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A POTENTIOMETRIC STUDY ON THE COMPLEX FORMATION OF GERMANIC
ACID AND GERMANATE ION WITH SUGAR ACIDS AND DISACCHARIDES
IN AQUEOUS SOLUTION

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ABSTRACT

The anionic complex formation of germanic acid and germanate ion with five sugar acids and eight disaccharides was studied potentiometrically at 25 °C in aqueous KCl medium of ionic strength 0.1. The results reveal that both 1:1 and 1:2 complexes are formed. The equilibrium constants were calculated with the program SCOGS or/and manually by graphical method. Comparisons are made with the results for boric acid.

INTRODUCTION

The complex formation of boric acid and borate with selected groups of disaccharides and sugar acids was described earlier.¹ Under the experimental conditions used in that investigation only 1:1 and 1:2 chelates formed. The present work describes the complex formation of germanic acid with the same sugar acids and disaccharides. The complex formation of germanic acid with many polyhydroxy compounds and the stability constants of these reactions have been widely reported in the literature.²⁻⁴ By contrast, the reactions between germanic acid and sugar acids and disaccharides have been poorly investigated.

The composition of aqueous germanic acid - germanate depends on the concentration of the total germanate⁵ and the pH.⁶ In dilute germanic acid solutions where concentration of the total germanium is below 0.005 M (0.5 M NaCl; 25 °C), only mononuclear species⁵ seem to be present, viz. germanic acid, $\text{Ge}(\text{OH})_4$, and the ions $\text{GeO}(\text{OH})_3^-$ and $\text{GeO}_2(\text{OH})_2^{2-}$. The more basic monogermanates form when the pH is greater than about 12.⁶ In the germanate - polyol system the distribution model of the different species

strongly depends on the ratio of germanate to polyol.^{5,7} With a great excess of polyol the species formed are AL^- and AL_2^- (where A^- is germanate and L a polyol).

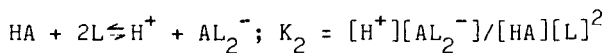
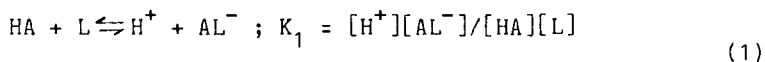
EXPERIMENTAL

Reagents. The sugar solutions were prepared from the following reagents: D(+)-cellobiose, D(+)-melibiose (Fluka AG, für Bakteriologie), maltose, saccharose (E. Merck AG, für biochemische Zwecke), gentibiose (Fluka AG, purum), lactose (BDH Chemicals Ltd. pa.), D(+)-trehalose, D(+)-turanose, D-gluconic acid, D-glucaric acid, D-glucuronic acid, mucic acid (galactaric acid) and D-galacturonic acid (Sigma).

Ge(IV) stock solutions were prepared from GeO_2 (Fluka 99.999%) and standardized by titration with alkali in saturated mannitol solution. Other reagents were of purest grade available. The concentration of the germanic acid was from 0.002 M to 0.005 M, and the concentrations of sugar acids and disaccharides were from 0.004 M to 0.1 M and 0.008 M to 0.3 M, respectively. The ratio of sugar acid to germanic acid varied between ten and twenty and the ratio of disaccharide to germanic acid between four and sixty. For determination of the stability constants, 20-60 points were taken from the buffer region, where the pH was for sugar acids from about 7 to 9.5 and for disaccharides from 7.2 to 9.6.

Apparatus. The details of apparatus used in potentiometric titrations have been described earlier.¹

Calculations. In aqueous solution, germanic acid (HA) and sugar (L) (used in excess) react in the following way:



The relation between the apparent protolytic constant K_a^* of the germanic acid and the total ligand concentration is shown by the equation⁸

$$p(K_a^* - K_{a1}) = pK_n - \log c_L^n \quad (2)$$

where n is the ratio of moles of ligand to one mole of germanic acid, K_n is the equilibrium constant of the complex-forming reaction and K_{a1} is the protonation constant of the germanic acid.

