REACTIONS OF Ge(IV) WITH AMINOCARBOXYLIC AND AMINOHYDROXYLIC CHELONES

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Reactions of GeO_2 with eight chelones were studied in dilute aqueous solutions by using the potentiometric neutralization titration method. The equilibrium formation constants were determined for the $Ge(OH)Y^-$ and $Ge(OH)(HY)$ complexes with EDTA, $Ge(OH)_2Z^-$ complex with NTA, and $Ge(OH)(OH_2)T$ complex with TEA. The conditions for formation of Ge(IV) chelates with chelones are discussed.

Germanic acid in aqueous solutions is commonly written as GeO_2, although the formulas $Ge(OH)_4(OH_2)_2$ or $H_2Ge(OH)_6$ represent its actual state in solutions with pH $2-8$ more properly. In alkaline solutions, two protons are consecutively detached[1], pK_{a1} 9·0 and pK_{a2} 12·2 ($I = 0·5$, $t = 25°C$). Polynuclear germanates are also formed at higher concentrations. In acidic solutions, pH < 3, cations have been observed to be formed through the reaction

$$Ge(OH)_i^{(4-i)+} + H^+ = Ge(OH)_{i-1}^{(5-i)+} + H_2O ; \quad K_{A,i} . \qquad (A)$$
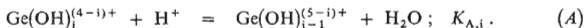
The values $pK_{A,i}$ $-0·17$, $0·22$, $0·47$, and $0·70$ ($i = 1, 2, 3,$ and 4, respectively) have been determined[2] for ionic strength $I = 0·5$.

Reactions of germanic acid with EDTA (H_4Y) are 2nd kind chelating reactions[3], water being created by condensation. In the anhydrous GeY compound, all the six coordination sites at the central atom are engaged in bonding to the Y^{4-} ligand[4]. In the monohydrate $Ge(OH)HY$ only the five-donor HY^{3-} ligand occurs, the sixth coordination site is occupied by the hydroxy group[4]. The reactions

$$GeO_2 + H_3Y^- = Ge(OH)Y^- + H_2O ; \quad K_B \qquad (B)$$

and

$$Ge(OH)HY = Ge(OH)Y^- + H^+ ; \quad K_C \qquad (C)$$
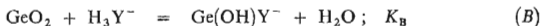
have been studied polarographically in aqueous solutions[5], log K_B 4·52, log K_C $-2·40$; the reaction (B) is very slow. For a study of the slowly establishing equilibrium

$$Ge^{4+} + H_4Y = GeY + 4H^+ ; \quad K_D \qquad (D)$$

titrimetric determination of the nonbonded EDTA has been used[6]; log K_D 5·3.

Chelones analogous to EDTA react with Ge(IV) similarly, only CDTA does not react[4]. NTA affords with Ge(IV) the 1 : 1 complex[7].

The reaction of Ge(IV) with EDTA proceeds slowly. For a determination of germanium, the reagent must be added in excess and the analysis must be conducted at elevated temperature; the mixture should be allowed to stand for about 10 min and the excess chelone titrated[8]. Addition of EDTA to solutions to be analyzed has also been used[9] for masking Ge(IV).

EXPERIMENTAL

C.p. preparations of cyclohexanediamine-N,N,N′,N′-tetraacetic acid (CDTA), nitrilotriacetic acid (NTA, H_3Z), and iminodiacetic acid (IDA), germanium dioxide, and triethanolamine (TEA, H_3T), and *p.a.* preparations of Na_2H_2Y and KNO_3, all products of Lachema, Brno, were used. Oxalamide-N,N′-diacetic acid (OADA) and nitrilotripropionic acid (NTP) were prepared in our laboratory[10,11]. Hydroxyethyliminodiacetic acid (HIDA) was supplied by the Department of Analytical Chemistry, Faculty of Pharmacy, Bratislava. The concentrations of the chelating agents in solutions were determined by potentiometric neutralization titrations.

Titrations with 0·1M-NaOH at 20 ± 1°C were carried out by using ABU-12, PHM-26, TTT-11, and SBR instruments (Radiometer, Copenhagen). The response of the G-202B glass electrode used in conjunction with a saturated calomel electrode was checked by titrating a strong acid (HNO_3) with a strong base (NaOH). Prior to each titration, the pH-meter was adjusted by using phosphate buffer, pH 6·50 (Radiometer). The various solutions, in which the equilibrium established slowly, were measured on the same apparatus. The ionic strength of the solutions measured was $I = 0·10 ± 0·01$ (KNO_3).

