COMPLEXES OF GERMANIC ACID WITH MANNITOL, SORBITOL, MALTOL AND WITH CHROMOTROPIC AND KOJIC ACIDS

Milena MIKEŠOVÁ and Miloš BARTUŠEK

Analytical Chemistry Department,
Purkyně University, 611 37 Brno

Received November 27th, 1978

Formation of complexes of Ge(IV) with chromotropic acid (GeL_3^{8-}), with maltol and kojic acid ($GeA_2(OH)_2$ and GeA_3^+) and with mannitol and sorbitol ($GeL_2(OH)^-$ and GeL_3^{2-}) has been studied by the method of potentiometric neutralization titration in diluted aqueous solutions. Equilibrium constants of the reactions of germanic acid with the mentioned regaents have been determined.

The complex GeL_3 (charges are omitted for simplification) is practically the only product of reaction between germanic acid and *o*-diphenols (H_2L) in diluted aqueous solutions[1] (Eq. (*A*)). The compounds type $GeL_2.x\,H_2O$, which were observed under special conditions[2,3], are not formed during alkalimetric titration of germanic acid in *o*-diphenol media[4]. The *peri*-diphenol chromotropic acid (H_2L) does not form complexes with Ge(IV) in diluted solutions at c_M 1 mM and c_L 5 mM (ref.[1]); c_M and c_L are total concentrations of Ge(IV) and the reagent in solution, respectively.

Germanic acid reacts with glycols (H_2L) according to Eq. (*B*) (ref.[5]), which is also used for alkalimetric determination of germanic acid[6]. Whereas in medium of *o*-diphenols germanic acid is titrated as a dibasic acid up to p*T* about 5, in solutions of glycols it behaves as a monobasic acid at p*T* about 8. Formation of the complex anion with the ratio glycol: Ge = 1 : 1 could not be proved in the work[6].

Hydroxy-γ-pyrones (including maltol and kojic acid) tropolone and *o*-hydroxyquinones (HA) in neutral solutions form complexes with Ge in the ratio 1 : 2 (Eq. (*C*)), whereas in acid medium the reaction (*D*) takes place to give complex germanium cation. Composition of these chelates was determined by the method of photometric study of the complexes in solution[7].

$$GeO_2 + 3\,H_2L = GeL_3^{2-} + 2\,H^+ + 2\,H_2O \quad K_A \qquad (A)$$

$$GeO_2 + 2\,H_2L = GeL_2(OH_2)(OH)^- + H^+ \quad K_B \qquad (B)$$

$$GeO_2 + 2\,HA = GeA_2(OH)_2 \quad K_C \qquad (C)$$

$$GeO_2 + 3\,HA + H^+ = GeA_3^+ + 2\,H_2O \quad K_D \qquad (D)$$

In this work formation of complexes of germanic acid in diluted aqueous solutions is studied by the method of potentiometric neutralization titration: the complexes with chromotropic acid at higher concentrations than those used in ref.[1], the complexes of mannitol and sorbitol also at pH > 10, and the complexes of maltol and kojic acid in acid and neutral media are investigated.

EXPERIMENTAL

The potentiometric titration with 0·1M-NaOH was carried out with the use of ABU 12, TTT 11, PHM 26 and SBR apparatus with a glass electrode G 202 B and a saturated calomel electrode (Radiometer, Copenhagen). The Nernst response of the glass electrode was checked by evaluation of a titration of strong acid with strong base (HNO_3 + NaOH), and the pH meter was adjusted with the use of a phosphate buffer pH 6·50 ± 0·02. Ionic strength of the solutions was adjusted by addition of potassium nitrate at the value I 0·1, if not otherwise stated. Temperature during titration 293 ± 1 K. For calculation of the constants given in this report activities of hydrogen ions and concentrations of the other components were used. The calculations were carried out with a pocket calculator Qualitron model 1419. Concentrations of germanic, chromotropic and kojic acids and maltol were determined by alkalimetric titration, those of D-mannitol and D-sorbitol were calculated from the weighings.

