Calorimetry

STRUCTURES OF THE BORATE COMPLEXES WITH A TETRITOL, PENTITOLS AND HEXITOLS IN SOLUTION. A CALORIMETRIC STUDY

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The molar heats for the reactions of borate with the polyhydroxy compounds pentaerythritol, L-arabinitol, xylitol, sorbitol and meso-inositol were determined by thermometric titrimetry. By means of the equilibrium constants, the corresponding Gibbs functions and entropies were also obtained. The results refer to aqueous medium at 25 °C and $I = 0.1$ M. The present data, together with previous data from this laboratory, lead to the conclusion that the differences in stability of these complexes are mainly determined by entropy, rather than by enthalpy factors. Unlike the other ligands (which are bidentate), pentaerythritol and meso-inositol seem to behave as tridentate ligands with borate. Nevertheless, their complexes exhibit very different stabilities, probably due to the different conformational freedoms of the two ligands in the uncomplexed form.

The reactions of borate with polyhydroxy compounds are of not only in analytical chemistry [1], but also in phytobiological chemistry, as the absorption of borate by many plants could take place through polyhydroxy molecules [2].

These equilibria have been investigated almost exclusively by means of the determination of stability constants. Some enthalpy and entropy data have also been obtained previously by the method of stability constant variation with temperature. Unfortunately, they are sometimes so inconsistent, as to differ, even in sign [3].

Among the spectral methods, NMR has recently provided information on the borate ester with D-mannitol and sorbitol [4], mainly from the point of view of internal, solute-solute factors.

Since enthalpies and entropies are often complementary with spectral data, as they can give details on external (i.e. solute-solvent) factors, it was considered of

interest to continue our recent investigation on the present subject [3] and to determine the enthalpies and entropies, by direct calorimetry, for the reactions of borate with a teritol (pentaerithritol), two pentitols (L-arabinitol and xylitol) and two hexitols (sorbitol and meso-inositol).

Experimental

Reagents. Analytical grade reagents were used throughout: boric acid, C. Erba RPE (>99.8% pure); pentaerythritol, xylitol, sorbitol (D-glucitol), L-arabinitol and meso-inositol, Fluka puriss. All solutions were prepared immediately before use. The background electrolyte was sodium nitrate (C. Erba RPE).

Equipment. Calorimetric measurements were performed at 25° with an LKB 8700–2 Precision Calorimetry System (isoperibol, incremental-titration type) and an LKB 8726–1 100 cm³ titration vessel. Fuller details on the instrument and the calibration have been reported elsewhere [5]. The calorimeter was equipped with a Radiometer ABU 12b autoburette for the addition of titrant. The calorimetric experiments were performed in a room kept at a temperature constant within ±0.3 deg (Branca Idealair "Zero" air-conditioning system).

Procedure. Successive portions of 2.505 ± 0.002 cm³ of sodium borate solution were added to 88.00 cm³ of polyol solution in the calorimetric cell, and the heat liberated in response to each addition was measured (for the borate and polyol concentrations, see Table 1). The pH of all solutions was brought to 11.5 ± 0.2 through the addition of sodium hydroxide before each measurement, and the ionic strength was adjusted to 0.1 M by the addition of sodium nitrate. At least three series of measurements were made for each polyol borate system. The corresponding heat of dilution was measured by adding the same amounts of sodium borate solution to 88.00 cm³ of 0.1 M sodium nitrate at pH 11.5, without any polyol. The following results were obtained under these conditions. (a) A negligible heat of neutralization between H^+ and OH^-. (b) A negligible association between the $[B(OH)_4]^-$ ion (which is the reacting species) and the proton, since the pK_a of boric acid is high (9.1 at 25° and $I = 0.1$ M [6]). (c) A negligible dissociation of the polyols, since the pK_a values are all above 14 [7]. (d) A negligible contribution to the measured enthalpies from the dissociation of polyborate species: since the borate concentration was lower than 0.025 M at the end of the mixing process, it must have reacted in the monomeric form [8] and, moreover, the heat of dissociation of any polyborates present in the initial solution is counterbalanced by an equal heat effect during the dilution experiment, so that it is eliminated in the calculation of the corrected heat (see below).

