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A Comparative Study on the Chelate Formation between Germanic Acid and Some Glycols and Polyalcohols in Aqueous Solutions

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The influence of a series of glycols and polyalcohols (hexoses) on the ionization of germanic acid has been studied potentiometrically in aqueous solution at 25°C. Germanic acid displays a tendency to form one-to-one and one-to-two chelate compounds with glycols, while the polyalcohols and their derivatives (aldoses and ketoses) seem to yield solely one-to-two chelate acids (one molecule of germanic acid combined with two molecules of polyol). It thus appears that the number of hydroxyl groups present in the organic ligand plays a very important part in determining the structure of the chelates formed. On the other hand, an increase in the number of carbon atoms in the ligand chain seems to increase the values of the chelate formation constants but not to affect the structure of the chelate. Furthermore, an increase in the number of hydroxyl groups in the ligand (*e. g.* propylene glycol and glycerol) seems to lead to increased values for the chelate formation constants. Additional functional groups as well as different configurations of the hydroxyl groups in the ligands apparently affect the values of the chelate formation constants. Lactol forms may be partly responsible for the observed differences in the chelating ability of germanic acid with carbohydrate substances.

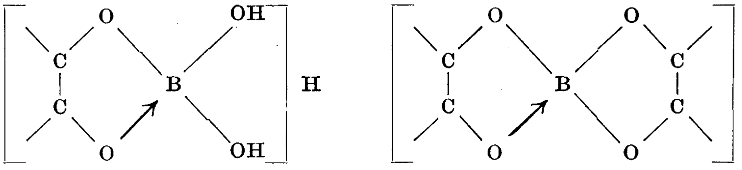
Analogously with boric acid [1] and telluric acid [2], germanic acid [3–7] forms chelate acids with di- or polyhydroxy compounds containing at least two hydroxyl groups in the *cis*-position. The structure and the formation constants of most of such chelate compounds of germanic acid seem to be still unknown. The object of the present investigation was to determine potentiometrically the structure and formation constants of the chelate acids formed by the interaction of germanic acid and the following alcohols in aqueous solutions: ethylene glycol, propylene glycol, 3-methoxy-1,2-propylene glycol, D-mannose, D-glucose and D-galactose. Furthermore an endeavour was made to establish the chelate-forming ability of germanic acid with these alcohols as related to that with glycerol, mannitol and fructose which has been studied previously by the author.

THEORY AND METHOD USED

The author [6] has previously observed that germanic acid is capable of forming one-to-one and one-to-two anionic chelate compounds with some polyalcohols:

$$\underset{\text{one-to-one}}{HGeD} \qquad \underset{\text{one-to-two}}{HGeD_2} \qquad (1)$$

These chelate compounds of germanic acid are generally strong mono-basic acids. However, germanium is also known to exhibit a cordination number six in complex formation, thus resembling boron, which has a tendency to form chelate acids with the co-ordination number four under corresponding conditions:



(2)

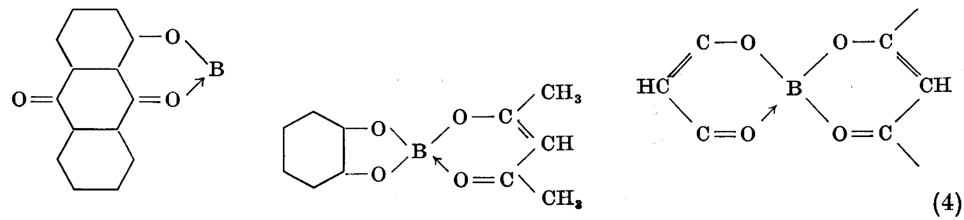
HBD one-to-one

HBD_2 one-to-two

These configurations are in good agreement with the concepts regarding the structure of the acid anions of boron and germanium in which these elements exhibit tetra- and hexacovalency, respectively [8,9]:

