THE REACTIONS OF OLIGOALCOHOLS WITH ARSENIC, ARSENOUS, BORIC AND GERMANIC ACIDS

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The reactions of sorbitol, mannitol, adonitol, dulcitol, glucose and glycerol with H_3AsO_4, H_3AsO_3, H_3BO_3 and GeO_2 acids in dilute aqueous solutions were studied by potentiometric neutralization titrations. The formation of the following chelates was demonstrated: $As(V)L_3^-$, $As(III)L(OH)_2^-$, $HAs(III)L(OH)_2$, BL_2^-, $GeL_2(OH)^-$ and GeL_3^{2-} and the equilibrium constants for their formation were found. Conditions for formation of these chelates of organic oligohydroxy compounds are discussed.

In the alkalimetric determination of boric and germanic acids their reactions with glycols are commonly used; the most marked are those with alcoholic sugars such as sorbitol and mannitol. Similar reactions have been described for arsenous acid[1] and for some further inorganic hydroxocomplexes such as telluric acid[2]. Reactions (*A*) and (*B*) of boric acid with mannitol (H_2L) have been studied in detail[3]. In solutions with excess reagent the 1 : 2 complex predominates and complex with 1 : 1 ratio is formed at small reagent excesses. Reaction with glycerol produces less stable chelates and the 1 : 1 complex predominates at reagent concentrations at which mannitol yields only the 1 : 2 complex. Complex acids $HBL(OH)_2$ and HBL_2 do not exist in aqueous solutions; solution acidification produces only complex decomposition.

$$B(OH)_3 + H_2L = BL(OH)_2^- + H^+ + H_2O \quad K_A \qquad (A)$$

$$B(OH)_3 + 2\,H_2L = BL_2^- + H^+ + 3\,H_2O \quad K_B \qquad (B)$$

$$GeO_2 + 2\,H_2L = GeL_2(OH)^- + H^+ + H_2O \quad K_C \qquad (C)$$

$$GeL_2(OH)^- + H_2L = GeL_3^{2-} + H^+ + H_2O \quad K_D \qquad (D)$$

With germanic acid the reaction with mannitol and with sorbitol proceeds in two steps[4], reactions (*C*) and (*D*). Reaction (*C*) is employed for the titration determination of germanic acid. Reaction (*D*) proceeds in very alkaline medium at $pH \geqq 10$. The $GeL_2(OH)^-$ complex is formed without intermediate formation; a chelate with a 1 : 1 ratio and the complex acids $HGeL_2(OH)$ and H_2GeL_3 were not found in aqueous solution.

With arsenous acid[5] the acidity of the solution is again increased by addition of oligoalcohols; the acidity increase is less than for boric acid or germanic acid. By analogy with the reaction of boric acid (*A*), the reaction of arsenous acid was described by reaction (*E*):

$$As(OH)_3 + H_2L = AsL(OH)_2^- + H^+ + H_2O \quad K_E \qquad (E)$$

$$As(OH)_6^- + n\,H_2L = AsL_n(OH)_{6-2n}^- + 2\,n\,H_2O \quad \beta_n\,. \qquad (F)$$

The reactions of arsenic acid with oligoalcohols have not yet been studied. An aqueous mannitol solution was found to be a suitable medium for the pulse polarographic determination of As(V) in trace amounts[6]. Reaction (*F*) between dihydrogenarsenate and *o*-diphenols[7] is known for $n = 2$ or 3. These reactions proceed slowly, best in weakly acid medium and only at large concentrations of diphenols (in 0·1M and more concentrated solutions) and the stability of the complexes formed is not large.

The molecules of alcoholic sugars contain a large number of functional groups and thus can bond more than one central atom. Examples of this type of compound are the very stable binuclear complex molybdates and tungstates[8] with the composition $M_2O_3(OH)_4LH^{2-}_{-2}$. Similarly, it is assumed that in boron chelates several boron atoms can be bonded to a single alcoholic sugar molecule[9]. The optimal conditions for the formation of polynuclear complexes are in quite concentrated solutions with a minimal reagent excess. In this work, the formation of chelates in dilute solutions with a sufficient reagent excess is studied, *i.e.* in media where the formation of polynuclear complexes is rather improbable.