RESULTS AND DISCUSSION

Reactions of Chromotropic Acid

Solutions of chromotropic acid were titrated in slightly acidic to neutral medium both in the presence and in the absence of germanic acid, their concentrations are given in Table I. At $c_M = 0$ it was found $pK_E = 5{\cdot}40$, $s(pK_E) = 0{\cdot}02$. The value $s(pK_E) = \frac{1}{2}\log(K_E + s) - \frac{1}{2}\log(K_E - s)$ where s is the standard deviation of the average of the K_E values calculated from the squares of deviations, in case of the dissociation constants of the reagents each s value was calculated from 8 to 12 experimental points. The titration curves of the solutions containing germanic acid are shifted to more acidic and more alkaline regions for ${}_L\bar{z} < 0{\cdot}6$ and ${}_L\bar{z} > 0{\cdot}7$, respectively, as compared with the titration curve of the pure reagent of the same concentration. This shift is the greater the greater is c_M. The curves for the same c_L and various c_M intersect in the point corresponding to ${}_L\bar{z} = 0{\cdot}66$.

If in the solution only one acid-base komplexation reaction (F) takes place besides the acid-base equilibrium (E) of the reagent, then the relation (1) is obeyed.

$$H_2L^{3-} \quad = \quad HL^{3-} + H^+ \qquad K_E \qquad (E)$$

$$GeO_2 + n\,H_2L \quad = \quad \text{complex} + h\,H^+ \qquad K_F \qquad (F)$$

$${}_L\bar{z}c_L = h[\text{complex}] + [HL]\,. \qquad (1)$$

The quantity ${}_L\bar{z}$ gives the average number of mol of protons split off from one mol of the reagent present in the form H_2L; if all reagent is present in the form H_2L, then ${}_{\mathrm{L}}\bar{z} = 0$; if $c_{\mathrm{L}} = [\mathrm{HL}]$, then ${}_{\mathrm{L}}\bar{z} = 1$. The analogous quantity $({}_{\mathrm{L}}\bar{z} - h/n)$ expresses the number of mol of protons split off from one mol of the reagent present in the form of the complex formed by the reaction (F). If the reagent is neutralized in such a way, that $({}_{\mathrm{L}}\bar{z} - h/n) = 0$, then no protons are liberated or consumed during formation of the complex, hence pH of the solution does not change in the reaction. It means that the value ${}_{\mathrm{L}}\bar{z} = h/n$ is reached in the reagent solutions at the same pH for any c_{M} value from the range $c_{\mathrm{M}} \geqq 0$. Formation of the complex makes itself felt by a pH decrease and a pH increase of the solution, if ${}_{\mathrm{L}}\bar{z} < h/n$ and ${}_{\mathrm{L}}\bar{z} > h/n$, respectively.

$$c_{\mathrm{L}}({}_{\mathrm{L}}\bar{z} - h/n) = -\frac{h}{n}[\mathrm{H_2L}] + (1 - h/n)[\mathrm{HL}]\,. \qquad (2)$$

TABLE I

Data about Systems Evaluated in Study of Complexes of Chromotropic Acid, Maltol and Kojic Acid (n number of experimental points)

Reaction	c_{L}, mM	c_{M}, mM	pH	n	log K	s (log K)
			Chromotropic acid			
(A)	33	20	3·8—6·6	14	—4·73	0·11[a]
	33	30	3·8—6·0	9	—4·69	0·07[a]
	30	10	4·1—6·9	11	—4·84	0·07[a]
	30	20	4·1—6·9	10	—4·72	0·13[a]
	30	30	4·1—6·9	10	—4·85	0·08[a]
	18	44	4·4—5·4	6	—5·13	0·08[b]
	18	21	4·4—6·0	6	—5·09	0·07[b]
			Maltol			
(C)	10·7	14·3	8·0—8·6	7	4·11	0·06
	5·2	13·9	8·0—8·6	7	4·43	0·06
	5·2	7·0	8·0—8·9	11	3·90	0·05
	4·4	5·3	8·0—8·9	7	4·23	0·03
	4·4	3·5	8·0—8·8	9	4·16	0·07
(D)	40	10	1·9—3·5	17	8·31	0·04
			Kojic acid			
(C)	35·8	10·3	6·8—8·1	13	3·15	0·08
	35·8	22·2	6·8—7·5	8	3·32	0·06
(E)	56·5	10·9	1·9—2·7	9	5·96	0·10
	37·6	10·9	1·9—2·7	8	6·02	0·10

I: [a] 0·15 ± 0·05; [b] 0·13 ± 0·03.