The $\bar{z}$ function represents the average number of mol hydrogen ions detached from one mol H_4T^+, H_4Y, or H_3Z acid. Only hydrogen ions detached as free protons, not those taken up in the condensation of water during the formation of the chelates, contribute to the value of $\bar{z}$. In the program used[12], a minimization procedure is employed to calculate the "optimum" constants for the complex equilibria considered. The U quantity characterizes the difference between the experimental $\bar{z}$ values and the $\bar{z}$ value calculated for the chosen constant of the equilibrium treated. The U value is minimum for the "optimum" constant chosen, which is regarded as correct. The calculations were carried out on a Tesla 200 computer at the Computer Laboratory, Technical University, Brno.

RESULTS

0·002M solutions of GeO_2 and the chelone in question with initial pH ~2 were prepared, and their potentiometric titration curve at pH 2−10 was recorded after 24 h. Complex formation was only observed with EDTA, NTA, and TEA (Fig. 1); in the case of the remaining reagents the titration curves for mixtures of the constituents were identical with those resulting from superposition of the titration curves for the individual components.

The same titrations were performed with $0.01\text{M-}H_3BO_3$ and 0.002M solutions of the chelones; inexpressive complexation was observed only for TEA. In solution of $0.02\text{M-}H_3BO_3$ and 0.03M-TEA, the equilibrium constant $\log K_E = 1.3$ for the reaction

$$H_3BO_3 + H_3T = \text{complex} + x\,H_2O\,; \quad K_E \qquad (E)$$
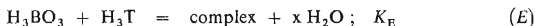
was found at pH $6.6-7.6$. We suppose that, most likely, the complex is BT, hence $x = 3$.

With regard to the slow establishment of equilibrium in the Ge(IV)–EDTA system[5], the solutions were mixed as given in Table I, heated to $30-35°C$ for $2-3$ h, and stored in closed vessels at room temperature. The pH was measured after $3-4$ days. It was considered equilibrium, if the results of three successive measurements did not differ more than ±0.01 pH unit. The equilibrium established usually in $4-5$ weeks. From the titration curves, during the recording of which the equilibrium was not attained, it follows that at pH ~4, one proton is consumed in the reaction of GeO_2 with H_2Y^{2-}.

The occurrence of a single reaction, (F), was therefore assumed:

$$GeO_2 + H_2Y^{2-} + H^+ = Ge(OH)Y^- + H_2O\,; \quad \log K_F = 7.46 \pm 0.01\,. \quad (F)$$
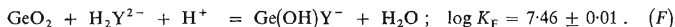
However, rather high differences were obtained between the experimental and the calculated values at pH ~3, the reaction (G) was therefore also taken into account:

$$GeO_2 + H_2Y^{2-} + 2\,H^+ =$$
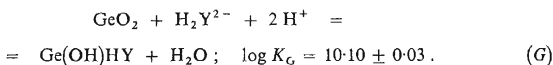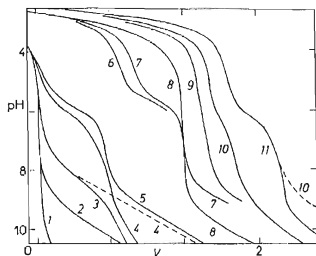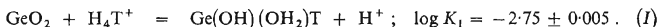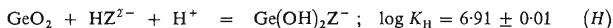$$= Ge(OH)HY + H_2O\,; \quad \log K_G = 10.10 \pm 0.03\,. \qquad (G)$$

Fig. 1

Titration Curves for GeO_2–Chelone Systems

Solid lines: experimental curves; dashed lines: calculated lines for nonreacting components. Volume of 0.1M-NaOH added to 25 ml solution: v for curves $1-8$, $v-0.5$ for curves $9-11$. $c_{HNO_3} = 2$ mmol/l. Chelone: 1, 2 no chelone; $3-5$ H_4T^+ (2 mmol/l), $6-8$ H_3Z (2 mmol/l), $9-11$ H_4Y (1.6 mmol/l); c_{GeO_2} (mmol/l): 1 0, 2 2, 3 0, 4 2, 5 4, 6 4, 7 2, 8 0, 9 4, 10 2, 11 0.