EXPERIMENTAL

Potentiometric titrations with a 0·1M-NaOH solution were carried out on automatic apparatus ABU 12, PHM 26, TTT 11 and SBR with G 202 glass and saturated calomel electrodes (Radiometer, Copenhagen). The Nernstian response of the glass electrode was verified by evaluation of titration of a strong acid with a strong base ($HNO_3 + NaOH$) and the pH meter was adjusted using a phosphate buffer with a pH of 6·50 ± 0·02. The ionic strength of the solutions was adjusted by addition of potassium nitrate to $I = 0{\cdot}1 \pm 0{\cdot}04$. The titrations were carried out at a temperature of 293 ± 1 K. Solutions of potassium dihydrogenarsenate and boric acid, germanic acid, arsenous acid and arsenic acid were standardized potentiometrically by neutralization titration. Solutions of the reagents glycerol, D-dulcitol, D-glucose, D-mannitol, D-sorbitol and D-adonitol were prepared from weighed amounts of the substances. All the chemicals used were products of Lachema, Brno, of *p.a.* purity or "pure". At $pH < 10$ the solutions had a negligible base consumption, only glucose behaved as a weak monobasic acid with pK_a approximately equal to 12.

The hydrogen ion activity and the concentrations of the other components were employed to calculate the constants found in this work. Function $\bar{z}$ gives[10] the average number of mol of hydrogen ions dissociated from one mol of the completely protonated inorganic acid whose composition was studied.

RESULTS AND DISCUSSION

Reactions of Arsenic Acid

Titration of arsenic acid to the first step, $H_3AsO_4 \rightarrow H_2AsO_4^-$, proceeds in concentrated alcoholic sugar solutions in somewhat more acid medium than in the absence of these reagents. The consumption of base for neutralization of arsenic acid to the first step remains unchanged. In the titration to the second step, $H_2AsO_4^- \rightarrow$

→ $HAsO_4^{2-}$, a decrease in the amount of titrable acid was observed in the complexing medium. This indicates an analogy between the arsenic acid–*o*-diphenol[7] and arsenic acid–alcoholic sugar systems.

The titration curves of arsenic acid titrated in the presence and absence of a complexing agent intersect one another at $\bar{z} = 1{\cdot}00$, *i.e.* at a solution pH optimal for the existence of $H_2AsO_4^-$ ions. The position of the intercept of the titration curves indicates that hydrogen ions do not participate in the reaction between the reagent and $H_2AsO_4^-$ and thus that the medium optimal for the formation of $H_2AsO_4^-$ also has optimal acidity for formation of the complex. Thus solutions prepared by mixing a solution of KH_2AsO_4 and the reagent were studied. Complex formation is slow; in a sorbitol solution with $c_M = 40$ mM and $c_L = 480$ mM (c_M and c_L are the overall concentrations of the compound of the central atom and the reagent) was found after 1/2 hour, 50%, after 1 hour, 34%, after 2 hours, 25% and after 24 hours or longer, 18% uncomplexed As(V). Thus As(V) solutions were always measured 24 hours after preparation. In these equilibrated solutions the amount of uncomplexed $H_2AsO_4^-$ was determined by neutralization titration, $H_2AsO_4^- \rightarrow$ $\rightarrow HAsO_4^{2-}$. The fraction of uncomplexed arsenate can be found only if it can be demonstrated that the complex does not decompose during the titration and that

TABLE I

The Solution Composition and Constants Determined for the $H_2AsO_4^-$–Oligoalcohol Systems

