

SORPTION OF GERMANIUM ON SILICA GEL FROM AQUEOUS AND MIXED AQUEOUS-ORGANIC SOLUTIONS*

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Sorption of germanium on silica gel has been studied from the solutions of perchloric, nitric, sulphuric, hydrochloric, and acetic acids as well as from the mixed aqueous-organic solutions of the hydrochloric acid with lower alcohols or with the acetic acid. The results obtained in these experiments can be explained by the sorption of neutral germanium complexes. In the mixed solutions the formation of ionic associates is assumed. The solubility of GeO_2 in mixed solutions of the hydrochloric acid with ethanol or 1-butanol has been determined.

Until now relatively few studies dealt with the sorption of germanium on inorganic sorbents¹⁻⁶ and, moreover, the main interest was concentrated solely to the sorption from solutions with pH 1-11. It was found⁴⁻⁶ that under these conditions the sorption of germanium on silica gel is very low so that it does not offer any possibility of a practical application and therefore very little attention has been given to this sorbent. However, in the studies of the coprecipitation of germanium with the silicic acid gel in the presence of sulphuric acid it was observed⁸ that the sorption of germanium increases with the increasing acidity so that in the solution of 10M- H_2SO_4 germanium is quantitatively removed from the solution. These experimental results inspired more detailed studies of the germanium sorption on silica gel from the strongly acidic solutions.

EXPERIMENTAL

Reagents and Apparatus

With the exception of the solubility determinations, the concentration of germanium remaining in the solution after the sorption was determined radiometrically using the radionuclide ^{68}Ge , prepared by the irradiation of metallic zinc by α -particles on cyclotron (Institute of Nuclear Research, Prague-Řež). Germanium was separated from the target material by extraction with tetrachloromethane from the 8M-HCl solution with a subsequent reextraction by water. The radioactivity was measured by a β counter with a GM tube. The nuclide ^{68}Ge was used in the form of an aqueous solution of the concentration of the order of 10^{-10} g-at. Ge/l. The stock solutions

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of non-active germanium were prepared by dissolving a given amount of the amorphous modification of germanium dioxide (made in USSR, GeO_2 content was $>99.99\%$) in 0.1M-NaOH . Dilution by the distilled water and labelling by the ^{68}Ge nuclide preceded every experiment.

All the reagents used were of the analytical grade. The acetic acid (99% solution) was used without any further purification. All other organic solvents were dried and distilled. The mixed solutions were always prepared immediately before the experiment. Silica gel CH (Spolana, Neratovice, with the specific surface of $360\text{--}400\text{ m}^2/\text{g}$) was washed first by the concentrated hydrochloric acid and then by the distilled water and dried at 110°C for 24 hours. The fraction with the mean size of the grain of 0.1 mm was used.

Procedure

The sorption was studied by shaking 2 ml of the liquid phase with 0.0225 g of silica gel for three days. The weighted amount of the sorbent was added using a calibrated dosing device (dosing precision $\pm 3\%$). The solutions were prepared by mixing the solvents in the following order: distilled water, the acid, the organic solvent, the stock solution of germanium. The experiments were carried out at $23 \pm 1^\circ\text{C}$, the sorption of germanium from the hydrochloric acid solutions was determined also at 10 ± 0.1 and at $40 \pm 0.1^\circ\text{C}$ in a thermostatted shaker.

The ratio of the adsorbed germanium γ was determined from the differences of the radioactivity before and after the sorption experiment. The radioactivity was measured always after the establishment of the equilibrium between ^{68}Ge and ^{68}Ga . To prevent any losses due to the volatility of GeCl_4 , the samples of chloride solutions were transferred on a paper disc and immediately sealed between two adhesive tapes.