Treatment of the experimental data. Some experimental data are collected, as an

example, in Table 1: the initial concentration of polyol in the calorimetric vessel (C_L); the concentrations of the complex species and of free polyol ($[BL^-]$, $[BL_2^-]$, $[L]$) after each addition of titrant; and the mean cumulative heat, corrected for dilution (ΣQ_c).

Table 1 Experimental data relating to the mixing of aqueous solutions of polyols (L) and sodium borate $(B^- = \text{borate ion})$ at $25°$[a]

Polyol	C_L, M	$[BL^-]$, $M \times 10^3$	$[BL_2^-]$, $M \times 10^3$	$[L]$, $M \times 10^2$	ΣQ_c, J
Pentaerythritol	0.100	1.49	1.24	9.32	7.41
		3.00	2.32	8.70	14.7
		4.50	3.26	8.11	21.9
		6.01	4.06	7.56	28.7
L-arabinitol	0.020	2.76	—	1.67	5.74
		5.38	—	1.35	10.5
		7.85	—	1.06	14.6
		10.2	—	0.78	17.7
Xylitol	0.200	—	2.77	18.9	9.81
		—	5.39	17.8	19.1
		—	7.87	16.8	28.6
Sorbitol	0.200	—	2.77	18.9	9.28
		—	5.39	17.8	18.3
		—	7.87	16.8	27.5
		—	10.2	15.9	36.6
Meso-inositol	0.100	2.23	—	9.50	0.72
		4.31	—	9.03	1.20
		6.23	—	8.59	1.77

[a] Initial concentration of borate in the titrant solution: 0.100 M; cumulative volumes of titrant added: 2.505, 5.010, 7.515, 10.020 cm³.

Molar enthalpies of association were determined from the experimental heats (ΣQ_c) and the concentrations of the complex species: the latter were calculated from values of the corresponding stability constants determined potentiometrically [6, 9–11] under the conditions of temperature and ionic strength used in the present study. The $\Delta H°$ values and the corresponding standard deviations were calculated by means of the numerical method of minimization of the error square sum for each measurement [12]. Entropies were calculated via the equation: $\Delta G° = \Delta H° - T\Delta S°$.

Results and discussion

The molar thermodynamic quantities relating to complex formation are collected in Table 2. No stepwise quantities are listed for xylitol and sorbitol, as only $[BL_2]^-$ was found for these ligands in [6, 9]. The thermodynamic quantities for the borate complexes of 1,2-ethanediol (ethylene glycol), 1,2-propanediol (1,2-propylenegly-col), 1,2,3-propanetriol (glycerol) and D-mannitol, obtained previously by calorimetry in this laboratory [3], are also given in the Table, for the sake of comparison.

No previous calorimetric data are available on the present equilibria.

The conclusions drawn in [3] for the reactions of the last four polyhydroxy compounds in Table 2 appear useful for the present discussion. They can be summarized in the following points. The log K, $\Delta H°$ and $\Delta S°$ data are increasingly more favourable for the formation of 1 : 1 borate-polyol complexes as the number

Table 2 Molar thermodynamic quantities relating to complex formation reactions of the borate ion $[B(OH)_4]^-$, with polyols (L) in aqueous solution at 25° and $I = 0.1$ M[a]