Ligand	c_M, mol l . 10^3	c_L, mol l . 10^3	$[M]/c_M$	β_3
Adonitol	8	480	0·982	
		680	0·947	0·3
		880	0·850	
Dulcitol	8	256	0·867	
		363	0·677	10
		469	0·541	
Mannitol	8	224	0·957	
		387	0·695	
		544	0·484	12
		704	0·282	
Sorbitol	40	96	0·951	
		160	0·858	
		256	0·632	80
		320	0·436	
		480	0·181	

only free $H_2AsO_4^-$ is titrated and not its mixture with another, possibly complex acid. The complex decomposes in neutral media after about one week. The kinetic stability of the complex during the titration, which does not take more than about 30 minutes, was demonstrated by Gran transformation[11] of the titration curves: the plot of the function $v \, . \, 10^{-\mathrm{pH}+\mathrm{const.}} = f(v)$ was linear for all the titrations and the intercept of the straight line with the horizontal axis, giving value v_e, was employed to calculate the concentration of uncomplexed arsenate (v is the volume of base added and v_e is v at equivalence). If the complex were to decompose to a marked degree during the titration, the Gran transformation would not be linear. The logarithmic dependence $\log v(v_e - v)^{-1} = f(\mathrm{pH})_{c_L=\mathrm{const.}}$ is linear for all the measured solutions and has a slope of unity. For $v = v_e/2$ a value of pH 6·70 ± 0·06 was found in solutions with various reagent concentrations, even in the absence of the reagents. Thus equally strong acid is titrated in every case. Formation of a complex acid which would have the same acidity as the uncomplexed component in solutions with various concentrations of various reagents is quite improbable. If the concentration of free arsenate determined by the titration is designated as [M] and reactions (*F*) proceed, then Eq. (*1*) is valid and can be rearranged to give (*2*).

$$C_M - [M] = \sum_{n=1}^{3} \beta_n [M][H_2L]^n \qquad (1)$$

$$(C_M - [M])/[M][H_2L]^2 - \beta_1/[H_2L] = \beta_2 + \beta_3[H_2L] \qquad (2)$$

$$(C_M - [M])/[M][H_2L]^2 = f([H_2L]) \qquad (3)$$

The experimental points yield a linear plot of transformation (*3*) and the straight line passes through the origin of the coordinate system. It follows from equation (*2*) that this dependence indicates $\beta_1 = \beta_2 = 0$ and formation of a single complex, AsL_3^-. The slope of the plot according to (*3*) yields the value of β_3. Solutions of 0·8M glycerol and 0·88M glucose and more dilute solutions of these reagents do not react with arsenate. Table I gives the composition of the studied solutions and the values of β_3 found.

Reactions of Arsenous Acid

Neutral solutions of arsenous acid (pK_a 9·25) exhibit an acidity increase on addition of chelating oligoalcohols. Potentiometric titration of the solutions whose composition is given in Table II exhibits a shift in the titration curve of arsenous acid to lower pH values after reagent addition. The reaction between arsenous acid and the oligoalcohols is rapid; only for glucose was slower equilibrium formation observed and equilibrium was attained in the titrated solution within 1 to 2 minutes. The logarithmic dependence $\log v(v_e - v)^{-1} = f(\mathrm{pH})$ at constant c_L is linear with

TABLE II

Solution Composition and Acidity and Constants Found for the Arsenous Acid–Oligoalcohol Systems

Ligand	c_M, mol l^{-1} . 10^3	c_L, mol^{-1} . 10^3	$pH_{\bar{z}=0,5}$	Constants
Adonitol	40	—	9·26	$\log K_G = -9{\cdot}26$
	8	16	9·17	$\log K_E = -8{\cdot}38$
	8	40	9·14	$\log K_I = -8{\cdot}70$
	8	60	9·10	$\log K_H = +0{\cdot}32$
	40	80	9·04	
	40	200	9·00	
	40	300	8·97	
Dulcitol	8	18·3	9·13	$\log K_G = -9{\cdot}25$
	8	36·6	9·08	$\log K_E = -8{\cdot}30$
	8	54·8	9·04	$\log K_I = -8{\cdot}60$
	40	91·4	9·01	$\log K_H = +0{\cdot}30$
	40	183	8·93	
	40	273	8·87	
Mannitol	8	20	9·14	$\log K_G = -9{\cdot}24$
	8	40	9·09	$\log K_E = -8{\cdot}20$
	8	60	9·01	$\log K_H = +0{\cdot}20$
	40	100	8·96	$\log K_I = -8{\cdot}40$
	40	200	8·84	
	40	300	8·77	
	40	600	8·65	
Sorbitol	8	20	9·05	$\log K_G = -9{\cdot}25$
	8	40	8·96	$\log K_E = -7{\cdot}96$
	8	60	8·88	$\log K_H = +0{\cdot}46$
	40	100	8·86	$\log K_I = -8{\cdot}42$
	40	200	8·73	
	40	300	8·68	
	40	600	8·56	
Glucose	6·7	33·3	9·24	$\log K_G = -9{\cdot}26$
	6·7	66·7	9·22	$\log K_E = -9{\cdot}21$
	6·7	100	9·21	$\log K_H = -0{\cdot}96$
	40	200	9·18	$\log K_I = -8{\cdot}25$
	40	400	9·12	
	40	600	9·08	
Glycerol	40	200	9·13	$\log K_G = -9{\cdot}26$
	40	400	9·04	$\log K_E = -8{\cdot}92$
	40	600	8·98	$\log K_H = -0{\cdot}70$
				$\log K_I = -8{\cdot}22$