Eq. (*2*) is analogous to Eq. (*1*). The latter does not involve explicitly concentration of the species H_2L which represent the basic state for the function ${}_L\bar{z}$. Similarly, Eq. (*2*) does not contain concentration of the complex formed in the reaction (*F*) which represents the basic state for the function $({}_L\bar{z} - h/n)$. If values of the quantities ${}_L\bar{z}$, h, n, c_L, c_M, pH and K_E are known, concentrations of the individual components are calculated from Eqs (*3*)–(*5*).

$$[H_2L] = ({}_L\bar{z} - h/n)\, c_L/(-h/n + (1 - h/n)\, K_E/[H])\,, \tag{3}$$

$$n[\text{complex}] = c_L - [H_2L](1 + K_E/[H])\,, \tag{4}$$

$$[M] = c_M - [\text{complex}]\,. \tag{5}$$

The values found experimentally show $h/n = 2/3$, which indicates that the reaction (*A*) takes place. The values $h = 2$, $n = 3$ and $K_E = 10^{-5 \cdot 40}$ as well as further values obtained experimentally were introduced into Eqs (*3*)–(*5*), and the calculated values of the equilibrium constant K_A show reasonable agreement within the whole concentration range used (Table I). This fact confirms that only two acid-base equilibria are established in the solution, *viz.* the reaction (*E*) and (*A*), and that the values h and n used in the calculation were properly chosen.

Reaction of Maltol with Kojic Acid

A series of solutions of germanic acid and hydroxypyrones was titrated, their concentrations and pH ranges being given in Table I. If the mixture of the both components is titrated, then neutralization to a certain pH in slightly basic region necessitates a smaller amount of base than it is needed for neutralization of solutions of the isolated components to the same pH at the same c_M and c_L values. If the values c_M and pH are sufficiently low to prevent formation of polynuclear hydrolysis products[8], then in weak alkaline solutions the reactions (*G*)–(*I*) take place.

$$GeO_2 + 4\,H_2O = Ge(OH)_5(OH_2)^- + H^+ \quad K_G \tag{G}$$

$$HA = A^- + H^+ \quad K_H \tag{H}$$

$$GeO_2 + n\,HA = \text{complex} \quad K_I \tag{I}$$

Concentration of base is denoted as q. At pH < 10 it is $q_1 = [Ge(OH)_5(OH_2)]$, $q_2 = [A]$ and $q_3 = [Ge(OH)_5(OH)_2] + [A]$. The indexes 1, 2 and 3 relate to solution of pure germanic acid, that of pure hydroxypyrone and their mixture, respectively. From pH dependence of q_1 and q_2 the values pK_G 9·27 and pK_H 8·62 and 7·77 for maltol and kojic acid, respectively, were evaluated, the value s (pK) being 0·02 for all these constants. The quantity Δq is calculated from Eq. (*6*) using the q values measured at the same pH and at $c_{M,1} = c_{M,3}$ and $c_{L,2} = c_{L,3}$. The quantities $[A]'$ and $[Ge(OH)_5(OH_2)]'$ represent that concentration of base originally present in solution of single component which reacted to the complex on addition of the other component at the given pH. From Eqs (*7*)–(*11*) it is then possible to calculate concentrations of all the components taking part in the reaction (*1*).

$$\Delta q = q_1 + q_2 - q_3 = [A]' + [Ge(OH)_5(OH)_2]' \qquad (6)$$

$$[\text{complex}] = [Ge(OH)_5(OH_2)]'(1 + [H]/K_G) = [A]'(1 + [H]/K_H)/n \qquad (7)$$

$$\Delta q/[A]' = 1 + (1 + [H]/K_H)/n\,(1 + [H]/K_G) = Q \qquad (8)$$

$$[\text{complex}] = (1 + [H]/K_H)\,\Delta q/nQ \qquad (9)$$

$$c_M - [\text{complex}] = [GeO_2]\,(1 + K_G/[H]) \qquad (10)$$

$$c_L - n[\text{complex}] = [HA]\,(1 + K_H/[H]) \qquad (11)$$

The values of equilibrium constants of the reaction (*1*) given in Table I are constant only for $n = 2$, *i.e.* the complexation (C) takes place in the solution.

