866. *The Chemistry of Quadrivalent Germanium. Part V.* Ion-exchange Studies of Germanate Solutions containing Polyhydric Alcohols.*

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Ion-exchange studies of solutions of germanates containing ethylene glycol, glycerol, and mannitol have been carried out over the pH range 6—12 with Amberlite I.R.A. 400-Cl. With ethylene glycol only chloride and germanate ions are taken up by the exchanger at all pH values. In presence of glycerol, chloride and germanate ions only are sorbed up to pH 9, whilst at higher pH values a doubly charged 1 : 1 monogermanic acid–glycerol complex is also sorbed. With solutions containing a germanium : mannitol mole ratio of 1 : 5 or 1 : 7 a singly charged 1 : 1 monogermanic acid–mannitol complex is taken up by the resin along with chloride up to pH 8. Above pH 10·6 a doubly charged 1 : 2 monogermanic acid–mannitol complex is sorbed together with chloride. A mixture of these ions is sorbed between pH 8 and 10·6. With solutions containing a germanium : mannitol mole ratio of 1 : 1 a singly charged monogermanic acid–mannitol complex is sorbed along with germanate and chloride at all pH values studied.

The formation of complexes between germanic acid and polyhydric alcohols has often been observed.[1,2] Their formation enhances the solubility of germanium dioxide and the acid strength of germanic acid and allows the latter to be quantitatively titrated with alkali as if it were a strong monobasic acid. In absence of mannitol, and with phenolphthalein as indicator, the titration of germanic acid gives an end-point of 2 moles of sodium hydroxide to 5 g.-atoms of germanium, *i.e.*, corresponding to the titration of pentagermanic acid. The pH of the phenolphthalein end-point is close to 9·2, at which value ion-exchange [3,4] and other methods [5] indicate that the proportion of germanic acid

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* Part IV, *J.*, 1957, 1820.

[1] Bardet and Tchakarian, *Compt. rend.*, 1928, **186**, 637; Tchakarian, *ibid.*, 1928, **187**, 229; Poluektov, *Mikrochemie*, 1935, **18**, 48; Cluley, *Analyst*, 1951, **76**, 517; Tchakarian, *Bull. Soc. chim. France*, 1943, **10**, 98.

[2] Tchakarian, *Ann. Chim.* (*France*), 1939, **12**, 415.

[3] Everest and Salmon, *J.*, 1954, 2438.

[4] *Idem, J.*, 1955, 1444.

[5] Lourijsen-Teyssedre, *Bull. Soc. chim. France*, 1955, 1118.

in solution present as pentagermanic acid is then a maximum. Addition of mannitol (M) appears to degrade the pentagermanic acid to form a complex formulated by Tchakarian[2] as $H_2[Ge_2O_5(M_n)]$, where n must be at least two. The stability of these polyhydroxy-complexes of germanic acid appears to be considerable; no precipitate of germanium dioxide is obtained on addition of ammonia (cf. preparation of activated germanium dioxide[6]) or of magnesium germanate with magnesium chloride; the precipitation of magnesium germanate from germanate solutions is normally quantitative.[7]

Similar complex formation with polyhydroxy-compounds has been observed with other inorganic acids (*e.g.*, between mannitol and molybdic,[8] bismuthic,[9] arsenious,[10] telluric,[11,12] niobic,[13] tantalic,[14] and zirconic acid[15] and between glycerol and telluric acid[11,12] in addition to the well-known mannitol– and glycerol–boric acids). It is significant that most of the above acid readily undergo condensation reactions under the correct conditions. We therefore studied the reaction of germanic acid, whose condensation reactions are now fairly well known, with three typical polyhydroxy-compounds: ethylene glycol, glycerol, and mannitol, to gain information about the complexes formed and the effect of these polyhydroxy-compounds on the normal condensation reactions of germanic acid. The success of ion-exchange methods in studying other complex systems[3,4,16] led us to use similar methods.