The low s and U values (Table I) indicate that the equilibria (F) and (G) describe the system under study properly.

In the reactions of GeO_2 with NTA and TEA, respectively, the equilibrium did not establish slowly. The solutions with the compositions as given in Table I were prepared; their acidity measured after 6, 24, and 48 h did not vary. The pH values obtained for these solutions were used in the calculations. In the plots, the points corresponding to the various solutions approach closely the titration curves obtained from automatic titration (hence, without waiting for the equilibrium to establish) for solutions of the same composition. For both reagents, formation of a single complex was observed, as described by the equations

$$GeO_2 + HZ^{2-} + H^+ = Ge(OH)_2Z^- \; ; \quad \log K_H = 6.91 \pm 0.01 \quad (H)$$

$$GeO_2 + H_4T^+ = Ge(OH)(OH_2)T + H^+ \; ; \quad \log K_I = -2.75 \pm 0.005 \, . \quad (I)$$

Detailed data are given in Table I.

DISCUSSION

Second kind chelating reactions proceed best at a pH at which the complex formation is only accompanied by condensation of water, while hydrogen or hydroxyl ions do not take part in the reaction[3]. The value found by us as optimum for reaction of GeO_2 with EDTA, pH 1·9, is in fair agreement with the paper[6], reporting 0·03M-HCl as the optimum medium.

The NTA and TEA reagents occupy four coordination sites at the central Ge(IV) atom. The reaction with NTA proceeds in acidic solutions, where the carboxy groups

TABLE I

Conditions of Study of Ge(IV)–Chelone Complex Formation

Chelone, pK_a	Total concentration mmol/l		pH	$\bar{z}$	Number of points	s^a	U
	chelone	GeO_2					
EDTA 2·40, 2·89	1·9	2·9—5·7	3·0—4·8	0·7—1·5	25	0·02	0·007
NTA 1·89, 2·49	7—10	10—22	4·1—6·3	1·2—1·9	16	0·02	0·008
TEA 8·01	5—30	6—36	3·0—5·1	0·1—0·7	8	0·01	0·002

^{a} Standard deviation calculated from the differences $\bar{z}_{exp} - \bar{z}_{cal}$.

of the reagent are not completely dissociated. Although formed in acidic medium, the $Ge(OH)_2Z^-$ complex involves no acidic proton from germanic acid, the two of them having been taken up in condensation of water. The decomposition of $Ge(OH)_2Z^-$ in insufficiently acidic medium is a result of deprotonation of the free NTA. The HZ^{2-} ion predominating in neutral solutions requires an addition of acid to react with GeO_2. The complex with TEA, on the other hand, appears at pH > 3; more acidic medium does not favour the detachment of a proton during the interaction of GeO_2 with H_4T^+. In the $Ge(OH)(OH_2)T$ complex, steady in neutral or weakly alkaline solutions, one of the acidic protons of germanic acid is preserved; its detachment was not observed at pH $\leq$ 10·5.

Carboxy groups are bonded to the central Ge(IV) atom more strongly than hydroxy groups. The Ge(OH)HY complex in aqueous solution exhibits acidic reaction, because the carboxy group that is not bonded in the complex dissociates. The analogous complex of Ge(IV) with N-hydroxyethylethylenediamine-N,N',N'- -triacetic acid[4] does not give an acidic reaction in water, as all of the three carboxy groups are bonded in the complex and the hydroxy group does not dissociate in aqueous solution. The tetradentate NTA reagent forms a complex with Ge(IV), in contrast to HIDA, in which one of the carboxy groups of NTA is replaced by the —CH_2OH group. The low reactivity of the hydroxy group of HIDA makes the compound actually a tridentate reagent, not forming complexes with Ge, similarly as the tridentate IDA and OADA reagents. Complexes of chromotropic acid and pyrocatechol have been used to demonstrate the lower stability of Ge(IV) chelates with six-membered rings as compared with those with five-membered rings[13]. NTA forms five-membered rings and reacts with Ge(IV), whereas NTP, forming six-membered rings, does not react. Steric reasons account most likely for the fact that CDTA does not react with GeO_2 or the reaction is extremely slow[4].