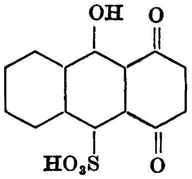
$$B(OH)_4^- \qquad Ge(OH)_6^{--} \qquad (3)$$

and also with the general tendency of these elements to form complex compounds with the co-ordination number four or six, *e. g.* the fluoborate and fluogermanate anions, BF_4^- and GeF_6^{--}. Chelates of type (2) require the hydroxyl groups to be of *cis*-configuration and attached to adjacent carbon atoms. Carbonyl groups may at times participate in chelate bonding as has been demonstrated for the following chelates of boric acid [10-13]

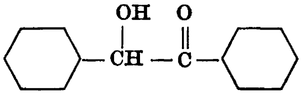


(4)

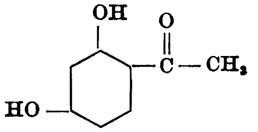
Germanic acid appears to behave in a similar manner as is evidenced by its reaction with the following compounds:



9-Hydroxynaphthacene-quinonesulphonic acid



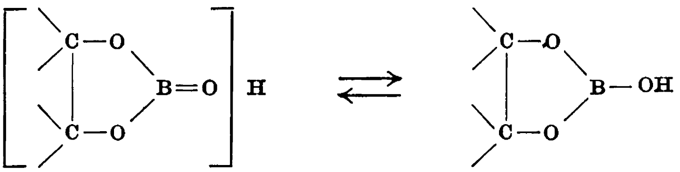
Benzoin



Resacetophenone

(5)

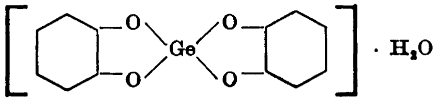
pH and conductivity measurements in general show the germanic acid-polyhydroxy chelates to be strong acids in aqueous solution. It has been noted that boric acid is also capable of forming neutral 1:1 chelates with certain glycols. In that case, according to Böeseken [14], a so-called pseudo acid is formed, which is in equilibrium with the strong chelate acid, the equilibrium being almost completely on the side of the pseudo acid



chelate acid pseudo acid

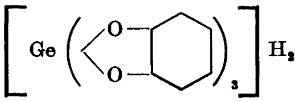
(6)

According to Bevillard [4] and others the existence of *o*-diphenol chelates of germanic acid, which possess the following structure



(7)

may be interpreted as indicating that similar neutral chelates may also be formed by this element. It has, however, not been possible to demonstrate the presence of such chelates in solution. It is thus obvious that germanic acid in solutions with polyhydroxy compounds generally forms strong chelate acids, the presence of which can be demonstrated, for instance, by pH measurements. Further, it is apparent from the above examples that the chelate acids formed are mono-basic acids. On the other hand, it is interesting to find that the germanic acid chelates which are formed with certain *o*-diphenols are of the following structure [4]



(8)

and act as strong di-basic acids. Summing up it may be said that the known polyhydroxy chelates of germanic acid are comprised of strong mono-basic acids of the one-to-one or one-to-two type and strong di-basic acids of the one-to-three type.

The author has previously used the so-called buffer capacity method [15,1,2] for the investigation of some polyhydroxy chelates of boric, telluric and germanic acid in aqueous solution. This method enables the stoichiometry of the reactions in question as well as the formation constants of the chelates formed to be determined.

When it is assumed that the germanic acid chelates formed are mono-basic acids, the reactions may be expressed as follows

$$H_2GeO_3 + nD \rightarrow HGeD_n$$

In this equation $HGeD_n$ designates the mono-basic acid formed and D the polyhydroxy compound; n represents the number of ligand molecules which combine with one molecule of germanic acid. If several different chelates are formed simultaneously, n designates the average number of ligand molecules per molecule of germanic acid. In such cases n is generally not a whole number. When the chelate formation reaction is expressed according to eqn. (9) the equilibrium constant for the reaction can be written as follows

$$K_k = \frac{[HGeD_n]}{[HGe] \cdot [D]^n} \tag{10}$$

When the real first-ionization constant of germanic acid is designated by K_1 and the corresponding constant for the chelate acid by K_1', the germanic acid solution containing chelate acids can be treated as an aqueous solution of an apparently mono-basic strong acid. The ionization constant, K^*, of this acid will consequently take the following form