EXPERIMENTAL

Equilibrium Experiments and Analytical Methods.—At least 14 days with frequent shaking was allowed for the establishment of equilibrium between the resin and solution. The solution was then decanted from the resin and the latter transferred to a short column and rapidly flushed with water to remove adhering solution. The resin was then eluted with 0·1N-sodium hydroxide (100 ml.) and 0·1N-sulphuric acid (100 ml.), both fractions being collected together. Germanium was determined iodometrically in an aliquot part of the eluate after reduction to the bivalent state with hypophosphorous acid[6] and chloride was determined gravimetrically as silver chloride. Polyhydric alcohols were determined by adding to an aliquot portion of the resin eluate (containing not more than 0·1 mmole of mannitol, 0·25 mmole of glycerol, or 0·5 mmole of ethylene glycol) 3N-hydrochloric acid (3 ml.) and 0·1N-potassium periodate (50 ml.). The mixture was kept for 30 min. at room temperature out of direct sunlight, solid potassium iodide (1 g.) was then added, and after 1—2 min. the liberated iodine was titrated with 0·1N-sodium thiosulphate. A blank experiment on the periodate solution was performed simultaneously.

Results

Ethylene Glycol–Germanate System.—In Table 1 are given the results for the sorption of germanium and chloride by Amberlite I.R.A. 400-Cl (0·25 g.) from solutions containing 2 mg.-atoms of germanium, 10 mmoles of ethylene glycol, and 0·75 mmole of chloride (as resin chloride) in 75 ml. of solution. The sorption of ethylene glycol by the resin was negligible at all pH values. The *R* values in Table 1 refer to the number of germanium atoms present in 1 equiv. of germanate ions sorbed by the resin; they were calculated as previously described.[3]

Glycerol–Germanate System.—Table 2 gives the results for the sorption of germanium, chloride, and glycerol by the resin (0·25 g.) from solutions containing 2 mg.-atoms of germanium, 10 mmoles of glycerol, and 0·75 mmole of chloride (as resin chloride) in 75 ml. of solution.

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[6] Everest, *J.*, 1953, 4117.

[7] Muller, *J. Amer. Chem. Soc.*, 1922, **44**, 2439.

[8] Darmois, *Bull. Soc. chim. France*, 1928, **43**, 1214.

[9] Vanino and Hauser, *Z. anorg. Chem.*, 1901, **28**, 210.

[10] Auerbach, *ibid.*, 1903, **37**, 353.

[11] Rosenheim and Weinheimer, *ibid.*, 1911, **69**, 266; Roy, Lafferriere, and Edwards, *J. Inorg. Nuclear Chem.*, 1957, **4**, 106.

[12] Antikainen, *Suomen Chem.*, 1956, **29**, *B*, 135.

[13] Hauser and Herzfeld, *Zentr. Min.*, 1910, 758.

[14] Hauser, *Z. anorg. Chem.*, 1908, **60**, 230.

[15] Tchakarian, *Bull. Soc. chim. France*, 1932, 846.

[16] Everest, *J.*, 1955, 4415; Everest and Harrison, *J.*, 1957, 1439, 1820.

TABLE 1. *Sorption of germanium and of chloride from solutions* (75 *ml.*) *by Amberlite* I.R.A. 400-Cl (0·25 g.).

pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	*R*	pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	*R*
3·95	—	1·0	—	9·8	1·53	0·35	2·35
6·1	0·67	0·76	2·8	10·1	1·32	0·37	2·1
6·95	1·23	0·56	2·8	10·85	0·56	0·50	1·1
8·2	1·79	0·365	2·8	11·4	0·33	0·46	0·61
8·8	1·88	0·32	2·75	12·05	0·28	0·43	0·49
9·5	1·78	0·32	2·6				

TABLE 2. *Sorption of germanium, chloride, and glycerol from solutions* (75 *ml.*) *by Amberlite* I.R.A. 400-Cl (0·25 g.).

pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Glycerol	Calc. capacity (equiv. per equiv. of resin)	pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Glycerol	Calc. capacity (equiv. per equiv. of resin)
5·5	—	1·0	—	—	11·25	0·20	0·615	0·21	1·02
7·0	1·27	0·565	0·04	1·01 *	11·5	0·20	0·57	0·205	0·97
8·2	1·56	0·42	0·04	0·98 *	11·75	0·215	0·58	0·18	1·01
8·9	1·33	0·48	0·04	0·99 *	12·0	0·215	0·55	0·20	0·98
9·5	0·82	0·56	0·09	1·02	12·1	0·23	0·53	0·18	0·99
9·85	0·30	0·585	0·17	0·98	12·2	0·22	0·53	0·18	0·97
10·6	0·20	0·595	0·195	0·99	12·3	0·215	0·52	0·185	0·95

* Calculated on the assumption that only free germanate and chloride are sorbed by the resin.

