THE STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF BORATE - CARBOHYDRATE COMPLEXES BY pH MEASUREMENTS

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Abstract

The complexation of borate with carbohydrates was studied potentiometrically at temperatures 298.15-328.15K in aqueous medium at constant ionic strength, I = 0.1M KCl. The stability constants (β) and thermodynamic parameters of borate-carbohydrate complexes were determined using the technique proposed by Verchere and Hlaibi. Carbohydrates such as D-fructose, D-Sorbitol, D-Mannitol, D-Galactose, D-Glucose and D-Raffinose were used as ligands in this study. The β_I values for the complexes at different temperatures were found to follow the order: D-fructose > D-Sorbitol > D-Mannitol > D-Galactose > D-Glucose > D-Raffinose. The ΔG^0 values were found to be negative and the negative values increased according to the above order. The values of ΔH^0 and ΔS^0 were both negative which indicated that the complex formation was an exothermic process and the spontaneity of its formation is driven by enthalpic contribution overcoming the negative contribution of ΔS^0.

Introduction

Knowledge of stability constant is very much important and has many applications such as in complexometric titration, colorimetric analysis, quantitative determination of the trace elements and analytical chemistry etc. The study of the formation of complexes between borate and polyhydroxy compounds has been received considerable attention since few decades[1-3]. Such studies provide an important tool in conformational analysis of carbohydrates and are used in a variety of separation and chromatographic techniques. Polyols and sugars have been used for the potentiometric determination of boric acid. Besides, the reaction with boric acid is known to be used in the field of bioinorganic chemistry. Most polyols possessing 1, 2 and 1,3-diol systems form 1:1 and 1:2 complexes with borate[4]. These reactions are used for the titrimetric determination of boron[5]. The formation of borate complexes of several mono-, di- and trisaccharides in aqueous solution at constant temperature and ionic strength using potentiometric method was reported in the literature[3]. A study was undertaken to investigate the complexation of borate with carbohydrates using pH measurements method. Similar procedure of the calculation of stability constants as reported in the literature[3] was followed in this study. The values of thermodynamic parameters of borate-carbohydrate complexes have also been presented.


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Experimental

D-fructose, D-Glucose and D-Galactose were obtained from BDH, England; D-Sorbitol, D-Mannitol and D-Raffinose were from Merck, Germany. Di-sodium tetraborate was obtained from Loba, Mumbai. All the solutions used in this study were prepared in distilled de-ionized water.

25 mL boric acid and 25 mL borate solutions were taken in a beaker and the ionic strength of the solutions was adjusted to 0.1M by using KCl solution. The carbohydrate solution or in some cases particular amount of solid was gradually added to the boric-borate mixture and the pH of the resultant mixture was measured with the help of a pH meter (Schott Gerate CG 820). After each addition of the carbohydrate solution (or solid), the mixture was thoroughly stirred and 5 minutes time was allowed for attaining equilibrium. The temperature of the system was maintained with the help of water thermostated bath. The experiments were extended at different temperatures at costant ionic strength.

Results and Discussion

When a carbohydrate is added to an aqueous solution of boric acid-borate mixture, a decrease of pH was observed with the increase of concentration of carbohydrate indicating the formation of anionic complexes. The H^+ ions are expected to be produced according to the following complexation reaction and hence the pH of borate solution was found to be changed with the

$$HB + nL = BL_n^- + H^+ \qquad (n = 1 \text{ or } 2) \qquad (1)$$
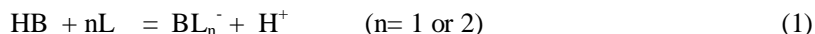
addition of carbohydrate as shown in Fig. 1.
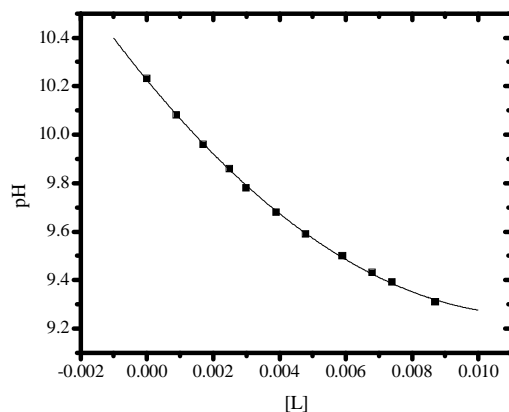
Fig. 1. A plot of pH versus [L] for D-fructose-borate complex at
T= 318.15K, I = 0.1M KCl and [B] = [HB] = 0.001M

The stability constants of borate-carbohydrate complexes were determined from general form of the following Antikainen polynomial equation[6]

$$K_a^/ = K_a (1+ \beta_1[L]+\beta_2[L]^2) \qquad (2)$$

Where [L] is the concentration of carbohydrate, β_1 and β_2 are the stability constants for 1:1 and1:2 borate-carbohydrate complexes respectively. In the absence of carbohydrate, the pH of the solution is equal to pK_a of boric acid.