$$K^* = K_k \cdot K_1' \ [D]^n + K_1 = K_n \cdot [D]^n + K_1 \tag{11}$$

It is therefore possible to determine the constants of this equation by measuring the apparent value of the ionization constant of germanic acid for various concentrations of the polyhydroxy compound. By using large concentrations of the ligand and small concentrations of germanic acid, it may be assumed that [D] is equal to the corresponding stoichiometric concentration, C_D, of the ligand and, eqn. (11) becomes

$$p(K^* — K_1) = pK_n — n \ . \log C_D \tag{12}$$

The expression $p(K^* — K_1)$ should, according to the above equation, be a linear function of $—\log C_D$, the slope of the curve giving the value of n, while the value of pK_n may be obtained from the point of intersection of this curve and the line obtained when $—\log C_D = 0$. The following assumptions have been made in the derivation of eqn. (12)

1. Both the germanic acid and its chelate acids are mono-basic acids.
2. $[D] = C_D$
3. Changes in the dielectric constants of the solutions as may possibly be caused by the ligand are too small to have any effect on the results. (High concentrations of the ligand have been avoided.)

In the event that these assumptions prove to be invalid eqn. (12) will, of course, no longer represent a straight line. This is especially true for assumption 2 (*cf.* Fig. 1).

If the chelate formation is almost complete, the apparent ionization constant, K^*, will approach the real ionization constant [1,2] of the chelate acid and the following equation is obtained

$$\lim_{C_D \to \gg C_{H_2GeO_3}} K^* \rightarrow K_1' \tag{13}$$

The graph of eqn. (12) may be curved for other reasons also. If, for instance, two chelates are formed simultaneously (one-to-one and one-to-two, for example) the graph takes a shape, in which the slopes of the ends of the curve approach the whole numbers. These slopes, n_1 and n_2, indicate the structures of the chelates formed in each reaction. Hence, eqn. (11) becomes

$$K^* = k_1 \cdot C_D^{n_1} + k_2 \cdot C_D^{n_2} + K_1 \tag{14}$$

by the aid of which both formation constants of the apparent chelate formation reactions may be determined in the manner described above. In this equation k_1 and k_2 correspond to the constant K_n in eqn. (11). For the determination of these constants n_1 and n_2 and, in addition, the apparent ionization constant, K^*, must be known for at least two different concentrations of the ligand. In practice, however, it is best to determine several points along the curve corresponding to eqn. (14) as well as its asymptotes which have the slopes n_1 and n_2, and then to calculate the constants k_1 and k_2 with these values for several pairs of K^*'s.

According to eqn. (11) the chelate formation constant, K_n, is equal to the product of K_1' and K_k. Hence,

$$K_n = \frac{[H^+] \cdot [GeD_n^-]}{[HGe] \cdot [D]^n} \tag{15}$$

The constants k_1 and k_2 of eqn. (14) also correspond to this equation. If the above equation is divided by the equation

$$K_1 = \frac{[H^+] \cdot [Ge^-]}{[HGe]} \tag{16}$$

which represents the first ionization constant of germanic acid, the following new expression is obtained for the chelate formation constant

$$K_n' = \frac{[GeD_n^-]}{[Ge^-] \cdot [D]^n} = K_n/K_1 \tag{17}$$

In eqns. (16) and (17) Ge^- designates the germanic acid anion ($H_2GeO_3^-$) and GeD_n^- the chelate acid anion formed. Again, both the germanic acid and its chelate acid are considered to be mono-basic acid. According to eqn. (17) the chelate formation reactions under investigation may be considered to take place between the germanic acid anion and the organic ligand as follows

$$Ge^- + nD \rightleftharpoons GeD_n^- \tag{18}$$

This equation corresponds to eqn. (9). The constant, K_n', gives a good indication of the extent of the chelate formation reaction, and is therefore employed in the final considerations. It should also be noted that, according to eqn. (18), the value of the constant, K_n', is not dependent upon the ionic strength. The constants obtained are therefore comparable to the corresponding thermodynamic constants.

