348. *The Chemistry of Quadrivalent Germanium. Part VII.*[1] *Further Studies of the Complexes formed between Germanium and Polyhydric Alcohols.*

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Ion-exchange studies of germanium in concentrated solutions of mannitol, glycerol, and ethanediol have shown that with mannitol and glycerol 3 : 1, 2 : 1, and 1 : 1 ligand–germanium complexes are formed at higher pH values. With ethanediol under the same conditions evidence for 2 : 1 and 1 : 1 complexes has been obtained. It has been confirmed that the stability order of these complexes is mannitol > glycerol > ethanediol. Evidence has been obtained for the sorption of polynuclear mannitol– and glycerol–germanium complexes by the resin at lower pH values. The glycerol complexes readily break down to give atypical polygermanates, but it is uncertain whether these occur in solution or are formed only in the resin phase. Tentative suggestions are advanced for the structures of the various species indicated.

A PREVIOUS study [2] of the interaction of germanic acid with mannitol, glycerol, and ethanediol by ion-exchange methods showed that a doubly charged 1 : 1 glycerol–germanium complex was sorbed by the resin above pH 9. In the mannitol system a singly charged mannitol–germanium complex was taken up by the resin below pH 8, a doubly charged 2 : 1 mannitol–germanium complex above pH 10·6; between pH 8 and 10·6 a mixture of these two ions was sorbed. Some evidence was also obtained for the presence of an uncharged mannitol–germanium complex in solutions containing excess of mannitol. In addition results obtained below pH 8 and given in section (*a*) of Table 3, ref. 2, indicate that the amount of mannitol sorbed by the resin is slightly, but significantly, above that of the germanium. As the amount of " free " mannitol taken up by the resin is negligible at the mannitol concentrations used, it is considered that this slight surplus of mannitol is

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[1] Part VI, Everest and Harrison, *J.*, 1959, 2178.

[2] Everest and Harrison, *J.*, 1957, 4319.

evidence that a small quantity of a singly charged 2 : 1 mannitol–germanium complex is sorbed by the resin, together with larger quantities of the 1 : 1 complex. No interaction was found between germanic acid and ethanediol at the concentrations used (26·6 mg.-atoms of germanium and 133 mmoles of ethanediol per l.). The normal condensation of germanic acid was suppressed by the polyhydroxy-compounds in the order mannitol > glycerol > ethanediol.

Interaction of germanic acid with a series of simple glycols and higher polyhydroxy-compounds has recently been studied by Antikainen, using pH methods.[3] He concluded that glycerol and the simple glycols formed monobasic 1 : 1 and 2 : 1 ligand–germanium complexes, whereas higher polyalcohols formed mainly 2 : 1 complexes.

In the present work the complexes formed between germanic acid and mannitol, glycerol, and ethanediol have been further investigated by ion-exchange methods, increasing concentrations of both germanium and polyhydric alcohols being used. The present study was initiated after the success of ion-exchange methods for investigating the chemistry of concentrated germanate solutions.[1]

EXPERIMENTAL

Solutions.—Where the germanium concentration was less than 40 mg.-atoms per l. a stock solution of germanium dioxide of this concentration was employed; to this solution were added the requisite quantities of ethanediol, glycerol, or mannitol, and the pH was adjusted with carbonate-free 3N-sodium hydroxide. For more concentrated germanium solutions weighed quantities of germanium dioxide and the required polyhydroxy-compound were boiled with water until an optically clear solution was obtained. Often it was easier to effect solution if excess of water was used, the clear solution obtained being then evaporated to the required volume.

Equilibrium Experiments and Analytical Methods.—These were carried out as previously described.[2] Chloride present was added as resin chloride. Amberlite I.R.A.-400 was employed in all experiments.

Polyalcohol and Chloride Controls.—These were determined as in the main experiments except that the germanium was omitted. When the amount of free polyhydroxy-compound exceeds 0·01 mole per equiv. of resin then the value is quoted at the head of the relevant table. No significant variation occurred in the quantity of free polyhydroxy-compounds found on varying the pH of the solution.