An analogous procedure was used also for the studies of the volatility of germanium from chloride solutions. The germanium solution of the initial concentration was transferred on a disc

TABLE I

Volatility of Germanium from the HCl Solutions and from the Mixtures of HCl and Ethanol

t min	$C_{\text{Ge}} = 10^{-10}\text{ mol/l}$			$C_{\text{Ge}} = 10^{-5}\text{ mol/l}$		
	1M-HCl	5M-HCl	10M-HCl	1M-HCl	5M-HCl	10M-HCl
HCl						
5	0	10	55	0	0	32
20	6	23	71	10	16	46
60	43	81	80	38	86	87
HCl + ethanol ^a						
5	—	0	0	—	0	0
20	—	0	54	—	13	22
60	—	31	65	—	21	56

^a Mixed solutions of the hydrochloric acid of the given concentration and ethanol in the ratio 1 : 1 have been used.

of filter paper glued to an adhesive tape and dried. The paper was then saturated with 0.1 ml of a solution with a certain variable concentration of the hydrochloric acid and the individual discs were after a certain time interval hermetically sealed by another adhesive tape.

The solubility of germanium dioxide in aqueous-organic solutions was determined by shaking the weighted amount (0.1–0.2 g) of GeO_2 and 5 ml of the solution for 3 weeks, which is sufficient for the equilibrium establishment. The solid phase was separated from the mother liquor by centrifugation.

Analytical Determination of Germanium

The concentration of solutions containing weightable amounts of germanium were determined by the complexometric titration: to 1–2 ml of the 0.05M-complexon III 0.3–1.0 ml of the analyzed germanium solution was added, the hydrochloric acid present in the solution was neutralized by 1M-NaOH (with phenolphthalein as an indicator), and then 0.3 ml of the 10M-HCl and 50 ml of distilled water were added. The solution was heated on a water bath for 30 min and after cooling down 1 ml of 0.05% solution of the xylenol orange was added and the microtitration was done using the 0.01M- $\text{Bi}(\text{NO}_3)_3$ solution.

RESULTS

Study of the Volatility of Germanium(IV) Chloride

Germanium(IV) chloride is highly volatile even at room temperatures. Preliminary experiments have been therefore made to determine such working conditions under which there are minimum losses of germanium and the experimental results are not affected by the volatility.

The germanium losses during the sorption studies under batch conditions can be caused directly during the sorption *via* a leakage through the stopper, during the pipetting of the solution after the sorption and during the preparation of samples, and, last but not least, during the period from the preparation of the sample up to the moment when the measurement of its radioactivity is finished. Sorption of germanium on the walls of probes makes the direct determination of losses in the course of sorption rather difficult. The losses in the concentrated hydrochloric acid were therefore determined by the desorption of ^{68}Ge adsorbed on the glass by the 5% solution of citric acid. Altogether up to 85% of the initial radioactivity was found. It follows from these experiments that the losses did not exceed 15%.

The method of sealing the samples between two adhesive tapes guarantees their storage without losses for a practically limitless period of time.

Eventual losses of germanium during the preparation of samples after the sorption were determined using the time dependence of the volatility of germanium from the hydrochloric acid solutions. From the results (Table I) it follows that in the course of drying the solutions germanium is volatile in the whole concentration range from 1M-HCl up to 10M-HCl; the higher is the acid concentration the higher is also the

volatility of germanium. On the other hand, the presence of a carrier or of an alcohol decreases the volatility.

As the time between the opening of the probe and the sealing of the sample did not exceed half a minute, we may expect that the losses of germanium(IV) chloride could not substantially affect the experimental results. The assumption is borne out by the fact that at higher temperatures the sorption of germanium is lower while the higher volatility of GeCl_4 would give higher values of γ .

Sorption from the HClO_4 , HNO_3 , H_2SO_4 , and HCl Solutions

Figs 1a, b, 2a,b present the dependences of the values of the germanium ratio sorbed under the batch conditions on silica gel and on the probe walls on the concentration of the respective acid. With the increasing concentration of HClO_4 , HNO_3 , and H_2SO_4 the fraction of germanium sorbed on silica gel also increases so that in the concentrated solutions the sorption is practically quantitative. The sorption on glass appears in a substantial degree only at higher concentrations of the acid. It is evident that the dependence of sorption on silica gel involves also the sorption on probe walls.