EXPERIMENTAL

All measurements were made by potentiometric titration using a quinhydrone electrode. A saturated calomel electrode served as reference standard. The temperature was regulated at 25 ± 0.05°C by means of a thermostat.

Carbon dioxide was removed from the test solutions effected by bubbling a stream of purified nitrogen through them for as many as 20 h previous to the titration. A slow, continuous flow of nitrogen was maintained during the titration. These precautions proved essential when working in ranges of small buffer capacity where the presence of even exceedingly low concentrations of carbon dioxide can lead to unreliable results.

The sodium hydroxide solution was added by means of a calibrated micro syringe designed by Ellilä [16]. With this syringe it was possible to attain an accuracy for small additions (0.0002 – 0.5 ml) of hydroxide solution that completely corresponded to the accuracy of the potentiometer. Addition of 0.003 – 0.08 ml of an approx. 0.1 N sodium hydroxide solution to the test solutions generally corresponded to a max. potential jump of 10 – 15 mV when the concentrations of germanic acid and polyhydroxy compounds were chosen to be within the molar ranges of 0.008 – 0.012 and 0.05 – 1.0, respectively.

The test solutions were prepared in 50 ml volumetric flasks by measuring with pipettes the appropriate amounts of germanic acid, polyhydroxylic compounds and potassium chloride from corresponding stock solutions. Small quantities of hydrochloric acid were also added before filling up the flasks. About 50 ml of these solutions were used for the titrations by emptying the calibrated volumetric flasks into the titration vessels. Whenever possible the reagents used were the best *pro analysi* products available. If these could not be obtained inferior products were purified.

The aqueous stock solution of germanic acid was prepared from Merck's germanium dioxide. Its concentration was determined by titration [3]. The stock solutions of the glycols were prepared by weighing out the appropriate quantities of dried glycols. The glycols were dried in small portions by being stirred on an oil bath at a temperature near the boiling point of each glycol (100 – 130°C) for about one hour and were then kept for a week in vacuum desiccators containing sulphuric acid and phosphorus pentoxide as drying agents. The molarities of the aqueous solutions prepared from these dried glycols were as follows:

ethylene glycol 2.290 (1.0160), propylene glycol 1.239 (1.0044),

butylene glycol 1.566 (1.0051), 3-methoxy-1,2-propylene glycol 2.422 (1.0347). (The numbers in brackets indicate the corresponding densities of the solutions.)

Because of the slow mutarotation of hexoses in aqueous solution, their solutions had to be prepared about 24 h before the measurements were made in order to permit the attainment of equilibrium.

Table 1. Values of the apparent ionization constant of germanic acid in approximately 0.1 M aqueous potassium chloride solutions with various concentrations of some di- and polyhydroxy compounds at 25°C. (In the calculations the value $K_1 = 2.63 \times 10^{-9}$ has been used[19].)

$C_{H_2GeO_3} \times 10^3$	C_D	$P_m \times 10^4$	$p(K^* - K_1)$
	Ethylene glycol		
11.96	0.1142	0.2882	9.194
11.93	0.2282	0.2973	9.076
11.87	0.3431	0.3129	8.900
11.90	0.5720	0.3402	8.528
11.88	0.9153	0.4111	8.395
	Propylene glycol		
11.91	0.1236	0.3005	9.032
11.93	0.2473	0.3158	8.889
11.95	0.3710	0.3300	8.604
11.89	0.6177	0.4099	8.398
11.98	0.9058	0.4545	8.177
	Butylene glycol		
11.97	0.09998	0.3255	8.817
11.91	0.1248	0.3373	8.728
11.87	0.2992	0.3920	8.463
11.93	0.4988	0.4810	8.188
11.89	0.6253	0.5144	8.107
11.99	0.7828	0.7636	7.834
	3-Methoxy-1,2-propylene glycol		
11.98	0.0960	0.3340	8.757
11.93	0.1814	0.3731	8.542
11.94	0.2723	0.4638	8.236
11.89	0.3630	0.5032	8.133
11.99	0.5456	0.5973	7.945
11.99	0.7275	0.7481	7.713
	D-Galactose		
3.996	0.09965	0.6535	7.300
3.994	0.1498	1.028	6.906
3.988	0.3990	2.050	6.305
3.986	0.5974	3.420	5.861
3.987	0.7976	3.830	5.762
	D-Glucose		
3.980	0.04978	0.4521	7.618
7.996	0.1998	0.7275	6.506
7.982	0.4496	1.530	5.860
7.975	0.6971	2.400	5.468
3.998	0.7992	2.240	5.228
	D-Mannose		
7.982	0.04995	1.209	7.065
7.963	0.09962	2.464	6.451
7.976	0.1496	3.720	6.090
7.950	0.1981	4.428	5.932
7.958	0.2984	5.901	5.678
7.948	0.3963	7.725	5.430