Polyol	j^b	log K_j^c	$-\Delta G_j^0$	$-\Delta H_j^0$	$-\Delta S_j^0$
Pentaerythritol	1	2.70 ± 0.12^d	15.4 ± 0.7	20.9 ± 1.2	$19. \pm 4$
	2	0.95 ± 0.17	5.4 ± 0.8	20.1 ± 2.1	49 ± 8
	1 + 2	3.65 ± 0.21	20.8 ± 1.1	41 ± 2	68 ± 9
L-arabinitol	1	4.51 ± 0.07	25.7 ± 0.4	18.9 ± 0.8	-23 ± 3
Xylitol	1 + 2	6.36 ± 0.06	36.3 ± 0.3	38.2 ± 0.2	6.3 ± 1.2
Sorbitol	1 + 2	5.65 ± 0.04	32.2 ± 0.2	36.7 ± 0.1	15.1 ± 0.8
Meso-inositol	1	1.64 ± 0.14	9.4 ± 0.7	1.4 ± 1.0	-27 ± 4
1,2-ethanediol	1	0.23 ± 0.01	1.30 ± 0.08	5.8 ± 0.5	15 ± 2
1,2-propanediol	1	0.46 ± 0.01	2.64 ± 0.08	9.3 ± 0.6	22 ± 2
	2	-0.35 ± 0.04	-2.0 ± 0.2	38.9 ± 1.7	138 ± 4
	1 + 2	0.11 ± 0.04	0.6 ± 0.2	48.2 ± 1.8	160 ± 4
Glycerol	1	1.30 ± 0.02	7.41 ± 0.12	10.2 ± 0.5	9.6 ± 1.6
	2	0.18 ± 0.05	1.0 ± 0.3	28.9 ± 1.7	92 ± 4
	1 + 2	1.48 ± 0.05	8.5 ± 0.3	39 ± 1.8	102 ± 4
D-mannitol	1	3.04 ± 0.08	17.3 ± 0.5	19.7 ± 0.2	7.9 ± 1.6
	2	1.50 ± 0.09	8.5 ± 0.5	23.4 ± 0.5	50 ± 2
	1 + 2	4.54 ± 0.12	25.8 ± 0.7	43.1 ± 0.5	58 ± 2.5

[a] Gibbs function and enthalpy are expressed in kJ mol^{-1}; entropy in J K^{-1} mol^{-1}. The thermodynamic parameters for 1,2-ethanediol, 1,2-propanediol, glycerol and D-mannitol are taken from Ref. 3 and refer to $I = 0.1$ M.

[b] $j = 1$ or 2 for stepwise reactions: $[BL_{j-1}]^- + L \rightarrow [BL_j]^-$ (B$^-$ = borate, L = polyol); $j = 1 + 2$ for overall reactions: B$^- + 2$ L $\rightarrow [BL_2]^-$.

[c] See Refs 6 and 9–11.

[d] The uncertainty given in each case is the estimated standard deviation.

of hydroxy groups in the polyol increases. In particular, the sequence of ΔH_1^0 values from ethylene glycol to mannitol may be justified by the presence of progressively stronger bonds between borate and polyol. In fact, in propylene glycol, besides the two hydroxy groups of ethylene glycol, a methyl group is present, which enhances the bond-forming properties with borate by inductive effects. Hydrogen-bonds too are present for glycerol and D-mannitol, in larger amount for the latter.

Furthermore, ΔH_2^0 was found to be more favourable than ΔH_1^0, while ΔS_2^0 is more negative than ΔS_1^0. This fact can be explained by a much lower degree of hydration of borate in the 1 : 1 complex than in the uncomplexed form, so that fewer borate-solvent bond ruptures take place when the second molecule of polyol enters the complex.

As concerns the present results, it can be observed that in this case too the enthalpy is favourable for complex formation, while the entropy is often unfavourable. The present data, on the other hand, do not show the regular variation of the thermodynamic quantities (which was observed previously [3]) for an increasing number of hydroxy groups in the polyol molecule. In particular (Table 2), a greater stability is observed for the complexes of pentitols than for those of hexitols: $\log K_1 = 4.51$ for arabinitol $vs.$ 3.04 for mannitol; $\log K_{1+2} = 6.36$ for xylitol $vs.$ 5.65 and 4.54 for sorbitol and mannitol, respectively. Comparisons between the corresponding enthalpies and entropies indicate that the latter are the determining factor of these differences in stability.

As regards the different stabilities for polyols with the same number of —OH groups, the importance of the presence of two —OH groups in the β and cis positions in the usual (i.e. "linear zig-zag") conformation of the polyol has at times been pointed out in the past. Such hydroxy groups, in fact, are in a parallel position and could form stable bonds with borate. Such an observation was made previously [6] in order to justify the higher stability of the complexes of xylitol (which possesses two —OH groups of this type) in comparison with the complexes of D- and L-arabinitol (which do not possess them). In the case of hexitols, the higher stabilities of the borate-sorbitol complexes in comparison with the complexes of D-mannitol were also explained in this way [9]. However, in this case too, the data of Table 2 do not agree with such explanations. The present results, in fact, seem to indicate entropy rather than enthalpy as the factor determining these differences in stability. In particular, the sequences of the ΔH_{1+2} and ΔG_{1+2}^0 values for sorbitol and mannitol are reversed, while the corresponding entropies determine the sequence of stabilities. For the formation of the present complexes, the importance is stressed of external factors in comparison with factors related with the borate-ligand bond strength.

