarboxylates with borate bound at the 2,3- (a) and 3,4-positions (b) are composed of two carboxylate oxygens and two borate-ester ring oxygens. In the case of a 2,3,4-*xylo* configuration [as in the left-hand carbon chain of (b)], the HO-2 also participates.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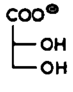
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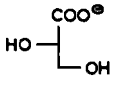
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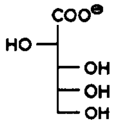
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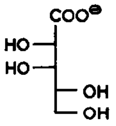
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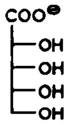
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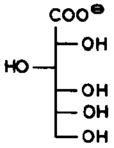
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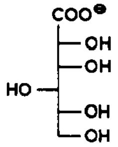
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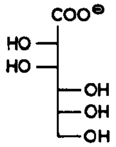
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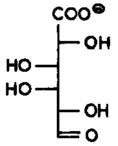
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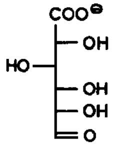
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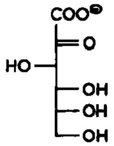
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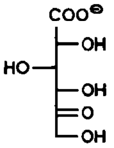
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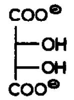
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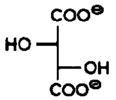
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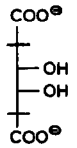
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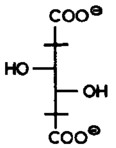
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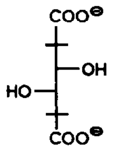
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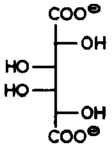
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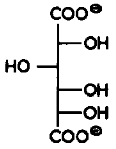
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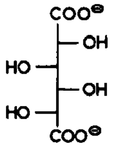
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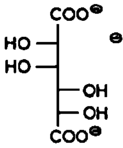
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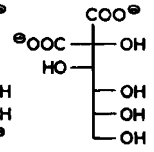
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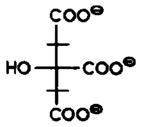
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RESULTS AND DISCUSSION

Calcium sequestering capacities. — Synergic sequestration of calcium in a borate–polyhydroxycarboxylate mixture can be demonstrated by the determination of the calcium sequestering capacity (CaSC)[22–24], using a titration procedure with

TABLE I

CALCIUM SEQUESTRATION CAPACITIES (CaSC) FOR POLYHYDROXYCARBOXYLATES IN THE ABSENCE AND IN THE PRESENCE OF 0.5 MOL OF BORATE[a]

Polyhydroxycarboxylate	*CaSC (g of Ca/100 g of L)*	
	Without borate	*With borate*
7 D-Gluconate[b]	2.9	6.8
8 D-Gulonate[b]	1.4	5.2
14 *meso*-Tartrate[b]	2.5	8.6
19 Galactarate	0.7	2.5 (2.5[c])
20 D-Glucarate	1.5	10.8 (>15[c])
20 D-Glucarate[d]	1.5	1.9
24 Citrate	5.5	5.6

[a] 8 g of polyhydroxycarboxylate/L, pH 11, 25°. [b] Taken from ref. 22; pH 9.5. [c] Without oxalate as indicator. [d] Phenylboronate instead of borate.

TABLE II

EFFECT OF THE ADDITION OF CALCIUM CHLORIDE ON THE COMPOSITION OF SAMPLES WITH BORATE AND A POLYHYDROXYCARBOXYLATE AS DETERMINED BY ^{11}B-N.M.R. SPECTROSCOPY[a]

