Carbohydrate Research, 241 (1993) 279–283
Elsevier Science Publishers B.V., Amsterdam

Note

Calorimetric study of the interactions of D-glucose, D-fructose, sucrose, and poly(vinyl alcohol) with borate ions

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(Received March 23rd, 1992; accepted September 2nd, 1992)

The formation of complexes between borate ions and organic compounds containing two or more hydroxyl groups (polyols) in dilute aqueous solutions has been investigated extensively. Roy et al.[1] and Conner and Bulgrin[2] assessed the thermodynamic functions of the formation of such complexes on the basis of the pH of aqueous solutions as a function of the concentration of the polyol. This method was also applied to poly(vinyl alcohol)[3]. Equilibrium dialysis[4], viscometry[5], and spectroscopic methods[6,7] have been used to study the formation of borate complexes.

Polyols interact with borate ion $B(OH)_4^-$ to give two types of complexes[1,2,7]:

$$B^- + P \leftrightarrow BP^- \quad (K_1)$$

$$B^- + 2P \leftrightarrow BP_2^- \quad (K_2)$$

where B^- is the $B(OH)_4^-$ ion, P is the polyol, BP^- and BP_2^- represent mono- and bis-diol complexes, respectively, and K_1 and K_2 are the equilibrium constants for the formation of each complex.

According to Conner and Bulgrin[2], K_1 and K_2 can be calculated from eqs *1* and *2*:

$$\left(\frac{[H^+]}{K_a} - 1\right)\frac{1}{[P]} = K' = K_1 + K_2[P] \qquad (1)$$

$$[P] = \frac{[P]_0 - 2[B]_0 + 2K_a[B^-]_0/[H^+]}{1 - K_1K_a[B^-]_0/[H^+]} \qquad (2)$$

where K_a is the first ionisation constant for boric acid, [P] is the concentration of the uncomplexed polyol, $[B^-]$ is the concentration of the borate ion, and subscript zero denotes the initial concentration. The equations are valid if it is assumed that the concentration of non-ionised boric acid [HB] does not vary with the concentration of the polyol, but remains equal to $[HB]_0$. Although the values of [P] and K are not known in eq. *2*, [P] may be determined by successive approximations,

TABLE I

Thermodynamic functions [a] for the formation of polyol–borate ion complexes

Polyol	K_1	$-\Delta G_1^0$	$-\Delta H_1^0$	$-\Delta S_1^0$
	K_2	$-\Delta G_2^0$	$-\Delta H_2^0$	$-\Delta S_2^0$
From the calorimetric data:				
D-Fructose	0			
	248325	30.8	37.4	22.2
D-Glucose	182	12.9	28.8	53.2
	1594	18.3	17.6	−2.4
Sucrose	28.7	8.3	21.7	44.7
	0			
Poly(vinyl alcohol)	12.3	6.2	26.7	68.8
	31.4	8.5	19.6	37.15
From the literature:				
D-Fructose[8]	0			
	222000			
D-Glucose[8]	165			
	1625			
D-Glucose[2]	135	12.2	14.7	8.4
	875	16.8	0.6	−54.4
Sucrose[8]	24.3			
	0			
Poly(vinyl alcohol)[8]	9.5			
	44.7			
Poly(vinyl alcohol)[3]	9.7			
	39.9			
Poly(vinyl alcohol)[9]	8 [b]	5.63	11.2	18.9
	39 [b]	8.92	39.6	103

[a] K_1 in $L \cdot mol^{-1}$; K_2 in $L^2 \cdot mol^{-2}$; ΔG^0 and ΔH^0 in $kJ \cdot mol^{-1}$; and ΔS^0 in $J \cdot mol^{-1}$. [b] The values of K_1 and K_2 were read from the graph.

assuming in the first step that $[P] = [P]_0$. From the dependence of K' on [P], values for K_1 and K_2 are obtained from eq *1*, and, from the well-known relations, the values ΔG^0, ΔH^0, and ΔS^0.

The use of calorimetry to study the thermodynamics of the interactions of polyols with borate ions allows direct measurement of the associated thermal effects. In comparison with other experimental methods that yield values of thermodynamic functions, calorimetry has the advantage that the degree of approximation used is lower and the data are obtained by thermodynamic and not by non-thermodynamic correlations. Four types of water-soluble polyols were investigated: D-fructose, D-glucose, sucrose, and poly(vinyl alcohol).

Table I contains the equilibrium constants K_1 and K_2, and the thermodynamic quantities ΔH^0, ΔG^0, and ΔS^0, together with values obtained by the pH method[2,3,8,9]. D-Fructose forms the strongest complex, but forms only the BP_2^- complex. In contrast, sucrose forms a rather weak complex only of the BP^- type.

On the other hand, D-glucose, which reacts in the furanose form, yields both types of complexes. In agreement with data in the literature[3,9], poly(vinyl alcohol) also forms both types of complexes.