$K_a^/ / K_a$ versus concentration of carbohydrate, [L] was plotted and a representative plot was shown in Fig.2. The parameters β_1 and β_2 were obtained from polynomial fitting of the experimental data using iteration method[3]. The values of β_1 for carbohydrates-borate complexes are presented in Table 1. For all the borate-carbohydrate complexes, the β_2 values were found to be higher in magnitude compared to that of β_1. This result indicated that 1:2 complexes were preferentially formed compared to that of 1:1 complexes. The formation of 1:1 and 1:2 complexes between boric acid and some diols was also reported by others[7]. The β_1 values for the borate complexes of carbohydrates at different temperatures were found to follow the order: D-fructose > D-Sorbitol > D-Mannitol > D-Galactose > D-Glucose > D-Raffinose, whereas the β_2 values did not follow the above order.
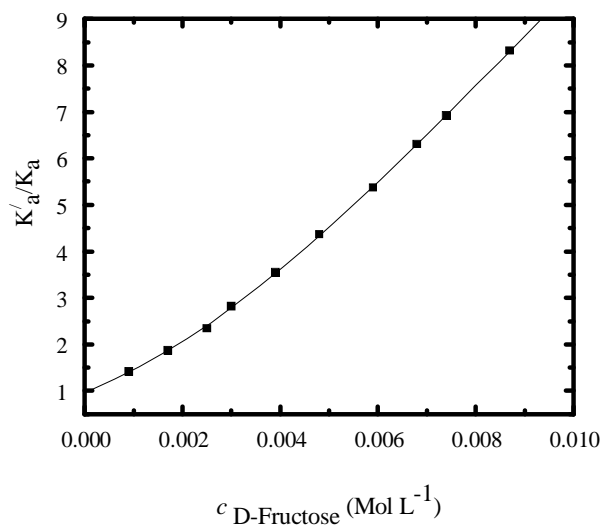

Fig. 2. A plot of $K_a^/ / K_a$ versus [L] for D-fructose-borate complex at
T= 328.15K, I = 0.1M KCl and [B] = [HB] = 0.001M

Table 1. The values of stability constants (β_1) for carbohydrate-borate complexes at different temperatures

Carbohydrates	β_1			
	298.15	308.15	318.15	328.15
D-Fructose	1523.4	627.0	571.22	451.95
D-Sorbitol	1123.8	368.46	257.81	175.91
D-Mannitol	851.77	369.39	245.38	52.28
D-Galactose	168.74	94.27	62.02	40.89
D-Glucose	59.18	45.59	33.82	11.85
D-Raffinose	39.68	21.99	17.75	8.78

The complexation with a borate ion requires two adjacent hydroxyl groups in adequate positions[8]. D-fructose forms complexes of higher stability than aldoses[9, 10]. D-Sorbitol and D-Mannitol do not form oxide ring like glucose and galactose but several of the available OH groups make them capable for complexation with the borate. Because of these facts, they have higher values of β_1. The less complexing ability of glucose and galactose is due to the presence of hemiacetal. The oxide ring developed through hemiacetal linkage hinders the approach of the borate for complexation and enhances steric hindrance and thus hinders the formation of borate complex. In all the cases, the β_1 values decreased with increase of temperature whereas the β_2 values decreased initially with increase of temperature but keeps on increasing after certain temperature.

The thermodynamic parameters of the borate-carbohydrate complexes were calculated from the standard thermodynamic equations. The values of ΔG^0, ΔH^0 and ΔS^0 are calculated using β_1 values and are presented in Table 2. log (β_1) vs. $1/T$ plot (Fig. 3) was used to calculate ΔH^0_m.
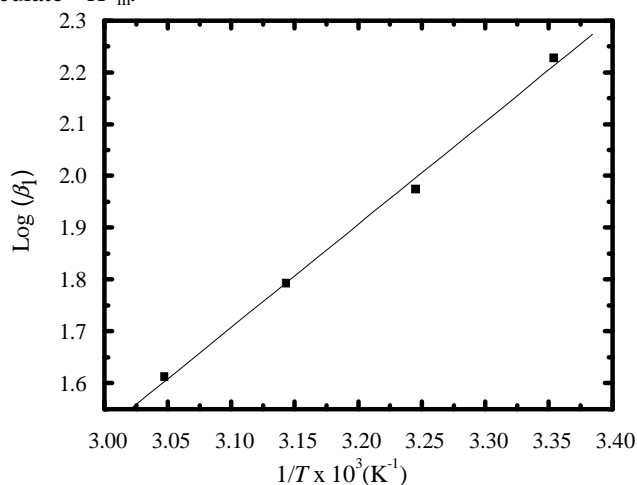
Fig. 3. Log β_1 versus $1/T$ plot fot borate-D-Galactose complexes