Polyhydroxycarboxylate		c_B (M)	c_L (M)	*pH*	$c_{Ca,max}$ (M)	% B^-[b]		% $B^-L_{1,2}$[b,c]		% $B^-(L_{1,3})_n$[b,d]		% $B(L_{1,2})_2$[b,e]	
						$c_{Ca,0}$	$c_{Ca,max}$	$c_{Ca,0}$	$c_{Ca,max}$	$c_{Ca,0}$	$c_{Ca,max}$	$c_{Ca,0}$	$c_{Ca,max}$
2 + 3	(±)-Glycerate	0.1	1.0	10.5	0.41	17	5	54	36			29	59
4	D-Arabinonate	0.1	0.2	11.0	0.54	9	3	65	21	2	2	34	74
5	D-Lyxonate	0.15	0.2	11.0	0.09	20	14	57	52	1	2	22	32
6	D-Ribonate	0.1	0.2	11.0	0.70	12	15	52	33	26	15	12	37
7	D-Gluconate	0.2	0.2	11.0	0.15	16	21	62	49	2	6	20	25
8	D-Gulonate	0.2	0.2	11.0	0.04	19	10	58	37	1	0	23	54
9	D-Mannonate	0.15	0.2	11.0	0.13	4	4	55	36	2	6	40	54
12	D-*arabino*-2-Hexulosonate	0.1	0.2	11.0	0.13	5	4	65	53	0	0	30	43
14	*meso*-Tartrate	0.1	1.0	11.0	0.09	32	9	55	24			13	67
15	D-Tartrate	0.1	0.1	10.5	0.05	77	69	22	10			1	21
16	*meso*-3,4-Dihydroxyadipate	0.1	0.5	11.0	0.05	39	35	54	50			7	16
17 + 18	(±)-3,4-Dihydroxyadipate	0.05	0.25	11.0	0.05	22	21	50	54			28	25
19	Galactarate	0.1	0.1	10.5	0.05	15	26	70	42	0	0	15	24
20	D-Glucarate	0.1	0.1	10.5	0.075	21	16	59	35	4	4	16	43
21	L-Idarate	0.1	0.2	11.0	0.05	22	21	55	45	3	10	21	24
22	D-Mannarate	0.1	0.2	10.5	0.06	29	21	53	40	0	0	19	39

[a] 64.19 MHz, D_2O, 25°. [b] The composition is given in % of c_B in the absence ($c_{Ca,0}$) and presence of calcium ($c_{Ca,max}$). [c] Sum of borate monoesters of the 1,2-diol functions, including the corresponding calcium complexes. [d] Sum of the borate esters of 1,3-diol functions, including the corresponding calcium complexes. [e] Sum of the borate diol functions of 1,2-diol functions, including the corresponding calcium complexes.

oxalate as the indicator. With the exception of citrate (**24**), the addition of borate led to substantially higher CaSC values (Table I). However, this method does not always give reliable results, as was observed in the system borate–galactarate (**19**); precipitation of a calcium borogalactarate defined the turbidity point. Furthermore, the ligands may inhibit the precipitation and the crystal growth of calcium oxalate[27], the change of the ionic strength affects the various equilibrium and solubility constants, and interactions of boric acid and oxalate result[25] in additional problems at pH <7.

Origin of the synergic calcium coordination in the borate–polyhydroxycarboxylate system. — The effect of increasing amounts of calcium chloride on the composition of the MLS were studied, using ^{11}B-n.m.r. spectroscopy, until precipitation occurred at $c_{\mathrm{Ca,max}}$ (Table II). Formulations were chosen so as to ensure an excess of borate monoester over diester, before the calcium chloride was added. For dicarboxylates, $c_{\mathrm{Ca,max}}$ was relatively low because the corresponding calcium salts are less soluble than those of monocarboxylates, probably as a result of self-association.

The exchange between the borate anion and the borate monoester and between the borate mono- and di-esters remained slow on the ^{11}B-n.m.r. time scale, but the exchange of the borate esters with the corresponding calcium complexes was fast. The calcium-induced shifts were negligible, but all signals were broadened on the addition of calcium chloride. Consequently, the resolution decreased and the error in assessing the intensity of the ^{11}B resonances increased. This, together with the occasional small changes in intensities, particularly when precipitation occurred at low $c_{\mathrm{Ca,max}}$, did not allow accurate quantitative analysis of the complex MLS on the basis of ^{11}B-n.m.r. data alone.

When c_{Ca} was increased, the total concentration of the borate diester-containing species (borate diesters and their calcium complexes) generally increased, whereas those of the borate monoester and free borate decreased (Table II, Fig. 3). This finding indicated the borate diesters to be the preponderant calcium-coordinating species, which accords with previous observations[1]. This inference is supported by the negligible effects both of adding calcium chloride to a mixture of phenylboronate and D-glucarate (**20**) as studied by ^{11}B-n.m.r. spectroscopy and of phenylboronate on the CaSC of D-glucarate (Table I). In the phenylboronate–D-glucarate system, only boronate monoesters can be formed[1].

The synergic effects, therefore, can be rationalised by the good calcium-coordinating properties of the borate diesters. The borate anion brings two polyhydroxycarboxylates together, resulting in one or two new calcium-coordinating sites. The denticity (number of coordinating donor atoms) of these sites ranges from 4 to 6 (Table III). Participating donor sites are two carboxylate oxygens (one of each polyhydroxycarboxylate) and two borate-ester ring oxygens. Moreover, the non-esterified HO-2 of a 2,3,4-*xylo*-configuration can participate in the coordination of calcium, when borate is bound at the 3,4-*threo* position (Fig. 2b).