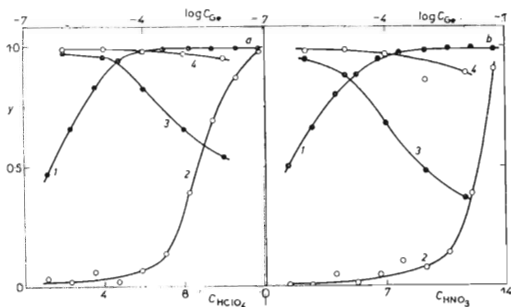


FIG. 1

Sorption of Ge on Silica Gel and on the Probe Walls

a From the HClO_4 solutions: C_{HClO_4} the molar concentration of HClO_4 , C_{Ge} the initial molar concentration of germanium, γ the ratio of the adsorbed germanium. Curves: 1 sorption of trace amounts of Ge on silica gel, 2 sorption of trace amounts of Ge on the probe walls, 3 the dependence of sorption from 5.90M- HClO_4 on C_{Ge} , 4 the dependence of sorption from 10.62M- HClO_4 on C_{Ge} . *b* from the HNO_3 solutions: C_{HNO_3} the molar concentration of HNO_3 . The notation and the curves 1 and 2 are analogous to those used in Fig. 1a. Curves: 3 the dependence of sorption from 6.67M- HNO_3 on C_{Ge} , 4 the dependence of sorption from 12.02M- HNO_3 on C_{Ge} .

Nevertheless, due to the high specific surface of silica gel we can assume that the predominant part of germanium is sorbed on silica gel even in the region of the maximum sorption on glass. This assumption has been confirmed in the case of protactinium sorption (unpublished results).

In the region from 1M-HCl to 6M-HCl the sorption of germanium also increases; however, from 7.5 to 8M-HCl there is a minimum on the dependence $y = f(C_{\text{HCl}})$. In the case of the hydrochloric acid, some experiments were also done at 10 and 40°C. From the results presented on Fig. 2b it follows that the minimum adsorption in diluted solutions is at 23°C. In the region 6–12M-HCl the increasing temperature decreases the sorption and simultaneously the minimum sorption is shifted towards lower concentrations of the hydrochloric acid. The sorption of germanium on glass from the HCl solutions is similar to that from the HNO₃ and HClO₄ solutions.

Sorption kinetics. The dependence of germanium sorption on the mixing time was studied only with the solutions in the hydrochloric acid. From the results (Fig. 3) it follows that in the concentrated acid the equilibrium is reached within about one hour. Under these conditions the sorption on glass proceeds similarly. In the diluted hydrochloric acid the establishment of equilibrium requires several days.

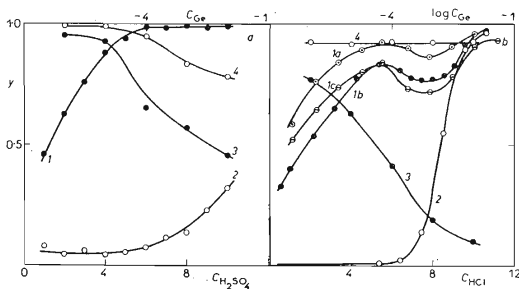


FIG. 2

Sorption of Ge on Silica Gel and on the Probe Walls

a From the H₂SO₄ solutions: $C_{\text{H}_2\text{SO}_4}$ the molar concentration of H₂SO₄. The notation and the curves 1 and 2 are analogous to those on Fig. 1a. Curves: 3 the dependence of sorption from 5.0M-H₂SO₄ on C_{Ge} , 4 the dependence of sorption from 9.0M-H₂SO₄ on C_{Ge} . *b* from the HCl solutions: C_{HCl} the molar concentration of HCl. The notation cf. Fig. 1a. Curves: 1a sorption of trace amounts of Ge on silica gel at 10°C, 1b at 23°C, 1c at 40°C, 2 sorption of trace amounts of Ge on the probe walls, 3 the dependence of sorption from 5.32M-HCl on C_{Ge} , 4 the dependence of sorption from 9.60M-HCl on C_{Ge} .