On equilibration of concentrated solutions of polyhydroxy-compounds with Amberlite I.R.A.-400, some desorption of chloride occurs, the quantity increasing with increasing pH of the solution (Table 1). It was considered that this release of chloride is due to the presence of a small quantity of a weakly acidic impurity, its affect being most apparent with the concentrated polyhydroxy-compound solutions. Within experimental error the chloride released was the same with all three polyhydroxy-compounds when their concentrations were >1000 mmoles per l. At high pH values the correction factors listed in Table 1 also include the effect of direct hydroxyl-ion competition (for hydroxyl-ion corrections in simple systems see ref. 4). All values for chloride quoted in this paper have been corrected for these effects.

TABLE 1. *Chloride corrections for concentrated polyalcohol solutions.*

pH	Cl^- desorbed (moles per equiv. resin) = A	$1/(1 - A)$ *	pH	Cl^- desorbed (moles per equiv. resin) = A	$1/(1 - A)$ *
3·0	0·065	1·07	10·7	0·175	1·21
4·2	0·07	1·08	11·2	0·222	1·29
6·1	0·075	1·08	11·7	0·301	1·43
7·9	0·08	1·09	12·0	0·358	1·56
9·6	0·11	1·125	12·5	0·452	1·82
10·2	0·137	1·16			

* $1/(1 - A)$ is the correction factor on the assumption that the ratio of chloride desorbed by impurities to the chloride retained by the resin is unaltered in presence of sorbed complexes.

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[3] Antikainen, *Suomen Chem.*, 1957, **30**, *B*, 147; 1958, **31**, *B*, 291.

[4] Everest and Salmon, *J.*, 1954, 2438; 1955, 1444; Everest, *J.*, 1955, 4415.

TABLE 2. *Sorption of germanium, mannitol, and chloride from solutions by Amberlite* I.R.A.-400(Cl).

	Species sorbed (moles or g.-atoms per equiv. resin)				
pH of soln.	Ge	Mannitol	Cl	Ratio mannitol : Ge in sorbed complex	Charge per Ge atom in sorbed complex
(*a*) Ge = 35 mg.-atoms, mannitol = 1050 mmoles, Cl = 10 mg.-atoms per l. Control sorption of mannitol = 0·04 mole per equiv. of resin.					
6·0	0·190	0·250	0·910	1·32	0·47
7·95	0·160	0·373	0·775	2·33	1·40
9·6	0·188	0·472	0·590	2·51	2·18
10·9	0·212	0·535	0·617	2·53	1·81
11·05	0·201	0·537	0·596	2·68	2·01
12·05	0·160	0·490	0·642	3·06	2·22
12·25	0·179	0·551	0·610	3·08	2·18
(*b*) Ge = 100 mg.-atoms, mannitol = 1050 mmoles, Cl = 20 mg.-atoms per l. Control sorption of mannitol = 0·04 mole per equiv. of resin.					
3·5	0·032	0·039	1·0	1·22	—
3·8	0·195	0·230	0·862	1·18	0·71
4·45	0·222	0·310	0·835	1·40	0·74
5·05	0·232	0·314	0·815	1·36	0·80
6·0	0·223	0·330	0·802	1·48	0·89
(*c*) Ge = 150 mg.-atoms, mannitol = 1200 mmoles, Cl = 20 mg.-atoms per l. Control sorption mannitol = 0·04 mmole per equiv. of resin.					
2·65	0·109	0·107	0·985	0·98	0·14
2·75	0·126	0·132	0·967	1·05	0·26
3·05	0·180	0·162	0·925	0·90	0·42
3·3	0·218	0·236	0·910	1·08	0·41
3·5	0·239	0·261	0·878	1·09	0·51
3·75	0·268	0·299	0·850	1·11	0·56
4·0	0·296	0·346	0·817	1·17	0·62
4·7	0·337	0·453	0·765	1·34	0·70
5·2	0·318	0·437	0·768	1·38	0·73
6·0	0·317	0·428	0·755	1·37	0·73
8·2	0·288	0·466	0·688	1·62	1·08
8·4	0·292	0·460	0·715	1·58	0·98

Mannitol–Germanic Acid System.—In Table 2 are given the results for the sorption of germanium, mannitol, and chloride from solutions containing mg.-atoms of germanium, mmoles of mannitol, and mg.-atoms of chloride per l. in the proportions (*a*) 35, 1050, 10; (*b*) 100, 1050, 20; (*c*) 150, 1200, 20, respectively.