In order to determine the number of calcium ions bound by the borate

TABLE III

ASSOCIATION CONSTANTS FOR CaL, OVERALL ASSOCIATION CONSTANTS FOR B^-L_2, AND DENTICITIES OF CALCIUM-COORDINATING SITES IN THE BORATE DIESTERS

	Polyhydroxycarboxylate	*log* $K_{CaL}^{a,b}$	*log* $\beta_{B^-L_2}^{c}$	*Denticities in the borate diester*[d]	
				R-*Diastereomer*	S-*Diastereomer*
1	Glyoxylate	1.6			
2 + **3**	(±)-Glycerate	1.6 (1.2)[28]	0.6		
4	D-Arabinonate	1.6	2.8	4	2
5	D-Lyxonate	1.6	3.8	4	2
6	D-Ribonate	1.5	1.8	2	4
7	D-Gluconate	1.6 (1.2)[28]	3.9	6	3
8	D-Gulonate	1.6	4.6	2	4
9	D-Mannonate	1.6	4.7	4	2
10	D-Galacturonate	1.3 (0.7–1.8)[29]	—	—	—
11	D-Glucuronate	1.1 (0.7–1.5)[29]	—	—	—
12	D-*arabino*-2-Hexulosonate	1.2	3.3	—	—
14	*meso*-Tartrate	2.5	−0.1	4 + 4	4 + 4
15	D-Tartrate	2.0 (1.8)[28]	2.3	4 + 4	4 + 4
16	*meso*-3,4-Dihydroxyadipate	1.6	0.1	4 + 4	4 + 4
17 + **18**	(±)-3,4-Dihydroxyadipate	1.6	1.7	4 + 4	4 + 4
20	D-Glucarate	2.2	3.7	5 + 5	6 + 4
21	L-Idarate	2.1	3.4	6 + 6	6 + 6
22	D-Mannarate	2.3	2.6	4 + 4	4 + 4
23	2-Carboxy-D-gluconate	3.2	2.3	6	3 + 3
	Borate	1.4 (1.1)[30]			

[a] c_{Ca} 5mM, c_L 10mM, pH 10, I 0.1, 25°. [b] Values taken from the literature for other ionic strengths and temperatures. [c] Ref. 26. [d] Two sites in borate diesters of dicarboxylates with the exception of (R)-B^-L_2 of **23**.

diesters, calcium complexation was studied with a calcium-ion-selective electrode (CaISE). For the dicarboxylates D-glucarate (**20**) and L-idarate (**21**), [Ca] is <2.5mM when $c_{Ca} = c_B = c_L = 5.0$mM (Fig. 4) and thus >2.5mM calcium is coordinated. Since the maximum concentration of the borate diester under these conditions is 2.5mM, these species must be able to bind two calcium ions, which is in agreement with previous ^{11}B-n.m.r. results[1]. In borate diesters of monocarboxylates, only a single calcium-coordination site is present in one of the two diastereomers and, as a result, [Ca] is >2.5mM for monocarboxylates under the present conditions (Fig. 4).

Quantitative analysis of the calcium–borate–polyhydroxycarboxylate MLS. — The CaISE measurements allow a more quantitative analysis of the MLS than the ^{11}B-n.m.r. data. The experiments were carried out at pH 10, since both the equilibria of borate ester formation[1] and those involving calcium coordination (Fig. 5) are then independent of pH. Furthermore, the experimental pH of 10 is in the range (9–10.5) of the standard washing process[6] and in the optimum region with respect to the CaISE sensitivity. The measurements were performed at c_{Ca} 5.0mM, which is the upper level of the hardness of Dutch tap-water and at $c_B + c_L = 10.0$mM.

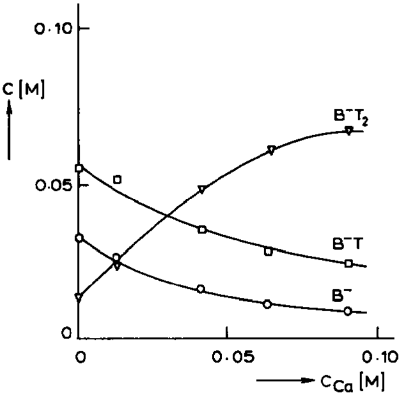

Fig. 3. Effect of the addition of calcium chloride on the borate ester equilibria for a sample with 0.1M boric acid and 0.1M *meso*-tartaric acid (14) in D_2O at pH 11 and 25° as determined with ^{11}B-n.m.r. spectroscopy.