In the case of pentaerythritol, the rather high stabilities of its complexes with borate in comparison with the complexes of other polyols with —OH groups in the

1,3 positions had already been pointed out previously [13]. It can also be observed that the H_1^0 value for this ligand is the most exothermic among those in Table 2, in accordance with the formation of very stable borate-ligand bonds. ΔS_1^0 is strongly negative, indicating a loss of conformational freedom of the ligand on complex formation. CPK models clearly indicate the possible formation of three C—O—B bonds in this case, in accordance with the experimental values of ΔH_1^0 and ΔS_1^0.

The thermodynamic quantities for meso-inositol (which is the only cyclic structure among the present polyols) are markedly different from the other values. The enthalpy contribution is near zero in this case, while the very positive entropy term determines the complex formation. As previously observed [14], cyclic hexitols such as meso-inositol can give tridentate complexes with three parallel axial —OH group in the 1, 3, 5 positions. Such bonds, which should in principle be strong, are weak in the case of meso-inositol, as indicated by the enthalpy value. The "chair" conformation present in the complex, in fact, shows both the —OH groups in the 1, 3, 5 positions and those in the 2, 6 axial positions:
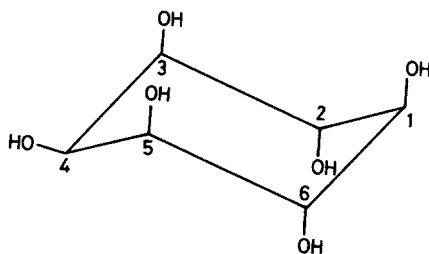
For steric reasons, such a conformation is markedly less stable than the usual one, in which the five —OH groups are equatorial.

The ΔS_1^0 value for meso-inositol, differently from that of pentaerythritol, is very positive, in spite of a possible tridentate structure of both ligands in the complex. This fact could be explained by considering that meso-inositol is the only one of the present ligands, which exhibits a semirigid structure in the uncomplexed form. The reaction with borate (besides the release of the three water molecules) takes place in this case with a smaller loss of conformational freedom by the polyhydroxy structure.

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Zusammenfassung — Mittels thermometrischer Titration wurden die molaren Reaktionswärmen für die Reaktionen von Borat mit den Polyhydroxyverbindungen Pentaerythrit, L-Arabinit, Xylit, Sorbit und meso-Inosit bestimmt. Mittels der Gleichgewichtskonstanten erhielt man auch die entsprechenden Gibbsschen Funktionen und Entropien. Die Ergebnisse beziehen sich auf 25 °C und $I = 0{,}1$ M. Auf Grund dieser und früherer Resultate der gleichen Autoren kann geschlußfolgert werden, daß die unterschiedliche Stabilität dieser Komplexe eher durch Entropie- als durch Enthalpiefaktoren bestimmt wird. Im Gegensatz zu den anderen Liganden (die zweizählig sind) scheinen sich Pentaerythrit und meso-Inosit gegenüber Borat als dreizählige Liganden zu verhalten. Trotzdem zeigen ihre Komplexe eine sehr unterschiedliche Stabilität, wofür der Grund wahrscheinlich in dem unterschiedlichen Freiheitsgrad der zwei nicht im Komplex gebundenen Liganden liegt.

Резюме — Методом термометрической титриметри определены молярные теплоты реакций бората с такими полиоксисоединениями как пентаэритритол, L-арабинитол, ксилитол, сорбитол и мезо-инозитол. С помощью констант равновесия были также получены соответствующие функции Гиббса и энтропии. Результаты относятся к водным средам с температурой 25° и $I = 0{,}1$ M. Представленные данные, вместе с полученными ранее в этой же лаборатории, приводят к заключению, что различия в устойчивости этих комплексов определяются главным образом скорее энтропийными факторами, чем энтальпийными. В отличие от других лигандов, которые являются бидентатными, пентаэритритол и мезо-инозитол в реакции с боратом ведут себя как тридентатные лиганды. Тем не менее их комплексы проявляют различную устойчивость, что возможно обусловлено их различными конформационными степенями свободы в некомплексированной форме.