The effect of germanium concentration on its sorption. The values of the ratio of the adsorbed germanium depend on its concentration as shown in Figs 1a, b 2a, b. The germanium sorption is practically independent on its concentration for $C_{Ge} < 10^{-6} M$ and $C_{H^+} > 5M$. Beyond this limit the function $y = f(C_{Ge})$ has a decreasing trend and its character is affected both by the acidity of the solution and by the nature of the acid used. The highest decrease was found in the diluted hydrochloric acid while in the concentrated hydrochloric acid the fraction of the adsorbed germanium is linear throughout the whole studied region of C_{Ge} .

Sorption of germanium from mixed solutions. The sorption of germanium on silica gel was also studied from the mixtures of water and acetic acid and of hydrochloric acid and acetic acid (Fig. 4). In the system H_2O-CH_3COOH and $2.13M-HCl-CH_3COOH$ the value of K_d increases linearly with the increasing fraction of the organic component and reaches maximum at 90% and 75% of CH_3COOH , respectively. In the system $5.32M-HCl-CH_3COOH$ the dependence of $\log K_d = f(C_{CH_3COOH})$ has also a maximum, which is, however, extended over a broad region of concentrations. In the sorption from the mixture of the concentrated hydrochloric and acetic acids the value of K_d decreases with the increasing fraction of the organic component, but at 80% of CH_3COOH it forms a small maximum. In the region of this maximum

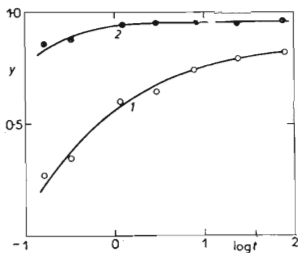


FIG. 3

Germanium Sorption Kinetics from the HCl Solutions

y Ratio of the adsorbed germanium, t the sorption time (hours). Curves: 1 5.32M-HCl, 2 10.65M-HCl.

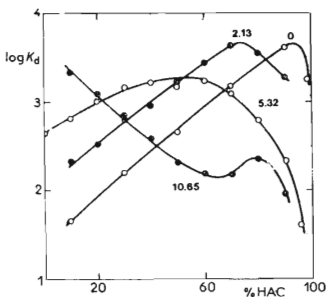


FIG. 4

Sorption of Germanium from the Mixture $HCl-CH_3COOH$ (HAc)

K_d Distribution ratio of germanium (ml/g). The numbers at curves indicate the molar concentrations of HCl. x-axis: the vol.% of HAc in solution.

the results were poorly reproducible and the values of K_d (Fig. 4) are the mean values of three experiments.

If the acetic acid is replaced by methanol or 1-propanol (Figs 5a, b), the addition of an alcohol leads to a nearly linear increase of the K_d value, if the diluted hydrochloric acid was used. On the other hand, a distinct minimum of sorption appears in the mixture with the concentrated acid. The presence of ethanol, 2-propanol, and 1-butanol in the mixture with 10.65M-HCl affects the sorption of germanium in an analogous way (Fig. 6). From these results it follows that the increase of the number of carbon atoms in the alcohol molecule increases the depth of the minimum. This fact is illustrated by Fig. 7, in which the values of $\log K_d$ are plotted against the molar ratio Q of the alcohol and the hydrochloric acid. For all primary alcohols the minimum appears close to the value $Q = 1$, in the case of 2-propanol the minimum lays at $Q = 0.5$.

Solubility of GeO_2 in aqueous-organic solvents. For the interpretation of the results of sorption in mixed solutions it was necessary to determine the solubility of germanium in the systems of hydrochloric acid with an organic solvent. The solubility of GeO_2 in the mixtures HCl-ethanol and HCl-1-butanol is presented in Fig. 8. In both cases the maximum solubility was found in solutions for which there is a minimum of sorption of germanium on silica gel. For low contents of the organic component in the mixture (<20 vol.%) the solution is in an equilibrium with the liquid GeCl_4 , for the higher contents the insoluble residue forms a compact white solid.