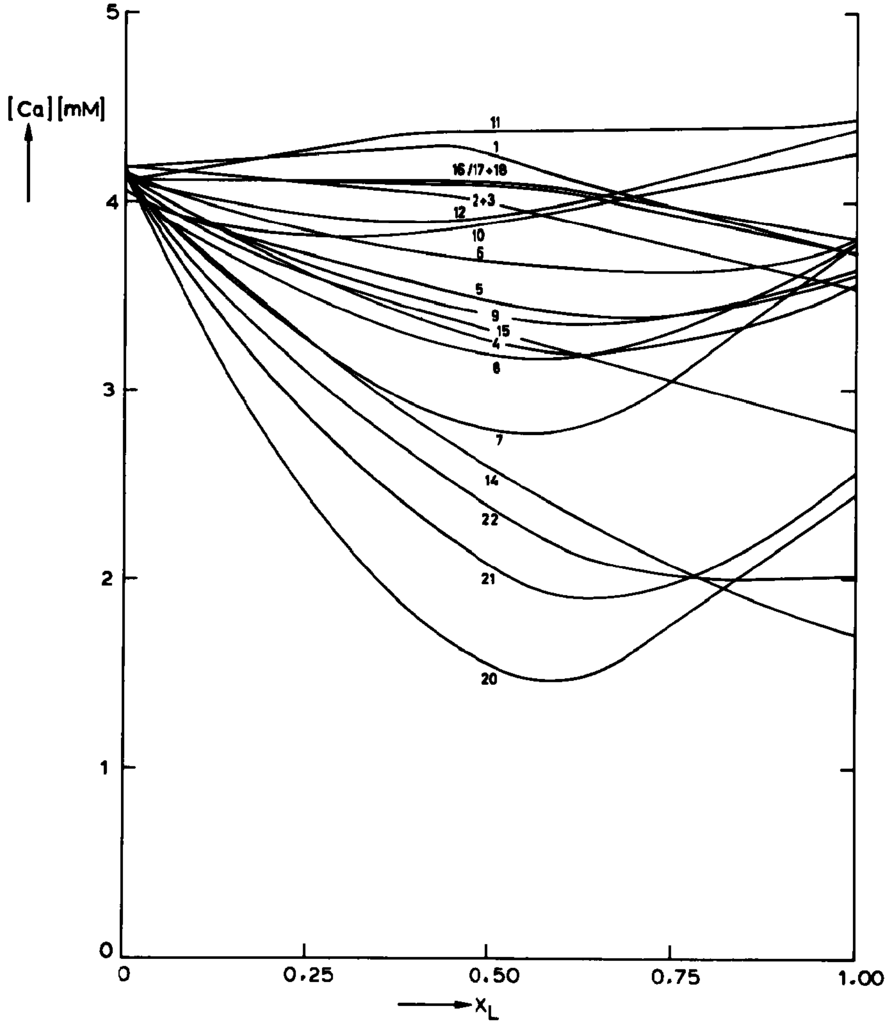

Fig. 4. Concentration of free calcium as a function of the molar fraction of polyhydroxycarboxylic acid for various MLS ($c_B + c_L$ = 10mM and c_{Ca} = 5.0mM at pH 10, I = 0.1, and 25°).

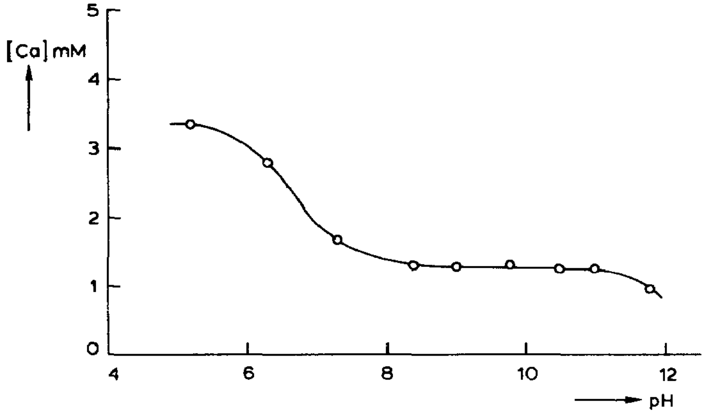

Fig. 5. Effect of pH on the concentration of free calcium for a solution with 6.67mM D-glucaric acid (**20**), 3.33M boric acid, and 5mM calcium at I = 0.1 and 25°.