The values of ΔG^0 were found to be negative which indicated that the complex formation processes were thermodynamically spontaneous. The values of ΔH^0 and ΔS^0 were found to be negative. The results showed that the negative values of ΔH^0 and ΔS^0 follow order: D-Mannitol > D-Sorbitol > D-Glucose > D-Raffinose > D-Galactose > D-fructose. Thus the free energy change was favoured only by the negative ΔH^0 overcoming the negative effect of ΔS^0. Therefore the borate-carbohydrate complexation was entirely enthalpy controlled. From the overall negative ΔH^0, it could be deduced that complexation process was associated with energetic forces such as hydrogen bonding and van der Waals forces[11] or some other form of chemical interaction. Andrews and keefer[12] had demonstrated that both ΔH^0 and ΔS^0 become more negative as the stability constant for molecular complexation increases. As the binding between borate and carbohydrate bomes

Table 2. The values of thermodynamic parameters for carbohydrate- borate complexes at different temperatures

Carbohydrates	T	G^0	H^0	S^0
	K	kJ. mol^{-1}	kJ.mol^{-1}	J. mol $^{-1}$. K^{-1}
D-Fructose	298.15	-18.15	-30.18	-40.35
	308.15	-15.96		-47.33
	318.15	-15.73		-48.51
	328.15	-15.15		-50.46
D-Sorbitol	298.15	-17.40	-47.67	-101.59
	308.15	-14.64		-110.86
	318.15	-13.76		-113.83
	328.15	-12.81		-117.01
D-Mannitol	298.15	-16.71	-69.27	-176.36
	308.15	-14.65		-183.31
	318.15	-13.63		-186.71
	328.15	-9.80		-199.56
D-Galactose	298.15	-12.7	-37.37	-82.76
	308.15	-11.26		-87.60
	318.15	-10.23		-91.08
	328.15	-9.19		-94.55
D-Glucose	298.15	-11.11	-40.16	-100.86
	308.15	-9.46		-103.03
	318.15	-8.72		-105.51
	328.15	-6.12		-114.24
D-Raffinose	298.15	-9.11	-37.6	-95.57
	308.15	-7.65		-100.47
	318.15	-7.12		-102.26
	328.15	-5.38		-108.11

stronger, ΔH^0 would be expected to have higher negative values. The higher negative values of both ΔH^0 and stability constants are a pointer to the strength of the binding between borate and carbohydrates as well as the high stability of the resultant complex.

The variation of the stability constants of carbohydrate molecules with boric acid may be explained by a likely interaction between the B atom of boric acid and O of hydroxyl group in carbohydrate molecules. Here boric acid acts as a Lewis acid and hydroxyl group of the carbohydrates that serve as Lewis bases to give Lewis acid-base adducts. One example is shown below (scheme 1).

Polyol   Boric acid   Lewis acid-base adduct
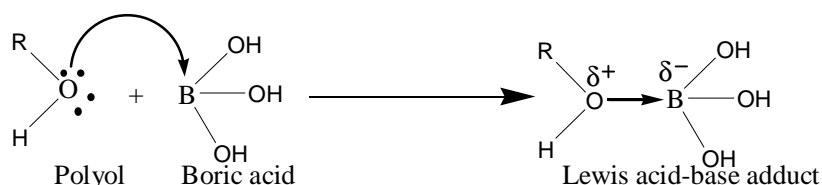
Scheme 1

In the cases of glucose and galactose, the oxide ring opposes the OH group to come in close contact with boron and therefore the stability constant of these two complexes are lower. On the other hand in sorbitol and mannitol all the OH groups are exposed and boron has a better chance of interaction with these groups. This causes a higher stability of these complexes. Similar argument can be given for raffinose where the three rings of the trisaccharides hides the OH groups from complexing with boron. Although fructose also forms a 5-membered oxide ring, it has two primary alcoholic groups extending outward from the ring and assists the formation of complex with boron.

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