Glycerol–Germanic Acid System.—In Table 3 are given results for the sorption of germanium, glycerol, and chloride from solutions containing: (*a*) and (*b*), corresponding concentrations to those used in sections (*a*) and (*b*) of the mannitol–germanic acid system; (*c*) 150 mg.-atoms of germanium, 2200 mmoles of glycerol, and 20 mg.-atoms of chloride per l.

Ethanediol–Germanic Acid System.—In Table 4 are given results for the sorption of germanium, ethanediol, and chloride from solutions containing mg.-atoms of germanium, mmoles of ethanediol, and mg.-atoms of chloride per l. in the proportions (*a*) 35, 1050, 20; (*b*) 35, 3000, 20, respectively.

DISCUSSION

Mannitol–Germanic Acid System.—In the experiments recorded in section (*a*) of Table 2, the ratio of mannitol to germanium in the sorbed complexes rises continuously from 1·35 to 3·08 : 1 on increase of pH from 6 to 12·25. This indicates that at high pH values and at high mannitol concentrations the germanium is sorbed by the resin exclusively as a 3 : 1 mannitol–germanium complex; within experimental error this complex is doubly charged. As the pH is reduced below 12 an increasing proportion of a lower complex is sorbed by the resin, this being probably the doubly charged 2 : 1 mannitol–germanium complex (see ref. 2). The result at pH 7·9 is consistent with the suggestion made on p. 1745 that a singly charged 2 : 1 complex is sorbed by the resin at low pH values.

TABLE 3. *Sorption of germanium, glycerol, and chloride from solutions by Amberlite* I.R.A.-400(Cl).

pH of soln.	Species sorbed (moles or g-atoms per equiv. resin)			Ratio glycerol : Ge in sorbed complex	Charge per Ge atom in sorbed complex	*R* value sorbed germanate
	Ge	Glycerol	Cl			
(*a*) Ge = 35 mg.-atoms, glycerol = 1050 mmoles, Cl = 10 mg.-atoms per l. Control sorption of glycerol = 0·085 mole per equiv. of resin.						
7·2	0·190	0·260	0·840	1·37	0·84	
7·9	0·178	0·255	0·770	1·44	1·29	
8·3	0·167	0·260	0·792	1·56	1·25	
10·75	0·172	0·340	0·715	2·00	1·66	
12·2	0·173	0·483	0·770	2·78	1·33	
12·8	0·178	0·423	0·720	2·40	1·57	
(*b*) Ge = 100 mg.-atoms, glycerol = 1050 mmoles, Cl = 20 mg.-atoms per l. Control sorption of glycerol = 0·085 mole per equiv. of resin.						
1·8	—	—	1·00	—	—	—
2·6	—	—	1·00	—	—	—
3·6	—	—	1·00	—	—	—
4·2	0·629	—	0·89	—	—	5·7
4·6	0·985	—	0·825	—	—	5·6
4·9	1·285	0·030	0·663	—	—	3·8
5·6	1·78	0·030	0·473	—	—	3·8
6·8	1·72	0·035	0·440	—	—	3·1
7·2	1·67	0·080	0·432	—	—	2·95
8·0	0·216	0·215	0·835	1·0	0·77	[1·3]
8·2	0·261	0·340	0·770	1·3	0·91	[1·1]
(*c*) Ge = 150 mg.-atoms, glycerol = 2200 mmoles, Cl = 20 mg.-atoms per l. Control sorption of glycerol = 0·100 mole per equiv. of resin.						
3·75	0·609	—	0·895	—	—	5·8
4·0	0·995	—	0·755	—	—	4·06
4·4	1·54	0·04	0·620	—	—	4·05
4·8	1·905	0·04	0·493	—	—	3·75
5·5	2·61	0·09	0·284	—	—	3·65
6·5	1·53	0·17	0·522	0·11	—	2·92
6·9	0·752	0·23	0·643	0·30	0·48	[2·1]
7·3	0·251	0·274	0·832	1·09	0·67	[1·5]

TABLE 4. *Sorption of germanium, ethanediol, and chloride from solutions by Amberlite* I.R.A.-400(Cl).