The overall stability constants are

$$\begin{aligned}\beta_1 &= K_1 \cdot K_{a1} = [AL^-]/[A^-][L] \\ \beta_2 &= K_2 \cdot K_{a1} = [AL_2^-] / [A^-][L]^2\end{aligned}\quad (3)$$

The values of the constants were calculated as overall stability constants with the program SCOGS.⁹ The results can also be treated graphically by expressing $p(K_a \cdot K_{a1})$ as a linear function of $-\log c_L$ (Eq. 2), where the slope of the curve gives the value of n and the point of intersection with the line at $-\log c_L = 0$ gives the value of pK_n .

RESULTS AND DISCUSSION

The first protonation constants of germanic acid was determined because of the wide divergence in the values reported in the literature.²⁻⁴ Many of the older measurements, at least, were made in too concentrated solutions, which resulted in polymerization.¹⁰ Our value $\log K_{a1} = 9.26(3)$ (0.1 KCl 25 °C) is in good agreement with the value reported recently by Mikesova and Bartusek ($\log K_{a1} = 9.27$ 0.1 M KNO₃ 20 °C).¹¹

The protonation constants of mucic acid and galacturonic acid were measured, too, and found in good accord with the values reported in earlier studies.^{12,13} The protonation constants of the other sugar acids were ones determined earlier.¹ The values measured here were mucic acid $\log K_{a2} = 3.165(2)$ and $\log K_{a1} = 3.861(6)$ and galacturonic acid $\log K_{a1} = 3.227(5)$.

The final values of the overall stability constants with their standard deviations, calculated by the program SCOGS, are given in Table 1. The values determined by the graphic method were in good accord with the values given in Table 1.

Both the graphic method and the computer calculations showed germanic acid to form 1:1 chelates with all disaccharides, and with melibiose and turanose also 2:1 chelates. The disaccharides with two vicinal hydroxyl groups in cis position--lactose, turanose and melibiose--formed the strongest complexes. The other disaccharides--cellobiose, gentibiose, maltose, trehalose and saccharose--were similar in stability. The stability order of saccharose, maltose and lactose is the same as Saito¹⁴ found by chromatographic method for complexes of germanic acid and further for complexes of boric acid.

Gluconic acid and glucuronic acid both formed 1:1 complexes with germanic acid when an excess of the sugar acid was used in the basic range. Galacturonic acid formed weak chelates with germanic acid ($\log \beta_1 < 1$)

TABLE 1.

Values of the Overall Stability Constants of Germanate Complexes with Sugar Acids and Disaccharides in Aqueous Solution at $I = 0.1 \text{ M}(\text{KCl})$ and $t = 25 \text{ }^\circ\text{C}$.

Carbohydrate	$\log \beta_1$	$\log \beta_2$	Carbohydrate	$\log \beta_1$	$\log \beta_2$
cellobiose	1.58(3)		saccharose	1.00(8)	
gentibiose	1.27(6)		trehalose	1.12(7)	
lactose	1.97(3)		turanose	2.32(3)	3.25(7)
maltose	1.48(6)		gluconic acid	2.06(5)	
melibiose	2.32(2)	3.24(7)	glucuronic acid	1.70(5)	

but the value of the stability constant could not be determined accurately. Glucaric acid and mucic acid did not form chelates with germanic acid under the conditions studied. The values of the stability constants for the germanate - disaccharide complexes were slightly higher than the corresponding constants for the borate - disaccharide complexes determined earlier.¹ The stoichiometries of the chelates of germanic acid and boric acid with disaccharides seem to be the same: turanose and melibiose formed 1:1 and 1:2 chelates, the other disaccharides only 1:1 chelates. The stability order of the germanate - disaccharide chelates is the same as for the corresponding chelates of borate¹ except that in the germanate series the cellobiose complex is more stable than that of maltose.

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