unit slope, indicating participation of a single proton in the equilibrium. The pH value for $\bar{z} = 0{\cdot}5$ (Table II) indicates that reagent addition in the region of small c_L leads to a marked increase in the acidity and that a further increase in c_L leads to only a small decrease in $pH_{\bar{z}=0.5}$. The plot of dependence $[H]_{\bar{z}=0.5} = f(c_L)$ for small reagent concentrations (c_L about 0·06M) increases almost linearly. At larger c_L the curve slope decreases and at sufficiently large c_L the function limits to a certain value of $H_{\bar{z}=0.5}$. If only reactions (*G*) and (*E*) occurred in solution, *i.e.* neutralization of arsenous acid and formation of the $AsL(OH)^-$ complex, then dependence $H_{\bar{z}=0.5} = f(c_L)$ would increase linearly. Formation of the AsL_2^- complex, provided it occurred parallel with reactions (*G*) and (*E*), would lead to an increase in the slope with increasing c_L. The actually observed decrease in the slope value at the largest c_L value indicates the presence of reaction (*H*) leading to formation of the undissociated complex acid.

$$As(OH)_3 + H_2O = As(OH)_4^- + H^+ \quad K_G \qquad (G)$$

$$As(OH)_3 + H_2L = AsL(OH) + 2\,H_2O \quad K_H \qquad (H)$$

If it is assumed that reactions (*G*) and (*H*) and (*E*) occur simultaneously, then function $\bar{z}$ is defined by relationship (*4*) which, after rearrangement, yields Eq. (*5*). The ionic charges are omitted for simplicity.

$$\bar{z} = ([As(OH)_4] + [AsL(OH)_2])/([As(OH)_3] + [AsL(OH)] + [As(OH)_4] + [AsL(OH)_2]) \qquad (4)$$

$$[H]_{\bar{z}=0.5} = (K_G + K_E[H_2L])/(1 + K_H[H_2L]) \qquad (5)$$

It follows from Eq. (*5*) that the slope of function $[H]_{\bar{z}=0.5} = f(c_L)$ yields the K_E value if the following conditions are fulfilled: $c_L \gg [AsL(OH)] + [AsL(OH)_2]$ and $1 \gg K_H[H_2L]$. Both of these conditions are fulfilled sufficiently well in the solutions employed with small c_L values (Table II). Consequently, quantity K_E could be evaluated from the slope of the linear initial part of function $H_{\bar{z}=0.5} = f(c_L)$. The intercept of this linear part of this function on the vertical axis yields quantity K_G, whose constant value found from plots for various reagents indirectly confirms the usefulness of this method for these systems. The plot of Eq. (*6*), also derived from equation (*5*), is linear. It has a unit intercept on the vertical axis and its slope corresponds to constant K_H. The determined values of K_E, K_G, K_H and K_I are given in Table II.