Addition of neutral solution containing mixture of germanic acid and hydroxypyrone brings about an acidity decrease in solutions of strong acid. The proton activities are lowered by the value Δh when the reaction (D) takes place, and the Eqs (*12*)–(*14*) are obeyed.

$$\Delta h = [GeA_3]\,, \qquad (12)$$

$$c_M - \Delta h = [GeO_2] + [GeA_2(OH)_2]\,, \qquad (13)$$

$$c_L - 3\,\Delta h = [HA] + 2[GeA_2(OH)_2]\,. \qquad (14)$$

For calculation of the quantities $[GeO_2]$ and $[HA]$ the approximation method was used; estimate of $[GeO_2]$ was introduced into Eq. (*13*), and the calculated value $[GeA_2(OH)_2]$ introduced into Eq. (*14*) enables calculation of $[HA]$. Such estimate was considered correct with which the calculated concentrations gave the values K_C 1·5 . 10^4 and 1·7 . 10^3 for the systems with maltol and kojic acid, respectively. These correct estimates were used for calculation of the equilibrium constant of the reaction (D) given in Table I.

TABLE II

Data about Systems Evaluated in Study of Complexes of Mannitol and Sorbitol (c_M = 4 mM)

pH	$\bar{z}$	$\mathrm{pH}_{z=0\cdot5}$	$[H_2L]_{z=0\cdot5}$ mM	$\mathrm{pH}_{z=1\cdot5}$	$[H_2L]_{z=1\cdot5}$ mM
		Manitol			
6·7—10·7	0·1—1·1	7·75	12·4	11·54[a]	6·3
6·7—10·7	0·3—1·2	7·10	28·7	11·32[a]	22·0
6·3—10·7	0·3—1·3	6·72	45·1	11·09[a]	37·7
6·1—10·7	0·3—1·3	6·46	61·4	11·00[a]	53·4
		Sorbitol			
6·7—10·9	0·2—1·6	7·44	12·4	10·82	6·3
6·3—10·7	0·3—1·7	6·78	28·7	10·35	22·0
6·3—10·5	0·5—1·8	6·35	45·1	10·03	37·7
6·3—10·5	0·6—1·8	6·07[a]	61·4	9·87	53·4

[a] The extracted values.

TABLE III

Survey of the Studied Equilibria

Reaction	Reagent	log K	
		this report	literature
$GeO_2 + 3H_2L^{2-} = GeL_3^{8-} + 2H^+ + 2H_2O$	chromotropic acid	—4·8	—
	tiron	—	—2·3 (ref.[1])
$GeO_2 + 3H_2L = GeL_3^{2-} + 2H^+ + 2H_2O$	mannitol	—13·7	—
	sorbitol	—12·3	—
$GeO_2 + 2H_2L = GeL_2(OH)^- + H^+ + H_2O$	mannitol	— 4·0	—4·0 (ref.[6]); —4·5 (ref.[10])
	sorbitol	— 3·7	—3·9 (ref.[10])
$GeL_2(OH)^- + H_2L = GeL_3^{2-} + H^+ + H_2O$	mannitol	— 9·7	—
	sorbitol	— 8·6	—
$GeO_2 + 2HA = GeA_2(OH)_2$	maltol	4·2	3·9 (ref.[7])
	kojic acid	3·2	2·8 (ref.[9])
$GeO_2 + 3HA + H^+ = GeA_3^+ + 2H_2O$	maltol	8·3	8·1 (ref.[7])
	kojic acid	6·0	—

Reactions of Mannitol and Sorbitol

Solutions 4 mM GeO_2 were titrated with standard solution of base in the presence of various concentrations of the hexitols, the detailed data being given in Table II. Titration curves show potential jump at $\bar{z} = 1$ at pH about 9. The quantity $\bar{z}$ gives the average number of mol of protons split off from one mol $GeO_2.x\ H_2O$. Increasing oligo alcohol concentration shifts the titration curves to more acidic region. The function $\log [\bar{z}/(1 - \bar{z})]_{c_L = \text{const}} = f(\text{pH})$ for $\bar{z} < 1$ and the function $\log [(\bar{z} - 1)/ /(2 - \bar{z})]_{c_L = \text{const}} = f(\text{pH})$ for $\bar{z} > 1$ are linear with slopes close to unity. The quantities $[H]_{\bar{z}=0 \cdot 5}$ and $[H]_{\bar{z}=1 \cdot 5}$ given in Table II were obtained by interpolation or extrapolation of the linear logarithmic dependences. Linear dependence of the function $[H]_{\bar{z}=0 \cdot 5} = f([H_2L]^2_{\bar{z}=0 \cdot 5})$ was also found for the lowest used c_L values, which indicates that the reaction (*B*) proceeds exclusively in the studied solutions at pH < 9 in accordance with literature data[6]. If the complex with the ratio Ge : H_2L = 1 : 1 were also formed in these solutions, then the mentioned linear dependence would be deformed, especially so at low c_L values. The K_B values given in Table III were determined from slope of this straight line.