pH of soln.	Species sorbed (moles or g.-atoms per equiv. resin)			Ratio ethanediol : Ge in sorbed complex	Charge per Ge atom in sorbed complex
	Ge	Ethanediol	Cl		
(*a*) Ge = 35 mg.-atoms, ethanediol = 1050 mmoles, Cl = 20 mg.-atoms per l. Control sorption of ethanediol = 0·080 mole per equiv. of resin.					
6·4	0·770	—	0·720	—	—
9·25	0·685	—	0·653	—	—
9·8	0·206	0·108	0·850	0·53	1·37
11·35	0·086	0·140	0·805	1·63	2·26
12·45	0·076	0·145	0·860	1·90	1·85
(*b*) Ge = 35 mg.-atoms, ethanediol = 3000 mmoles, Cl = 20 mg.-atoms per l. Control sorption of ethanediol = 0·180 mole per equiv. of resin.					
6·45	0·615	0·061	0·770	—	—
8·55	0·129	0·108	0·825	0·84	1·35
9·1	0·127	0·162	0·845	1·27	1·22
10·95	0·112	0·105	0·825	0·94	1·55
11·7	0·122	0·111	0·895	0·91	0·86
12·25	0·067	0·175	0·870	2·6	1·95

Of particular interest in section (*a*) of Table 2 is the result at pH 6, where the overall charge per germanium atom falls below one and the mannitol : germanium ratio in the sorbed complex approaches one. It is not possible to account for this low charge per germanium by assuming that a mixture of free germanate and any singly charged mononuclear mannitol–germanium complex is sorbed by the resin. In any case sorption of free germanate is unlikely from such a concentrated mannitol solution for, as previously observed,[2] no free germanate was sorbed from a solution of the same pH containing only one-fortieth of the concentration of mannitol. If no free germanate is taken up by the resin, then it is necessary to assume that there is more than one germanium atom per charge in the sorbed mannitol complex, *i.e.*, a polymeric mannitol–germanium ion is being sorbed. An approximate fit for the result at pH 6 is obtained by postulating sorption of a doubly charged 4 : 3 mannitol–germanium complex, although the charge per germanium in such a complex is greater than the observed value (0·66 as against 0·47). A singly charged 3 : 2 mannitol–germanium complex would give a better value for the charge per germanium (0·5 as against 0·47) but a poorer value for the mannitol : germanium ratio (1·5 as against 1·32).

The existence of such polynuclear complexes in this lower pH region is confirmed by the results given in sections (*b*) and (*c*) of Table 2. In section (*b*), at pH values between 6 and 3·8, complexes are sorbed by the resin with ratios of mannitol : germanium of 1·48—1·18 : 1 and with charges per germanium of 0·9—0·7. These results suggest sorption of a doubly-charged 3 : 2 or a 4 : 3 mannitol–germanium complex, the charge per germanium being rather too high for sorption of a singly-charged polynuclear complex. Below pH 3·5 sorption of germanium and mannitol falls to zero.

In section (*c*) of Table 2 are shown results obtained by using the highest concentrations which could be obtained at the lower pH values. The increasingly polynuclear character of the species sorbed by the resin on decreasing the pH is clearly demonstrated by the steady reduction in the charge per germanium atom from 0·98 at pH 8·4 to 0·14 at pH 2·65. The value of 0·14 corresponds to sorption of a doubly-charged Ge_{14} polymer or to a singly-charged Ge_7 polymer. It is significant that the mannitol : germanium ratio in the sorbed complexes progressively decreases towards 1 as the pH is reduced. This would be consistent with the formation of $Ma_{n+1}Ge_n$ polymers * which would tend towards a mannitol : germanium ratio of unity at high values of *n*.

Glycerol–Germanic Acid System.—The results given in section (*a*) of Table 3 closely resemble those for the corresponding mannitol system [section (*a*) of Table 2]. The self-condensation of germanic acid, which is less affected by glycerol than by mannitol, is completely suppressed at the high glycerol concentrations used in the present work. The ratio glycerol : germanium in the sorbed complexes rises from 1·4 to 2·8 as the pH increases from 7·2 to 12. These results indicate that at pH values of *ca.* 12 at least part of the germanium is sorbed by the resin as a 3 : 1 glycerol–germanium complex, whilst a 2 : 1 complex is the principal species sorbed at *ca.* pH 10—11. At pH 8·3 and 7·9 a singly-charged 1 : 1 complex appears to be taken up by the resin. It seems that glycerol resembles mannitol in forming 1 : 1, 2 : 1, and 3 : 1 complexes with germanium; in both cases formation of the higher complex is favoured by increasing the concentration of the polyhydroxy-compound or the pH of the solution. As previously concluded,[2] glycerol–germanium appear less stable than mannitol–germanium complexes. The charge on the 2 : 1 and 3 : 1 glycerol–germanium complexes is rather uncertain. The charge per germanium atom appear to be about 1·5; this fractional value could result from difficulty in ionising the second hydrogen from these complexes, or from cumulative errors in calculating the charge per germanium atom at high pH values.