Mannitol–Germanate System.—Results for the sorption of germanium, chloride, and mannitol by the resin from (*a*) 1 : 5 solutions, (*b*) 1 : 1-solutions and (*c*) 1 : 7 solutions are given in Table 3. For the 1 : 7 solution the sorption of chloride and germanium only was measured. In all cases the minimum of resin chloride was present, *ca.* 0·75 mmole.

TABLE 3. *Sorption of germanium, chloride, and mannitol from solutions* (75 *ml.*) *by Amberlite* I.R.A. 400-Cl (0·25 g.).

pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Mannitol	Calc. capacity (equiv. per equiv. of resin)	pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Mannitol	Calc. capacity (equiv. per equiv. of resin)
(*a*) 2 mg.-atoms of germanium and 10 mmoles of mannitol present (1 : 5).									
3·6	—	1·0	—	—	8·0	0·32	0·575	0·44	0·895 1·215 *
5·3	0·15	0·86	0·21	1·01	10·1	0·39	0·46	0·54	0·85 1·24 *
5·75	0·25	0·765	0·31	1·01	10·6	0·32	0·43	0·59	1·07 *
6·1	0·32	0·725	0·37	1·04	11·2	0·30	0·38	0·59	0·98 *
6·6	0·37	0·66	0·43	1·03	11·5	0·29	0·36	0·59	0·94 *
(*b*) 2 mg.-atoms of germanium and 2·0 mmoles of mannitol present (1 : 1).									
3·9	—	1·0	—	—	11·0	0·76	0·214	0·595	0·99
6·5	0·615	0·67	0·16	0·99	11·6	0·765	0·18	0·665	1·02
7·4	0·79	0·445	0·345	0·97	11·85	0·73	0·17	0·70	0·93
7·6	0·84	0·405	0·38	0·96	11·95	0·705	0·15	0·655	0·93
8·0	0·85	0·34	0·46	0·95	12·05	0·69	0·17	0·66	0·89
8·4	0·85	0·335	0·53	0·99	12·15	0·685	0·175	0·585	0·96
(*c*) 1·4 mg.-atoms of germanium and 10 mmoles of mannitol (1 : 7).									
5·0	0·115	0·91	—	1·02	6·0	0·255	0·77	—	1·02
5·4	0·16	0·85	—	1·01	6·3	0·34	0·73	—	1·07
5·7	0·20	0·79	—	0·99	6·8	0·28	0·74	—	1·02

* Sorption of a bivalent 1 : 2 monogermanic acid–mannitol complex postulated.

DISCUSSION

Ethylene Glycol–Germanate System.—The results in Table 1, together with the fact that no ethylene glycol is taken up by the resin, indicate that only germanate and chloride are taken up. The *R* values calculated are consistent with the sorption of pentagermanate (*R* 2·5) at *ca.* pH 9, whilst an increasing proportion of the sorbed germanium is present as monogermanate ($HGeO_3^-$, *R* 1·0; or GeO_3^{2-}, *R* 0·5) at higher pH values owing to the depolymerisation of the pentagermanate ion: That *R* remains at a little above 2·5 when the pH falls below 9 is similar to the behaviour of germanate solutions with large amounts of chloride present.[3] These high *R* values may be due to the sorption of traces of a higher germanate polymer of greater *R* value, but they are more probably due to the sorption of small quantities of $HGe_5O_{11}^-$ (*R* 5·0) at these lower pH values. The presence of ethylene glycol appears to inhibit the sorption of monogermanate ions by the resin just as do chloride ions.[3] Monogermanate ions are taken up by the resin at these lower pH values in presence of small or zero amounts of chloride.[4]