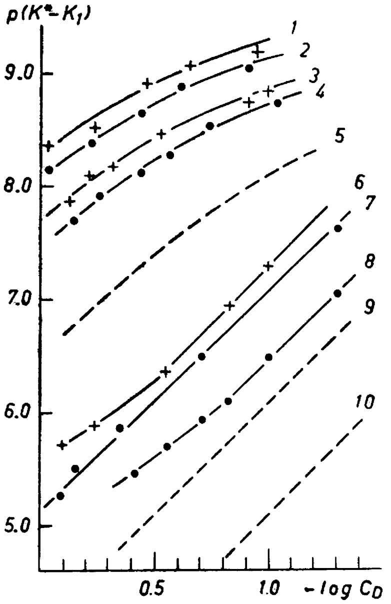


Fig. 1. The dependence of the apparent ionization constant of germanic acid on the concentrations of 1) ethylene glycol, 2) propylene glycol, 3) butylene glycol, 4) 3-methoxy-2,3-propylene glycol, 5) glycerol, 6) D-galactose, 7) D-glucose, 8) D-mannose, 9) D-mannitol, 10) D-fructose (*cf.* Table 1 and Ref.[6]).

RESULTS AND DISCUSSION

Table 1. gives the values of the apparent ionization constant of germanic acid in approx. 0.1 M potassium chloride solutions at different concentrations of various glycols and polyalcohols. These values are in good agreement with eqn. (14) as is illustrated by Fig. 1. Furthermore, it appears that the glycols have a weak tendency to form one-to-one and one-to-two chelates, while the polyalcohols (hexoses) seem to possess a strong tendency to form one-to-two chelates only, as has been expressed previously by the author [6] (*cf.* D-galactose and D-mannose and eqn. 13). Thus it appears that the chelate-forming abilities of the glycols and polyalcohols investigated increase in the order

> ethylene glycol, propylene glycol, butylene glycol, 3-methoxy-1,2-propylene glycol, glycerol, D-galactose, D-glucose, D-mannose, D-mannitol, D-fructose. (19)

The different chelating abilities of these ligands with germanic acid may also be seen from Table 2 which lists the calculated values of pk_1, pk_2, $\log k_1'$ and $\log k_2'$ (employing eqn. 14). Here k_1 and k_2 correspond to the constants in eqn. (17). Thus it becomes apparent that the number of hydroxyl groups in the organic ligand has a very important influence on the structure of the chelates formed. In the case of aliphatic alcohols an increase in the number of hydroxyl groups in the ligand molecule apparently favours the formation of one-to-two chelates and also tends to increase the chelate formation constants (*cf.* propylene glycol, 3-methoxy-1,2-propylene glycol and glycerol). It is interesting to note here that according to Bevillard [4] the aromatic dihydroxy compounds

Table 2. Chelate formation constants of chelates formed by germanic acid and some di- and polyhydroxy compounds. The values in Table 1 and eqns. (12), (14) and (17) have been used in the calculations, the values of n, n_1 and n_2 being 2, 1 and 2, respectively, *c. f.* Ref.[6].