The result at pH 7·2 is similar to that at pH 6 in the mannitol system [section (*a*), Table 2] in that sorption of a polynuclear species is indicated.

In the experiments at the higher germanium concentrations [section (*b*), Table 3] only the results at pH 8·2 and 8·0 indicate polynuclear formation. Below pH 8 sorption of glycerol falls to low values and the resin contains virtually only chloride and germanates

* Here, and later, Ma = mannitol.

of high R value (for definition of R see refs. 1, 4, and 5). This sorbed germanate shows two features of interest. Not only do the R values found rise considerably above those found in germanate systems in absence of polyhydroxy-compounds, but germanate sorption also occurs below the minimum pH at which it occurs in simple germanate systems.[1,4]

Similar interpretation is given to the results obtained at the highest concentrations used [section (*c*), Table 3]. Polynuclear glycerol–germanium complexes appear to be sorbed at pH 7·5 and 7·3, but at lower pH values atypical germanates of high R value are sorbed by the resin. In both sections (*b*) and (*c*) of Table 3 the R values tend to a maximum value of about 5·8, possibly indicating that a discrete polygermanate species is sorbed at low pH values, *e.g.*, $H_2Ge_{11}O_{24}^{2-}$ ($R = 5{\cdot}5$) or $H_2Ge_{12}O_{26}^{2-}$ ($R = 6$). These results provide evidence that polygermanates higher than heptagermanate can exist under some conditions, although it is not certain from our work whether such high polygermanates exist in solution or are only formed under special conditions in the resin phase. Slight evidence has been previously obtained for the existence of polygermanates higher than heptagermanate.[1]

Ethanediol–Germanic Acid System.—By employing higher concentrations of germanium and ethanediol than previously,[2] complex formation has been detected in this system. The results given in section (*a*) of Table 4 indicate that above *ca.* pH 11 a mixture of 1 : 1 and 2 : 1 ethanediol–germanium complexes are sorbed by the resin, both species carrying a charge of 2. At lower pH values polygermanate and chloride are sorbed by the resin; even ethanediol concentration of 1050 mmoles per l. do not form a complex with the germanium sufficiently strongly to inhibit the normal condensation except at high pH values. The results obtained with 3000 mmoles of ethanediol per l. [section (*b*), Table 4] confirm that germanium–ethanediol complexes are sorbed by the resin. At this ethanediol concentration self-condensation of germanic acid is largely suppressed, only appearing at the lowest pH studied (6·4). Quantitative interpretation of the results in section (*b*) of Table 4 is difficult, largely because the control correction for " free " ethanediol is of the same order of magnitude as of the ethanediol sorbed as complex. The relatively low sorption of germanium and the possibility of a small sorption of polygermanate also add to the quantitative uncertainty. Sorption of ethanediol appears to be slightly less from the more concentrated ethanediol solution, constituting evidence that uncharged germanium–ethanediol complexes also occur (cf. mannitol–germanic acid system, ref. 2).

Although the results obtained for this system do not allow complete quantitatve interpretation, they indicate that ethanediol forms complexes with germanium when present in large excess, and that such complexes are weaker than mannitol- and glycerol-germanium complexes. The difficulties of quantitative interpretation illustrate the limitations of the ion-exchange method for very weakly complexing systems.

Structure of the Polyhydroxy-germanium Compounds.—Although ion-exchange data provide little information concerning the structure of particular complexes, comparison of the results obtained under different conditions and with different ligands enables reasonable suggestions to be made concerning structure.

The 2 : 1 and 3 : 1 polyalcohol–germanium complexes, which normally carry two negative charges, are probably derived from the octahedral $Ge(OH)_6^{2-}$ species by elimination of water between the hydroxyl groups of the germanium and two of the hydroxyl groups on each ligand. That such octahedral complexes are most readily formed at high pH values is consistent with the fact that the $Ge(OH)_6^{2-}$ ion becomes the major species in a germanate solution only at high pH values.[4,6] Evidence has also been obtained that mannitol, glycerol, and ethanediol form uncharged complexes with germanium. These complexes may be of the 2 : 1 type derived from uncharged tetrahedral orthogermanic acid

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[5] Russell and Salmon, *J.*, 1958, 4708.