Glycerol–Germanate System.—At pH 8·9 and below, the sorption of glycerol by the resin (Table 2) is only slightly greater than the trace quantity (*ca.* 0·02 mmole per equiv. of resin, cf. ref. 16) of glycerol physically entrained inside the resin. Between pH 7 and 8·9 the capacity of the resin can be reasonably accounted for in terms of the sorption of chloride and pentagermanate ions by the resin. Above pH 9 the sorption of glycerol by the resin increases whilst the sorption of germanium falls off relatively more quickly than in the ethylene glycol system (Table 1). This behaviour indicates that a germanium–glycerol complex is being taken up by the resin, and that formation of this complex increases the extent of depolymerisation of the pentagermanate ion. The capacity of the resin above the pH 9 can be accounted for to within 5% by assuming the sorption of a doubly charged 1 : 1 monogermanic acid–glycerol complex by the resin, together with chloride and free germanate. The *R* value of this free germanate (*i.e.*, the ratio of pentagermanate to monogermanate taken up by the resin) was taken from the values found in the ethylene glycol system (Table 1). The method of calculating the resin capacities from the experimental results followed the method previously described.[3, 4, 16]

Although addition of glycerol does not appear to affect the condensation of monogermanic acid below pH 8, it considerably reduces the degree of condensation at higher pH values by complexing with monogermanic acid. This is illustrated by the fact that the maximum sorption of germanium in presence of glycerol was 1·6 g.-atoms per equiv. of resin at pH 8·0. This is in contrast to the behaviour found in the ethylene glycol system where a maximum germanium sorption of 1·9 g.-atoms of germanium occurred at pH 9·2. The concentration of pentagermanate in solution and its sorption by the resin is normally a maximum at pH 9·2 in non-complex-forming systems.[3, 4, 5]

Our results are similar to Antikainen's for the telluric acid–glycerol system.[12] He showed from potentiometric and cryoscopic experiments that only a 1 : 1 complex was formed in this system, no higher complex being detected.

Mannitol–Germanate System.—In solutions containing a germanium : mannitol mole ratio of 1 : 7 or 1 : 5 (Table 3) the resin capacity below pH 8 can be satisfactorily accounted for in terms of the sorption of a singly charged 1 : 1 monogermanic acid–mannitol complex by the resin together with chloride, no free germanate being sorbed. These calculations were based on the germanium sorption figures rather than those of mannitol as the former were considered the more accurate. The mannitol figures confirm, however, that it is just a mixture of these two ions which is taken up by the resin. Above pH 10·6 the capacity of the resin can be quantitatively accounted for in terms of the sorption of a doubly charged 1 : 2 monogermanic acid–mannitol complex by the resin together with chloride, but again no free germanate. Between pH 8·0 and 10·6 a mixture of these two complexes is sorbed by the resin together with chloride. It is evident that in these 1 : 7 and 1 : 5 solutions the mannitol forms complexes so strongly with the monogermanic acid that the normal condensation reactions of germanic acid are entirely repressed, and no free monogermanate or pentagermanate remains in solution.

Similar results have been observed in mannitol–boric acid solution.[17] Either a 1 : 1 or a 1 : 2 boric acid–mannitol complex is formed, depending upon the conditions.

In the solutions containing a germanium : mannitol mole ratio of 1 : 1 the resin capacity can be accounted for over the whole pH range by assuming a singly charged 1 : 1 monogermanic acid–mannitol complex to be sorbed by the resin together with chloride and free germanate. As before, R for the free germanate taken up by the resin was taken from those obtained in the ethylene glycol system (Table 1).

It is obvious from Table **3** that more germanium and mannitol are taken up by the resin from solutions with the lower mannitol concentration. This apparently anomalous behaviour can be explained if it is assumed that appreciable quantities of an uncharged germanium–mannitol complex are formed in solutions containing excess of mannitol. Formation of such a complex would decrease the effective concentration of available mannitol and germanium in solution and allow relatively more chloride to be taken up by the resin.

Mannitol evidently forms complexes more strongly with monogermanic acid than does glycerol, and ethylene glycol forms complexes extremely weakly. This is in the same general order as found in other systems (*e.g.*, ref. 18). These three polyhydric alcohols affect the condensation of germanic acid in a similar order—the stronger the complex formed the greater is the degree of suppression of the normal condensation process.

It is noteworthy that the rate of polymerisation of silicic acid above pH 8 is considerably reduced by addition of glycerol and other polyols.[19] This probably indicates that monosilicic acid forms complexes with them under similar conditions to monogermanic acid.

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