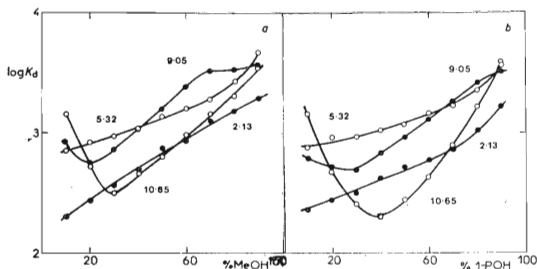


FIG. 5

Sorption of Germanium from the Mixtures: *a* HCl - Methanol (MeOH), *b* HCl - 1-Propanol (1-POH)

Notation and conditions: *cf.* Fig. 4.

DISCUSSION

Sorption from Aqueous Solutions

The behaviour of germanium in aqueous solutions has so far been studied rather insufficiently. No transfer has been detected by the electrophoresis of germanium in the solution of the perchloric, nitric, and sulphuric acids⁹, what indicates that only neutral molecules are present. However, in the hydrochloric acid solutions a transfer towards the anode has been observed already for the acid concentrations higher than 1M. The increase of the distribution ratio for the sorption of germanium on strongly basic anexes from the concentrated hydrochloric acid solutions is explained by the formation of chloro germanate anions¹⁰. However, the most interesting results were obtained from the studies of the solubility of germanium dioxide. In the perchloric and nitric acids the solubility of GeO_2 gradually decreases with the increasing concentration of the acid, but the composition of the solid phase remains the same⁹. In the system $\text{GeO}_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ the solubility decrease has been also observed in the region from 1 to 9M- H_2SO_4 ^{9,11-14,20}. The formation of complex anions in the more concentrated region has been proved spectrophotometrically¹¹.

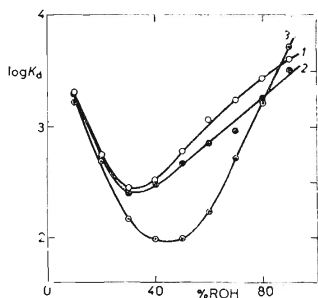


FIG. 6

Sorption of Germanium from the Mixtures of 10.65M-HCl with Ethanol (1 EtOH), 2-Propanol (2 2-POH), and 1-Butanol (3 1-BuOH) Notation and Conditions: *cf.* Fig. 4

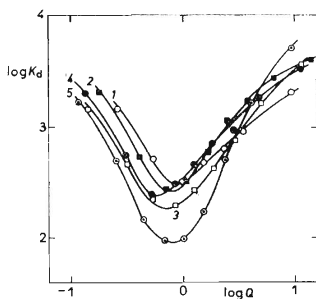


FIG. 7

Dependence of the Distribution Ratio of Ge K_d on the Molar Ratio of HCl-Alcohol

Q Molar ratio of HCl and the respective alcohol in the solution. The values are given for the mixtures of 10.65 M-HCl with a variable content of the alcohol. Notation and conditions: *cf.* Fig. 4. 1 MeOH, 2 EtOH, 3 1-POH, 4 2-POH, 5 1-BuOH.

A similar character of solubility dependence has been found also in the hydrochloric acid. Several authors studied the solubility of GeO_2 and GeCl_4 in the hydrochloric acid^{9,14-19} but the published data are difficult to compare, namely in the most interesting region of the solubility maximum at 6–8M-HCl. Most authors agree that the maximum on the solubility curve of GeO_2 lays at 8.1M-HCl. In the system $\text{GeCl}_4\text{-HCl-H}_2\text{O}$ the solubility of germanium is somewhat higher and the maximum corresponds to 6.7M-HCl. In both cases the maximum are very distinct and they correspond to the reversible change of the solid phase composition according to the reaction $\text{GeO}_2 \rightleftharpoons \text{GeCl}_4$. This behaviour of germanium is explained¹⁴ by the formation of chloro complexes of the $\text{Ge}(\text{OH})_x\text{Cl}_y^{4-x-y}$ type. For the acid concentrations lower than 6M-HCl these complexes are stepwisely hydrolyzed up to $\text{GeO}_2 \cdot x\text{H}_2\text{O}$ or to H_2GeO_3 . The formation of chlorogermanate complexes can be used also for the explanation of an other interesting effect, *i.e.*, the inverse temperature dependence of the solubility^{15,17-19}.