[Ca] was determined for the various MLS (Fig. 4) as a function of the molar fraction of polyhydroxycarboxylate x_L:

$$x_L = c_L/(c_L + c_B). \qquad (1)$$

The accuracy of the experimental method was demonstrated by the excellent overlap of the two partial curves, constructed from data of experiments starting at $x_L = 0.0$ and 1.0, respectively. For galactarate (**19**) and D-*xylo*-5-hexulosonate (**13**), clear starting solutions could not be prepared due to precipitation of calcium salts. For 2-carboxy-D-gluconate (**23**), the formation of a calcium borate-ester precipitate occurred.

As to the species in the MLS (Fig. 6), the concentrationsof $Ca(B^-)_2$, CaL_2, Ca_2B^-, Ca_2L, and $(B^-)_2L$ were neglected. The overall association constants of CaL_2

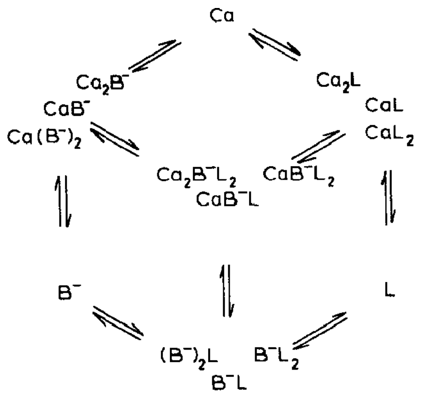

Fig. 6. Species in the calcium–borate–polyhydroxycarboxylate (Ca–B⁻–L) MLS.

and $Ca(B^-)_2$, obtained by fitting the curves for titration of free D-glucarate and borate with calcium, are only ~20 and ~1M^{-2}, respectively. Those of Ca_2L and Ca_2B are expected to have similar or lower values. The overall association constant of $(B^-)_2L$ for L = D-mannitol is relatively large ($2 \times 10^4\text{M}^{-2}$) (refs. 31, 32). When L = polyhydroxycarboxylate, however, the concentration of $(B^-)_2L$ can be neglected even at $c_B = c_L = 0.1\text{M}$, due to the smaller number of hydroxyl groups and to Coulombic repulsion of the BO_4 moiety and the carboxylate group[26].

As a result, our mathematical model includes the three material-balance equations for calcium, borate, and the polyhydroxycarboxylate, and the equilibrium constants for the species Ca, B^-, L, CaL, CaB^-, B^-L, B^-L_2, CaB^-L, CaB^-L_2, and $Ca_2B^-L_2$. The *K* values are defined as:

$$K_{B^-L_n} = [B^-L_n]/([B^-L_{n-1}][L]) \qquad (n = 1,2) \qquad (2)^{26,*}$$

$$K_{CaZ} = [CaZ]/([Ca][Z]) \text{ with } Z = L, B^-, B^-L, B^-L_2, \text{ or } CaB^-L_2. \qquad (3)$$

K_{CaZ} with Z = B^- or L was determined from [Ca] at x_L = 0.0 or 1.0, respectively (Fig. 4), and the relation:

$$K_{CaZ} = (c_{Ca} - [Ca])/\{[Ca](c_Z - c_{Ca} + [Ca])\}. \qquad (4)$$

The agreement with literature values is good (Table III). In addition, two assumptions were made:

$$K_{CaB^-L} = K_{CaL} \qquad (5)$$

and, for dicarboxylates, $K_{Ca_2B^-L_2} = \alpha K_{CaB^-L_2}$, $\qquad (6)$

with $\alpha = 0.25$ on statistical grounds.

When [Ca] is measured for a MLS, our mathematical model reduces to a set of three equations with three variables, *viz.*, $[B^-]$, [L], and $K_{CaB^-L_2}$. Although accurate fitting of the experimental data (Fig. 4) was not possible, this model gave log $K_{CaB^-L_2}$ and log $K_{Ca_2B^-L_2}$ values of 3.8–5.0 and 3.3–3.6, respectively. These values are comparable with those of other calcium-coordinating ligands with four oxygen donor atoms, such as citrate or carboxymethoxysuccinate (log K_{CaZ} = 3.4 and 4.1, respectively[11]). Both the imposed proximity of the carboxylate groups in the borate diester and the relatively large partial charge on the coordinating oxygens of the borate-ester rings (−0.37 in a borate ester ring *vs.* −0.25 in a free diol, as calculated with CNDO[33]) contribute to this. Variation of α (equation *6*) did

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*The ^{11}B chemical shifts (p.p.m.), line widths (Hz), and association constants[26] (M^{-1}) of the various borate esters of D-*arabino*-2-hexulosonate (**12**): $B^-(L_{1,2\text{-diol}})$ – 12.5, 50, and 150; $B^-(L_{1,2\text{-diol}})_2$ – 7.9, 120, and 9; $B^-(L_{1,2\text{-diol}})$ −13.6, 60, and 200; $B^-(L_{1,2\text{-diol}})_2$ – 8.6, 90, and 2; $B^-(L_{1,3\text{-diol}})$ – 18.1; and of 2-carboxy-D-gluconate (**23**): $B^-L_{3,4}$ – 13.1, 30, and 60; $B^-(L_{3,4})_2$ – 8.8, 110, and 9; $B^-L_{4,5}$ – 14.4, 50, and 13; $B^-L_{4,6}$ – 18.1, 50, and 5.