D-Mannitol is reported to be the strongest complex-forming polyol[2,10], but the K_2 for D-fructose by comparison is almost double that of D-mannitol, although the estimation of K values $> 10^4$ could be uncertain[11]. The reason for the high value of K_2 for D-fructose is associated with the favourable conformation of pairs of OH groups of the β-D-fructopyranose form which preponderates in the aqueous solution[12]. The low K_1 for the BP^- complex and the non-formation of a BP_2^- complex by sucrose is caused by the limited possibility for the formation of the planar complex mainly due to the pyranose form of the glucose moiety of sucrose.

D-Glucose gives rise to both BP^- and BP_2^- complexes. A comparison of the values of K_1 and K_2 in Table I shows that almost the same values were found by calorimetry and by the pH method, but the value of K_2 determined by the pH method[2] is approximately half that determined by calorimetry. The more probable value for K_2 seems to be 1.6×10^2, which was determined by both calorimetry and the pH method[8].

The equilibrium constants for poly(vinyl alcohol) correspond approximately to that in the literature; the calorimetric method gave a slightly higher value of K_1 and lower K_2 value than the pH method.

The thermodynamic parameters for formation of the BP^- and BP_2^- complexes can be compared only for D-glucose and poly(vinyl alcohol). The value of ΔH^0 is negative for each system and for each type of complex, i.e., the formation of the complexes involves exothermic reactions. Considerable differences are seen between the ΔH^0 values obtained by calorimetry and by the pH method. The trend of ΔH_1^0 and ΔH_2^0 values for D-glucose is preserved in agreement with the literature data[2]. The formation of a BP^- complex is accompanied by a higher thermal effect than the formation of a BP_2^- complex, but the numerical values of ΔH^0 determined calorimetrically are much higher. Poly(vinyl alcohol) showed the reverse trend in the values of ΔH_1^0 and ΔH_2^0 to that described by Ochiai et al.[3,4]. The values obtained by calorimetry indicate that the formation of the BP^- complex is more exothermic than that of the BP_2^- complex for D-glucose and other systems[2]. The numerical values of these quantities also differ: ΔH_1^0 is double, whereas ΔH_2^0 is only half of the value determined by the pH method. Similar results[2] have not been explained satisfactorily.

The values of ΔS^0 are negative for all of the systems except for the formation of the BP_2^- complex of D-glucose, where the change in entropy is positive. The decrease in entropy is probably caused by higher ordering of the system during the formation of complexes both by limiting the motion of the components and by orientation and hindrance of the segmental motion of the backbone of poly(vinyl alcohol). The decrease in entropy is only partially compensated by the release of water when complexes are formed. For D-glucose, the effect of the release of water or the destruction of solvated shell during the formation of the BP_2^- complex predominates, which leads to a positive change in entropy. Conner and Bulgrin[2] have come to similar conclusions, although the numerical values of ΔS_2^0 are substantially different.

The values of ΔS^0 for poly(vinyl alcohol) calculated from the calorimetric data show the opposite trend to that of the pH method in that a higher negative change in the entropy was found during the formation of the BP^- complex than in the formation of the BP_2^- complex. The numerical values of these quantities differ considerably, ΔS_1^0 being approximately threefold and ΔS_2^0 about one-third when compared with the corresponding values determined by the pH method.

The differences between the thermodynamic quantities determined by calorimetry and the pH method may be due to several effects. The calculation of the differences in pH is based on the assumption that the concentration of non-dissociated sodium tetraborate does not change during the formation of complexes. This assumption is valid only within a narrow concentration level[9]. The calculation of the values of ΔH^0 is based on the Van't Hoff equation, assuming that ΔH^0 does not vary with temperature. This assumption may be valid over only a narrow range of temperature where the determination of the slope of temperature dependence for equilibrium constants is subject to considerable error. The precise measurement of changes in pH in a media of varying viscosity also presents problems. Calorimetry is not subject to these potential errors and a wider range of concentrations can be investigated. Thus, we believe that thermodynamic functions obtained by calorimetry characterise the formation of complexes between polyols and borate ions more precisely.

EXPERIMENTAL

Materials.—D-Glucose, D-fructose, and sucrose were analytical grade. Poly(vinyl alcohol), obtained from Fluka, had a dp of 300. Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$, analytical grade) was recrystallised from distilled water. For the preparation of solutions, redistilled water was used.

Calorimetry.—A low-temperature model of a Calvet–Setaram microcalorimeter was used at 298.19 K. Complexation reactions were carried out in a special cell[13]. The error in the measurement of the heats of formation of the complexes was ±10%. The concentration of each polyol varied between 0.005 and 0.2 M, two monomeric units of poly(vinyl alcohol) being taken as a basis for the calculation of its concentration. The concentration of $Na_2B_4O_7$ was 0.01 M.

The method of dilute solutions[11,14,15] was used for calculating the heats and thermodynamic functions of the formation of complexes. The values ΔH^0, K_1, and K_2 were obtained by the optimisation method. The measured heats, the overall concentrations of the components, and the associated model expected were used in the computer calculation[15]. From this calculation, ΔH, K_1, and K_2 (or ΔG^0) were determined for each complex. The values of ΔS^0 were calculated according to $\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$.

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