[6] Brintzinger, *Z. anorg. Chem.*, 1948, **256**, 98.

units by interaction of the germanium's hydroxyl groups with two hydroxyl groups on each ligand. Such a tetrahedral complex is of necessity uncharged unless either a germanium–ligand bond is broken, thus allowing ionisation of one of the germanium's hydroxyl groups, or the complex is converted into the octahedral configuration based on $Ge(OH)_6^{2-}$. It is significant that the existence of neutral 2 : 1 α-hydroxy-acid–germanium complexes has been demonstrated;[7] such complexes may also be tetrahedral.

The considerable stability of the 1 : 1 mannitol–germanium complex, and the fact that it carries only a single charge over a wide pH range [*i.e.*, 5—12, see section (*b*), Table 3, ref. 2], can be explained by assuming the complex to be derived from the tetrahedral orthogermanic acid. The mannitol acts as a tridentate group binding three of the four germanium hydroxyl groups, leaving the fourth free to ionise; for this complex to gain a second charge would entail breaking one of the germanium–ligand bonds. However, in presence of a 5 : 1 molar excess of mannitol [section (*a*), Table 3, ref. 1] the 1 : 1 complex is the principal species only up to pH 8·6; at higher pH values the complex acquires a second charge by binding an additional mannitol and becoming octahedral in configuration, each mannitol acting as a tridentate group. The relative difficulty in forming the 3 : 1 mannitol–germanium complex from the 2 : 1 complex results from the necessity for breaking the germanium–mannitol bonds in the latter compound, each mannitol acting as a bidentate group in the 3 : 1 complex.

In contrast to the 1 : 1 mannitol–germanium complex, the similar glycerol complex is doubly charged. This complex is the major species sorbed by the resin from relatively dilute glycerol solutions.[2] This double charge arises from inability of glycerol to bind more than two hydroxyl groups on the orthogermanic acid unit, leaving the other two free to ionise. Such a complex is evidently only stable in the ionic form, for it is sorbed by the resin only above pH 9; below this pH, only free germanate is sorbed,[2] unless a large excess of glycerol is present.

The marked difference between the mannitol and the glycerol system in the region where polynuclear complexes are formed is of significance. Mannitol forms a range of polymers $Ma_{n+1}Ge_n$ which strongly suggest their possessing a linear structure consisting of alternating mannitol and germanate units. It is difficult to decide whether the germanium has an octahedral or a tetrahedral configuration in these polymers. A tetrahedral structure based on orthogermanic acid would lead to an uncharged complex, whilst an octahedral configuration would imply a charge per germanium of 2, which is too high. Possibly these polymers contain both tetrahedral and octahedral germanium units, or the ionisation of the octahedral-based polymers may be partly suppressed by the low pH of the system.

With glycerol, polymers consisting of alternate germanium and ligand units cannot occur, for glycerol cannot simultaneously bind two germanate units, no evidence ever having been obtained that germanium can form a complex with a ligand containing only one hydroxyl group as co-ordination centre. Polymerisation in the glycerol system can be envisaged as originating from the 1 : 1 glycerol–germanium complex if it is assumed that the pH at which the latter breaks down into glycerol and germanate is reduced by increasing the concentration of germanium and glycerol in solution. As the pH is reduced below 9, condensation occurs between the free germanium hydroxyl groups of neighbouring complexes. The resulting polymers are similar to those formed by condensation of dialkylsilanediols,[8] the glycerol masking two of the hydroxyl groups on the germanium and making it effectively bifunctional. Any charge carried by these polymers will result from ionisation of the hydroxyl groups on the terminating germanate units. Increasing the concentration of the solution only retards the loss of glycerol from the germanium complexes, thus further decreasing the pH required for complete displacement of glycerol

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[7] Pflugmacher and Rohrman, *Angew. Chem.*, 1957, **69**, 778; Clark, *Nature*, 1959, **183**, 536.

[8] Hardy and Megson, *Quart. Rev.*, 1948, **2**, 25.

and formation of atypical chain polygermanates which are taken up by the resin. Such chain polygermanates are in contrast to normal polygermanates which have a globular structure.[9]

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[9] Nowotny and Wittman, *Monatsh.*, 1952, **83**, 568; 1956, **87**, 654.