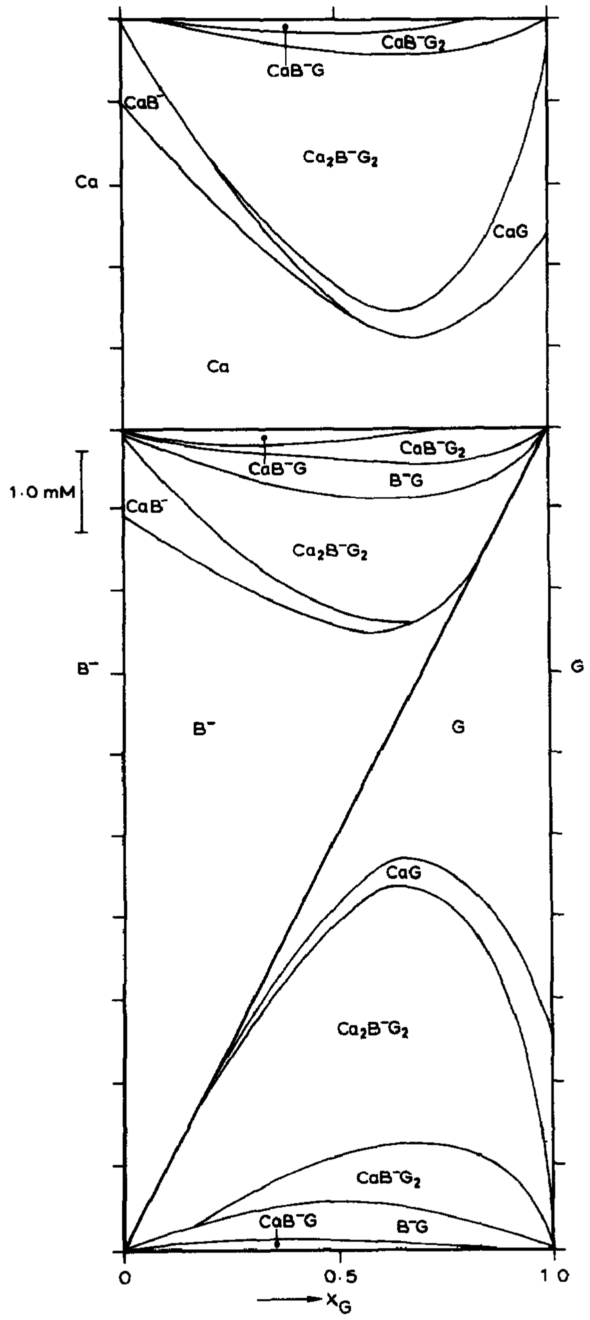

Fig. 7. Calculated distribution of species in the system calcium (5mM), borate (B^-), and D-glucarate (G) ($c_B + c_G$ = 10mM) at pH 10 with log $K_{B^-G} = 2.3$, log $K_{B^-G_2} = 1.4$, log $K_{CaB^-} = 1.4$, log K_{CaG} = log $K_{CaB^-G} = 2.1$, log $K_{CaB^-G_2} = 4.2$, and log $K_{Ca_2B^-G_2} = 3.8$. The concentrations of the calcium, borate, and glucarate species are expressed as $p[Ca_p(B^-)_qG_r]$, $q[Ca_p(B^-)_qG_r]$, and $r[Ca_p(B^-)_qG_r]$, respectively.

not improve the fit, and increase of $K_{\mathrm{CaB^-L}}$ only resulted in a better fit when $K_{\mathrm{CaB^-L}} > K_{\mathrm{CaB^-L_2}}$, which can be rejected on the basis of the ^{11}B-n.m.r. and CaSC data.