Comparing the data of the GeO_2 solubility in various acids with the sorption of germanium on silica gel one observes a distinct correlation: the sorption is inversely proportional to the solubility. This correlation is evident namely in the hydrochloric acid solutions where the solubility maximum corresponds to the sorption minimum. Assuming the most probable composition of the individual germanium complexes and its dependence on the hydrochloric acid concentration, these results can be explained supposing the sorption of two different types of neutral complexes:

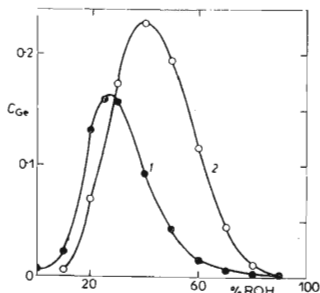


FIG. 8

Solubility of GeO_2 in the Solution of 10.65M-HCl with a Variable Content of EtOH and 1-BuOH

C_{Ge} Molar concentration of Ge in the solution, % ROH the content of the respective alcohol in the mixture vol.%. Curves: 1 EtOH, 2 1-BuOH. The solubility was measured by shaking the mixture at $23 \pm 1^\circ\text{C}$ for three weeks.

a) in the region of 1–6M-HCl germanium is sorbed in the form of partially hydrolyzed chloro complexes $[\text{Ge}(\text{OH})_x\text{Cl}_{4-x}]^0$, or, eventually, $[\text{GeO}(\text{OH})_x\text{Cl}_{2-x}]^0$. The increase of sorption with the acid concentration can be explained by the increase of the number of neutral molecules or by the increasing salt-out effect of the hydrochloric acid. In this region germanium behaves in an exactly opposite way than, *e.g.*, zirconium or hafnium²¹; b) with the increasing concentration of the hydrochloric acid germanium is dehydrolyzed up to GeCl_4 and the chlorogermanate anions are being formed. Due to the very high concentration of hydrogen ions these complexes are evidently from the most part associated and form the $\text{H}_{y-4}\text{GeCl}_y$ molecules. It may therefore be assumed that any further sorption of germanium on silica gel in the concentrated region, similarly as its sorption on the probe walls from solutions of >8M-HCl, are due to the molecular sorption of the non-dissociated molecules of the chlorogermanic acids that are being salted-out from the solution. In this case we may observe a certain analogy to the behaviour of protactinium²².

The sorption of at least two different types of complexes is indicated also by the differences in the sorption kinetics in 5M- and 10.65M-HCl (Fig. 3), by the dependence of sorption on the germanium concentration (Fig. 2b), and by the sorption from the aqueous-organic solutions.

Because the solubility of GeCl_4 in the hydrochloric acid decreases with the increasing temperature, an increase of sorption could be expected under these conditions. In fact, an exactly opposite dependence has been found (Fig. 2b, curves 1a–c). However, one should keep in mind that the sorption was studied using solutions with trace amounts of germanium while the solubility measurements were made with saturated solutions. The differences in sorption at different temperatures could be ascribed to the changes of the dissociation and sorption constants of individual complexes at the given concentration of the acid. In the case of solubility the higher temperature affects the decomposition of the chlorogermanic acids up to GeCl_4 . From this point of view it is remarkable that at higher temperatures the sorption minimum is shifted towards lower concentrations of the acid, similarly as the maximum on the solubility curve.