Chelating agent	pk_1	pk_2	$\log k_1'$	$\log k_2'$
Ethylene glycol	8.410	8.954	0.170	−0.374
Propylene glycol	8.298	8.521	0.282	0.059
Butylene glycol	7.943	8.187	0.637	0.040
3-Methoxy-2,3-propylene glycol	7.745	8.000	0.835	0.580
Glycerol	7.320	6.636	1.212	1.944
D-Galactose	—	5.295	—	3.285
D-Glucose	—	5.120	—	3.460
D-Mannose	—	4.453	—	4.127
D-Mannitol	—	4.050	—	4.530
D-Fructose	—	3.100	—	5.480

(*o*-diphenols) form solely one-to-three chelates in aqueous solutions. The occurrence of such one-to-three chelates has also been observed by the author and his co-worker [17] through potentiometric measurements.

Apart from the number of hydroxyl groups in the ligand molecule, the size of the carbon chain also seems to be an important factor in the stability of the chelates. An increase in the number of carbon atoms appears only to increase the stability of chelates but not to affect the structure of the chelates, as may be seen from the fact that all glycols as well as glycerol, independent of the number of carbon atoms, form both one-to-one and one-to-two chelates. On the other hand, an increase in the number of hydroxyl groups seems to favour the formation of one-to-two chelates, as has been found earlier [18].

In a more critical study of the observed differences in the stabilities of the chelates formed it must be born in mind that the hexoses will occur in aqueous solutions mainly in their lactol forms (*cf.* Ref.[6]). Thus, the real ligands in the case of hexoses consist of heterocyclic molecules. Such structural differences have naturally considerable influence on the stability of the chelates formed. In some cases the presence of the necessary hydroxyl groups in the *cis*-position depends on lactol formation, *e. g.* for D-glucose; of its two anomeric forms only the α-form possesses two hydroxyl groups in the *cis*-position. It is therefore apparent that glycosidic hydroxyl groups may also participate in chelate formation. Mutarotation alters the space configuration of the glycosidic hydroxyl groups and thus affects chelate formation. Since the mutarotation is dependent on pH, the chelate formation of hexoses will also be affected by pH and it is therefore important to mention the conditions under which the measurements were performed. In this investigation the measurements were made in acidic solutions, only exceedingly small quantities of base being added to germanic acid-ligand solutions.

From Fig. 1 and Table 2 it can be seen that of all the chelate formers investigated fructose showed the greatest chelating effect on germanic acid. This may be attributed to the fact that fructose, in contrast to the other hexoses, occurs in aqueous solution almost entirely in the open-chain form.

It may therefore be concluded that lactol formation diminishes the ability of the ligand to form chelates with germanic acid. This is supported by the fact that although D-mannitol and D-mannose have very similar space configurations with respect to the hydroxyl groups, mannose possesses a lower chelate-forming ability than mannitol. A similar reduction in chelate formation owing to lactol configuration has been observed earlier by the author [6] in the hexose chelates of boric acid. Boric acid and germanic acid display similar behaviour in chelate formation in other respects also. Thus, for instance, the chelating effect of the chelate formers seems to increase according to series (19) for both acids. It must, however, be noted that, as may be seen from the chelate formation constants obtained, the germanic acid chelates are more stable than the corresponding chelates of boric acid.

According to Saito [5], the hydroxyl groups in positions 1 and 2 play a very important part in the chelate formation between sugars and germanic acid. This becomes evident from the chelating ability of fructose as compared with its two glycosidic derivatives inuline and sucrose, which display a noticeably smaller chelating ability than does the parent sugar. Accordingly it is also possible that fructose undergoes chelation by virtue of its lactol form, even though this form may be present to only a minor extent in aqueous solution. The fact that the aldohexoses display a considerably smaller chelating ability than does fructose may possibly be explained that in the case of the aldoses C-atoms 1 and 2 are both incorporated in the rigid lactol ring, while C-atom 1 of fructose is outside the ring. The hydroxyl groups of C-atom 1 of the ketoses may therefore, owing to their less restricted state, assume a sterically more favourable position for chelate formation than is possible for the corresponding hydroxyl groups of the aldoses. That flexibility in structure plays an important part in chelate formation is furthermore evidenced from the chelate formation constants of D-mannitol and D-mannose. The great importance of the hydroxyl groups in positions 1 and 2 for the formation of germanic acid chelates of ketoses has also been observed polarographically by Saito [5].

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