For D-glucarate (G: **20**) as the ligand, Fig. 7 shows the concentrations of the various species calculated with the model described above as a function of x_G. Most of the coordinated calcium is bound as $\mathrm{Ca_2B^-G_2}$. Calculations for $x_G = 0.5$ ($c_B = c_L = 5.0$mM) demonstrate that, in the absence of calcium, the concentration of $\mathrm{B^-G_2}$ is 0.05mM, whereas for $c_{Ca} = 5$mM the concentrations of $\mathrm{B^-G_2}$, $\mathrm{CaB^-G_2}$, and $\mathrm{Ca_2B^-G_2}$ are 0.012, 0.25, and 1.4mM, respectively. Hence, the amount of borate diester-containing species in dilute solutions is only significant when calcium is present. This finding agrees with the results of previous ^{11}B-n.m.r. experiments[1] and stresses the high stability of $\mathrm{Ca_nB^-G_2}$ ($n = 1,2$). Supporting evidence for this phenomenon is obtained from ion-exchange experiments in the presence of borate–D-glucarate[11]. The calcium coordinating system generated in the presence of calcium resembles the ternary calcium–calmodulin–enzyme system[34].

More concentrated solutions (>0.1M) of borate and a polyhydroxycarboxylate (as in the n.m.r. experiments) in the absence of calcium generally contain substantial amounts of the borate diester. On addition of calcium, the induced equilibria changes will be relatively small (Table I and Fig. 3) compared with the more diluted solutions.

Synergic coordination of calcium as a function of the polyhydroxycarboxylate. — $K_{\mathrm{CaB^-L_2}}$ and $K_{\mathrm{Ca_2B^-L_2}}$ cannot be calculated with the required accuracy for a discussion of the effect of the polyhydroxycarboxylate in the MLS. In order to quantify the synergic effect of borate and a polyhydroxycarboxylate, the experimental concentrations of calcium ($[\mathrm{Ca}]_{\mathrm{exp}}$) are compared with values obtained by calculation, in which only equilibria with $\mathrm{CaB^-}$ and CaL are taken into account

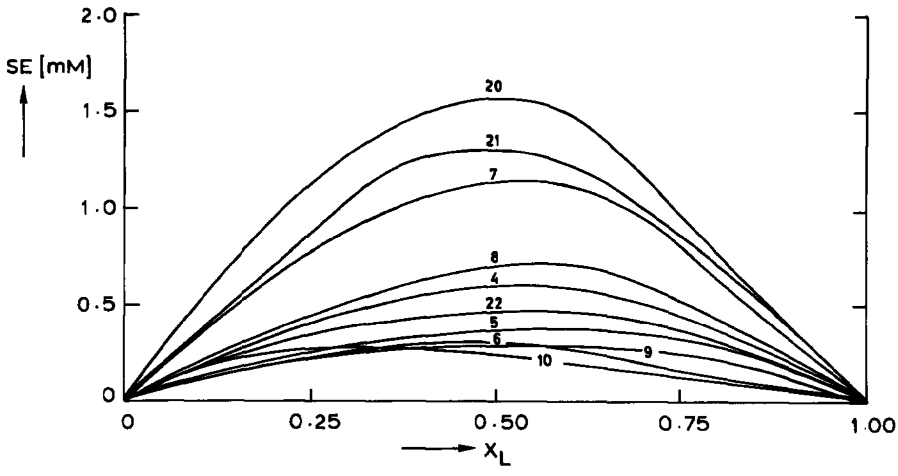

Fig. 8. Synergic effect (SE) as a function of the molar fraction of polyhydroxycarboxylate for various MLS ($c_B + c_L = 10$mM and $c_{Ca} = 5$mM at pH 10, I = 0.1, and 25°).

($[\mathrm{Ca}]_{\text{non-syn}}$), *i.e.*, discarding all extra interactions such as the formation of borate esters. The synergic effect (SE) is then defined as:

$$\mathrm{SE} = [\mathrm{Ca}]_{\text{non-syn}} - [\mathrm{Ca}]_{\text{exp}}. \tag{7}$$

The SE appears to be maximal at $x_L = 0.45 - 0.65$ (Fig. 8). Theoretically, this optimum is at $x_L = 0.67$ (c_B/c_L equals the ratio B^-/L in B^-L_2), although the curve of SE *vs.* x_L is rather flat at $x_L = 0.5$–0.7.