$$(K_G + [H_2L]\,K_E)/[H]_{\bar{z}=0.5} = f([H_2L]) \qquad (6)$$

$$AsL(OH) + H_2O = AsL(OH)_2^- + H^+ \quad K_I \qquad (I)$$

Reactions of Boric Acid

The titration curves for the neutralization of boric acid are shifted on addition of oligoalcohols to a more acid region as indicated by the $[H]_{\bar{z}=0.5}$ value in Table III. Formation of the BL_2^- complex predominates in the mannitol–boric acid system with excess reagent[3], *i.e.* reaction (*B*). If the possibility of formation of $BL(OH)_2^-$ is also considered, reaction (*A*), then function $\bar{z}$ is defined by Eq. (*7*) which can be rearranged to give (*8*):

$$\bar{z} = ([B(OH)_4] + [BL(OH)_2] + [BL_2])/([B(OH)_3] + [B(OH)_4] + + [BL(OH)_2] + [BL_2]) \qquad (7)$$

$$[H]_{\bar{z}=0.5} = K_J + K_A[H_2L] + K_B[H_2L]^2 \qquad (8)$$

$$B(OH)_3 + H_2O = B(OH)_4^- + H^+ \quad K_J\,. \qquad (J)$$

The experimental values yield a linear dependence $[H]_{\bar{z}=0.5} = f([H_2L]^2)$ for all the studied reagents and for all the c_L values studied. Thus only formation of the BL_2^- complex occurs in solution. The determined values of constant K_B and of the concentrations of the components employed in its determination are given in Table III.

The reactions of boric acid with oligoalcohols are very rapid; only for glucose, similarly as for the reactions of arsenous acid, was slower equilibrium formation observed.

The Reactions of Germanic Acid

The titration curves of solutions with the compositions given in Table IV exhibit a potential break at $\bar{z} = 1$ corresponding to titration to the first step, reaction (*C*). A further neutralization occurs at pH < 9, reaction (*D*). Interaction between the components occurs very rapidly; only for glucose at pH < 9, the pH stabilizes after 1–2 min. Quantities $pH_{\bar{z}=0.5}$ and $pH_{\bar{z}=1.5}$ reflect the dependence of the acidity of the Ge(IV) solution on the reagent concentrations. The values of equilibrium constants K_C and K_D were found analogously to quantity K_B. The determination procedure is given in the work by Mikešová and Bartušek[4].

CONCLUSION

Table V gives a survey of the equilibrium constants for the studied systems. The values of K_B and K_C published in the literature are in good agreement with the values found in this work. The K_E values published in the literature were determined by methods which did not consider the formation of molecules of complexes arsenous acid.

TABLE III

The Solution Compositions and Acidity and Constants found for the Boric Acid–Oligoalcohol Systems

c_M, mol l^{-1} . 10^3	c_L, mol l^{-1} 10^3	$pH_{z=0,5}$
Adonitol, log K_B —5·48		
1·98	4·95	8·79
3·92	9·8	8·63
3·92	29·4	8·33
3·92	39·2	8·12
18·2	45·5	8·01
18·2	90·9	7·53
18·2	135	7·20
Dulcitol, log K_B —4·03		
3·92	17·6	7·86
3·92	35·3	7·46
3·92	52·9	6·58
18·2	81·8	6·34
18·2	164	5·66
18·2	246	5·38
Sorbitol, log K_B —3·78		
1·98	9·9	7·50
3·92	19·6	7·09
3·92	39·2	6·50
3·92	58·8	6·14
18·2	90·9	5·96
18·2	182	5·32
18·2	273	4·97
Glucose, log K_B —6·33		
1·98	19·8	8·80
3·92	39·2	8·59
3·92	78·4	8·30
3·92	118	8·11
18·2	182	7·82
18·2	364	7·26
18·2	564	6·85

The presence of undissociated complex acid in aqueous media was demonstrated only for As(III) and not for B(III) and Ge(IV). The formation of this complex acid can be correlated with the presence of a lone electron pair on the central atom. The arsenate complex is formed in acid media; decomposition is observed in neutral solutions. In the other systems the chelates are formed in neutral or alkaline media. In all the systems the complexes are formed at pH values close to the pK_a value for the parent inorganic acid. Dissociation of the first proton of arsenous, germanic and boric acid occurs at the same solution acidity, $pK_{a1} \approx 9$. After addition of oligohydroxy compounds only a slight increase in the solution acidity is observed for arsenous acid solutions and a much larger increase in the acidity for boric and germanic acid solutions. This is a result of the fact that As(III) forms chelates of low stability and only solutions of As(III) also contain undissociated molecules of the complex acid. Of the studied reagents, sorbitol forms the most stable complexes. As sorbitol is also produced commercially and is cheaper than mannitol, it can