The sorption of germanium from the HClO_4 , HNO_3 , and H_2SO_4 solutions can be explained in two different ways: by the sorption of $\text{GeO}_2 \cdot x \text{H}_2\text{O}$ molecules (or $\text{GeO}(\text{OH})_2 \cdot x \text{H}_2\text{O}$), or by the sorption of neutral complexes of the $\text{Ge}(\text{OH})_x\text{A}_{4-x}$ types, eventually of the $\text{GeO}(\text{OH})_x\text{A}_{2-x}$ type (where A is a univalent anion of the respective acid). The evident coincidence of the individual dependences on Figs 1a, b, 2a, b justifies the assumption that the sorption mechanism of germanium is the same for all the acids under study and this fact corroborates the second possibility. If, however, this is the case, it must be expected, that in the concentrated solutions of perchloric and nitric acids germanium is present predominantly in the form of $\text{Ge}(\text{ClO}_4)_4$ and $\text{Ge}(\text{NO}_3)_4$ complexes associates, respectively. The fact that during the dissolution of GeO_2 in HNO_3 and HClO_4 the solid phase remains unchanged

at all concentrations of the acid need not disprove the existence of these complexes in the solution. Even in the case of the sulphuric acid, where the complexes $\text{Ge} \cdot (\text{SO}_4)_2$ and $\text{Ge}(\text{SO}_4)_3^{2-}$ are undoubtedly formed, the analysis of the solid phase¹¹ yields the composition of GeO_2 even in concentrated solutions and the shape of sorption curves is completely analogous to those measured in the perchloric and nitric acids.

Sorption from Aqueous-Organic Solutions

The assumption of the sorption of two different types of neutral complexes of germanium is corroborated even by the results obtained with the aqueous-organic solutions. When 1–6M-HCl was used as the base electrolyte, the results are presented on Figs 5a and b and they could be explained by a decrease of the hydration of $\text{Ge}(\text{OH})_x\text{Cl}_{4-x}$ complexes due to the lower concentration of water in the mixed solution. On the other hand, the sorption minima on the $\log K_d = f(C_{\text{ROH}})$ dependences in the solutions where GeCl_x^{4-x} complexes predominate (Figs 7–9) could be explained by the formation of ionic associates of the $[\text{SH}(\text{H}_2\text{O})_n]_{x-4} \cdot \text{GeCl}_x$ type, where S is the alcohol molecule. A similar behaviour was observed even for the protactinium sorption²³; in this case, however, K_d reaches minimum for $Q = 2$. The fact that the minima for protactinium and germanium appear at different values of Q could be caused by the different stability of the corresponding associates.

Certain difficulties arise if the anomalous behaviour of 2-propanol has to be explained. Because in this case a secondary alcohol is being dealt with, we may *a priori* expect the formation of an oxonium ion, composed of two protons and one molecule of the alcohol, e.g., of the structure of $\text{H} \dots \text{C}(\text{CH}_3)_2 \text{—} \overset{+}{\text{O}}\text{H} \dots \text{H}$. The evident analogy between the sorption of germanium on silica gel and the solubility of germanium dioxide in mixed solutions can be taken as an evidence for the formation of oxonium associates. As the used solutions represent an analogy of the isomolar series, the higher solubility of GeO_2 in solutions with $Q = 1$ indicates that germanium is dissolved in the form of a chlorogermanic acid solvated by the respective alcohol. Nevertheless this assumption can be definitely proved only by a direct evidence of the presence of these associates in the solution, or, eventually, by their isolation. The solid phase produced by the action of the hydrochloric acid in mixture with an alcohol on GeO_2 is probably composed of the solvated chlorogermanic acid.

The correspondence between the solubility and sorption is fully valid even for the sorption of germanium from the aqueous solutions of acetic acid²⁴. Similarly as in the case of alcohols, even in the sorption from the mixtures of acetic acid and diluted hydrochloric acid, the values of K_d gradually increase. If, however, 5.32M-HCl is used as the base electrolyte (in which the hydrolysis of germanium is substantially suppressed) the dependence of $\log K_d = f(C_{\text{CH}_3\text{COOH}})$ has a convex character. In the mixture with the concentrated hydrochloric acid the addition of the acetic acid

causes a sharp decrease of sorption. In this case the acetate or mixed chloro-acetate complexes of germanium are probably formed, which have a lower sorption ability on silica gel under the given conditions.

The observed behaviour of germanium could be exploited in various separation procedures²⁵ because in strongly acidic solutions only a limited number of elements is sorbed on silica gel.

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