The SE is determined by both the overall stability constant of the borate diester,

$$\beta_{B^-L_2} = [B^-L_2]/([B^-][L]^2) = K_{B^-L}\,K_{B^-L_2}, \tag{8}$$

and the calcium-coordinating strength of the borate diester,

$$\beta^{\mathrm{Ca}}_{\mathrm{Ca}_nB^-L_2} = [\mathrm{Ca}_nB^-L_2]/([\mathrm{Ca}]^n[B^-L_2]), \qquad \text{with } n = 1,2, \tag{9}$$

which depends on the denticity of the coordination sites (Fig. 2. Table III). Combination of equations *8* and *9* shows that the SE is related with:

$$B^- + 2\,L \rightleftharpoons B^-L_2 \overset{n\mathrm{Ca}}{\rightleftharpoons} \mathrm{Ca}_nB^-L_2$$

$$\beta_{\mathrm{Ca}_nB^-L_2} = [\mathrm{Ca}_nB^-L_2]/([\mathrm{Ca}]^n[B^-][L]^2) = \beta_{B^-L_2}\,\beta^{\mathrm{Ca}}_{\mathrm{Ca}_nB^-L_2}. \tag{10}$$

Borate esters of glyoxylate (**1**) and citrate (**24**) involve the carboxylic acid functions and are not stable at pH >10, according to the pH rule-of-thumb derived earlier[25]. For each compound, only the free borate signal was observed in the ^{11}B-n.m.r. spectrum at pH 10. As a result, $[B^-L_2] = 0$ (pH = 10) and thus SE = 0.

Calculations demonstrate that no significant SE occurs (SE <0.2mM) if $\beta_{B^-L_2} < 60$, assuming log $K_{\mathrm{CaB}^-L_2} = 4.2$. This applies to (±)-glycerate, *meso*-tartrate, and *meso*- and (±)-3,4-dihydroxyadipate (**2** + **3**, **14**, **16**, **17** + **18**: $\beta_{B^-L_2} < 60$). Furthermore, the denticities of the coordinating sites for calcium are only 2 or 4 for the diastereomeric borate diesters. For borate–*meso*-tartrate (**14**), the calculated curve (assuming no synergy) follows that obtained experimentally (Fig. 4) closely, and therefore the calcium-coordinating properties of this system are entirely due to the *meso*-tartrate. D-Ribonate (**6**) is a border-line case with $\beta_{B^-L_2} = 66$ and SE <0.24mM.

For the aldonates with borate bound at positions 2 and 3 [D-arabinonate (**4**) and D-ribonate (**6**)] and for the aldarates [D-glucarate (**20**), L-idarate (**21**), and D-mannarate (**22**)], the value of $\beta_{B^-L_2}$ seems to determine SE: **4** > **6** and **20** > **21** > **22**, respectively. But for the aldonates with borate bound at positions 3 and 4 [D-lyxonate (**5**), D-gluconate (**7**), D-gulonate (**8**), and D-mannonate (**9**)], differences in the denticity of the calcium-coordinating site seem to be of major importance: **7** > **5** = **8** = **9**. With the exception of D-mannarate (**22**), the C_6-aldarates have a larger SE than the aldonates, since both diastereomeric borate diesters of the former are able to bind two calcium ions. Discussion of the SE of D-*arabino*-2-hexulosonate (**12**) and the uronates is complicated due to acetal formation. The antagonistic effect for D-glucuronate (**11**) and the maximal SE for D-galacturonate (**10**) at x_L = 0.35 are exceptional.

EXPERIMENTAL

The carboxylic acids were commercial products or prepared as described in refs. 2 and 26. Sodium D-*arabino*-2-hexulosonate (2-keto-D-gluconate), calcium D-*xylo*-5-hexulosonate (5-keto-D-gluconate), and disodium 2-carboxy-D-gluconate were gifts from Akzo.

The ^{11}B-n.m.r. spectra of samples with boric acid (0.05–0.20M), a polyhydroxycarboxylic acid (0.1–1.0M), and increasing amounts of calcium chloride (until precipitation occurred) were recorded with a Nicolet NT-200 WB spectrometer at 64.2 MHz and 25°, using a 12-mm sample tube. The total volume of each sample in D_2O at adjusted pH (NaOD) was 5 mL. ^{11}B Chemical shifts were measured against external 0.1M boric acid in D_2O. Base-line correction was applied for all spectra and, when necessary, a deconvolution programme was used to obtain all signal characteristics.

Calcium sequestering capacities were determined according to Wilham and Mehltretter[35] at pH 11.0 (NaOH). Concentrations of free calcium were measured at 25° with a Radiometer F2112 Ca or a Philips IS 561-Ca CaISE, a HNU ISE-40-01-100 single-junction reference electrode, and a Corning digital 112 pH meter. The CaISE was calibrated as a function of pH. The desired MLS were obtained by mixing solutions with c_{Ca} 5.0mM, pH 10.0 (NaOH), I 0.1 (KCl), and c_B 10.0mM or c_L 10.0mM, respectively, and were flushed with nitrogen. The measurements were performed under nitrogen. Linear drift correction was applied using standard solutions with c_{Ca} 10.0mM at pH 10.0 and I 0.1.

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