TABLE IV

The Solution Compositions and Acidity and the Constant Values Found for the Germanic Acid–Oligoalcohol Systems

	c_M mol l^{-1} . 10^3	c_L mol l^{-1} . 10^3	pH	pH $\bar{z} = 0·5$	pK $\bar{z} = 1·5$	pH_C	pK_D
Adonitol	3·6	10	8·0—10·0	9·03		5·43	10·6
	3·6	20	7·6— 9·6	8·70			
	3·6	30	7·4—11·2	8·45	12·23		
	18	50	7·0—11·2	8·31	12·36		
	18	100	6·4—11·2	7·67	12·07		
	18	150	6·2—11·2	7·27	11·86		
Dulcitol	3·6	10	6·8— 8·8	8·01		3·88	10·0
	3·6	20	6·4— 8·4	7·39			
	3·6	30	6·0— 8·0	7·03			
	18	50	5·6—11·8	6·83	11·71		
	18	100	5·2—11·8	6·10	11·42		
	18	150	4·8—11·8	5·73	11·26		
Glucose	1·8	20	7·9— 9·9	8·99		6·33	10·6
	3·6	40	7·7— 9·7	8·79			
	3·6	80	7·3— 9·3	8·46			
	3·6	120	7·1— 9·1	8·18			
	18	200	6·9—10·7	7·92	11·82		
	18	400	6·3—10·7	7·26	11·00		
	18	600	5·9—10·5	6·87	10·86		

TABLE V

Survey of the Equilibrium Constants for the Complexes of As, B and Ge with Oligoalcohols

Reagent	$\frac{[H^+][AsL(OH)_2^-]}{[As(OH)_3][H_2L]}$	$\frac{[AsL(OH)]}{[As(OH)_3][H_2L]}$	$\frac{[AsL_3^-]}{[H_2AsO_4^-][H_2L]^3}$	$\frac{[BL_2^-][H^+]}{[B(OH)_3][H_2L]^2}$	$\frac{[GeL_2(OH)^-][H^+]}{[GeO_2][H_2L]^2}$	$\frac{[GeL_3^{2-}][H^+]}{[GeL_2(OH)^-][H_2L]}$
	$\log K_E$	$\log K_H$	$\log \beta_3$	$\log K_B$	$\log K_C$	$\log K_D$
D-Sorbitol	—7·96	+0·46	+1·90	—3·78	—3·70[a]	— 8·6[a]
D-Mannitol	—8·20	+0·20	+1·08	—4·04[b]	—4·08[b]	— 9·7[a]
D-Dulcitol	—8·30	+0·30	+1·0	—4·03	—3·88	—10·0
D-Adonitol	—8·38	+0·32	—0·52	—5·48	—5·43	—10·6
D-Glucose	—9·21	—0·96	[c]	—6·33	—6·33	—10·6
Glycerol	—8·92	—0·70	[c]	[d]	—7·15[b]	—

[a] Ref.[4]; [b] ref.[3]; [c] does not react; [d] at $c_L \leqq 0{\cdot}4$M only[3] $BL(OH)_2^-$.

be recommended that mannitol be replaced by sorbitol in titration determinations of boric and germanic acids. Glucose and glycerol form less stable compounds than the alcoholic sugars.

The complexes of As and Ge have a coordination number of 6; the coordination number for B is 4. In aqueous solution, water molecules occupy those coordination sites not occupied by other ligands. There is a lone electron pair in one of the coordination sites of the As(III) complex and this lone electron pair can interact with hydrogens of the surrounding ligands and solvent molecules. The formulae $GeL_2(OH).(H_2O)^-$, $As(III)L(OH)_2(H_2O)^-$ and $As(III)L(OH)(H_2O)_2$ best describe the complexes formed in solution. Simpler formulae were used in the text because of the convention of not giving the coordinated solvent in formulae.

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