At pH > 9 neutralization of the germanic acid bound in the complex $GeL_2(OH).(OH_2)$ proceeds to the second degree with simultaneous coordination of another ligand (Eq. (*J*)).

$$GeL_2(OH)(OH_2)^- + H_2L = GeL_3^{2-} + 2\,H_2O + H^+ \quad K_J \qquad (J)$$

The reaction course is confirmed by linear dependences $\log((\bar{z} - 1)/(2 - \bar{z})) = f(\text{pH})$ and $[H]_{\bar{z}=1 \cdot 5} = f([H_2L]_{\bar{z}=1 \cdot 5})$ the slope of the latter giving the K_J values given in Table III.

CONCLUSIONS

The *peri*-diphenol chromotropic acid as well as *o*-diphenols form complexes GeL_3 with Ge(IV). The marked difference between K_A values (Table III) of the complexes with 1,8-dihydroxynaphthalene-3,6-disulphonic acid and with pyrocatecholdisulphonic acid indicates that the complex of *o*-diphenol is formed in much more acidic medium and, hence, is more stable than that of *peri*-diphenol which is not formed at all in more diluted solutions of the components. The stability difference of these complexes is due to higher stability of five-membered chelate cycles than the six-membered ones in case of complexes with Ge(IV). It is noteworthy that neither the more stable complexes with *o*-diphenols nor the less stable ones with chromotropic acid showed any stepwise formation of the complexes with the components ratio Ge : L = 1 : 1 and 1 : 2.

Also in case of mannitol and sorbitol we could not prove all members of stepwise complex formation in the solutions, the compound with the ratio 1 : 1 being not formed. Gradual coordination with 2 and then with 3 ligands is connected with stepwise dissociation of 2 acidic protons of germanic acid. The complexes of Ge with oligo alcohols, which are not formed until in neutral and alkaline medium, are less stable than the chelates with diphenols, which are formed in acidic media, too. The difference $\Delta pH = pH_{\bar{z}=1\cdot5} - pH_{\bar{z}=0\cdot5}$ at constant concentration of the same oligo alcohol has a value close to 4 (Table II), hence the reaction (*B*) can be used analytically for titration; contribution of the reaction (*J*) is negligible in the Ge determination. For such titrations mannitol is more suitable than sorbitol, ΔpH is greater for mannitol, and sorbitol forms more stable complexes.

The reagents type H_2L, as diphenols and glycols, are bound to the central atom by means of 2 oxygens of hydroxyl groups. In case of hydroxypyrones the ligand is bound by one oxygen of hydroxyl group and one oxygen of carbonyl group, the both acidic hydrogen atoms of germanic acid being consumed for condensation to water molecules in the reaction (*C*). The hydrogen ions do not participate in the reaction (*C*), and the product $GeA_2(OH)_2$ has no acidic hydrogens. Coordination of a third ligand HA is only possible with assistance of external proton (Eq. (*D*)). Therefore, in cases of the reagents HA coordinated through hydroxyl and carbonyl functional group the coordination of the third ligand is only possible in acidic medium. On the contrary, in case of polybasic alcohols coordinated through two hydroxyl groups coordination of the third ligand necessitates alkaline medium. With hydroxypyrones as well as with oligo alcohols formation of chelate with the components ratio 1 : 1 was not proved in aqueous solution.

REFERENCES

1. Stejskal V., Bartušek M.: This Journal *38*, 3103 (1973).
2. Antikainen P. J.: Suom. Kemistilehti B *32*, 211 (1959).
3. Pichet P., Benoit R. L.: Inorg. Chem. *6*, 1505 (1967).
4. Šprta F., Bartušek M.: Chem. Listy *68*, 867 (1974).
5. Antikainen P. J.: Suom. Kemistilehti B *30*, 147 (1957).
6. Šprta F., Bartušek M.: Scrip. Fac. Sci. Nat. Univ. Brno, Chemia *3*, 91 (1973).
7. Beauchamp A., Benoit R. L.: Can. J. Chem. *44*, 1615 (1966).
8. Ingri N.: Acta Chim. Scand. *17*, 597 (1963).
9. Cleoux B., Benoit R. L.: Bull. Soc. Chim. Fr. *1976*, 2920.
10. Antikainen P. J., Rossi V. K. M.: Suom. Kemistilehti B 32, 182, 185 (1959).

Translated by J. Panchartek.