Stability of ML type complexes is commonly mutually compared in terms of the stability constants $K = [ML]/[M][L]$, characterizing the equilibrium between the free, nonbonded M and L species and the ML complex, in which the two constituents are mutually bonded. There is only one difference between the state of the free and the bonded species, namely, the bonding between M and L. In the solutions under study, however, equilibria other than that represented by the stability constant establish, and consequently, additional differences are observed between the state of the free component, predominating in the solution, and the state of the component bonded in the complex. Many ligands are protonized in aqueous solutions. For instance, EDTA in solutions pH $\sim$5 exists predominantly in the H_2Y^{2-} anion form; in such solutions, the equilibrium constant of the reaction between the M and H_2Y^{2-} components is directly obtained. Since solutions in which the predominating species are HY^{3-} or Y^{4-} can be prepared and measured, there is no problem in converting the primarily determined equilibrium constant into the stability constant. The central ions in aqueous solutions are largely solvated by water (*e.g.*,

$Cu(OH_2)_4^{2+}$) or complexed by dissociation products of water (e.g., $B(OH)_3$ and CrO_4^{2-}). Formation of mixed complexes such as $As(OH)_5(OH)_2$, $Ge(OH)_4(OH_2)_2$, or $MoO_2(OH)_4^{2-}$ has been frequently encountered. The prevailing $Ge(IV)$ species in aqueous solutions with pH $1-8$ is hydrated molecule of GeO_2; in this form it takes part in the equilibria measured. Conversion of the equilibrium constant into the stability constant requires that the dissociation of germanic acid to the Ge^{4+} cation be known quantitatively. The dissociation constants $K_{A,i}$ have been determined[2] for various ionic strength values, among them for $I = 0.1$. Taking into account that in solution with $I = 0.1$, pH > 1 and all of the four $pK_{A,i}$ values lie in the range of 0.26 ± 0.44, we find that only a negligible fraction of the $Ge(IV)$ present can occur as Ge^{4+}. As a consequence, the $K_{A,i}$ values cannot have been determined precisely, and the $K_{A,1}$ values may involve errors of orders of magnitude. Transforming the obtained equilibrium constants of the Ge–EDTA system into the stability constants, different values are obtained for the $Ge(OH)HY$ and GeY complexes. In the case of such transformed stability constants, the way in which the transformation has been performed may not be unique. Use of little reliable data in the transformation reduces the quality of information on the complex system in question. In view of this, we cannot recommend transformation of equilibrium constants into stability constants if it may be carried out in several ways or if the constant characterizing the conversion of the species prevailing in the solution into that whose activity is involved in the stability constant is not known reliably enough.

If the dissociation of the species prevailing in the solution to the aquo complex of the species that is involved in the complex (e.g., $B(OH)_3 \rightarrow B(OH_2)_4^{3+}$, $H_3AsO_4 \rightarrow As(OH_2)_6^{5+}$, $MoO_4^{2-} \rightarrow MoO_2(OH_2)_4^{2+}$) cannot be evaluated reliably at least for one of the complex components, the complex equilibria should be characterized by the equilibrium constants rather than by the stability constants. Regarding the fact

TABLE II

Equilibrium Constants of Ge(IV)–Chelone Complexes

$I\ 0.10 \pm 0.01$, $t = 20 \pm 1°C$.

Chelone		Reaction	$\log K$	
			this work	ref.[5]
EDTA	(H_4Y)	$GeO_2 + H_3Y^- \rightarrow Ge(OH)Y^-$	4·57	4·25
		$Ge(OH)HY \rightarrow Ge(OH)Y^- + H^+$	—2·64	—2·40
NTA	(H_3Z)	$GeO_2 + H_2Z^- \rightarrow Ge(OH)_2Z^-$	4·42	
TEA	(H_3T)	$GeO_2 + H_3T \rightarrow Ge(OH)(OH_2)T$	5·26	

that a chemical equilibrium may be described adequately by several different chemical equations (Eqs (B) and (F)), the following rules can be recommended for selection of chemical equilibria:

$a)$ Simple acid–base reactions of the type HA → A⁻ + H⁺, such as Eq. (C), should be favoured

$b)$ If rule $a)$ cannot be applied, an equation is chosen such that a minimal number of H⁺ and OH⁻ ions are involved. For instance, reactions $(F)–(I)$ are not suitable.

$c)$ If several possibilities emerge from rule $b)$, an equation is chosen such that the species involved represent best the actual species in the solutions. For instance, reaction (B) is preferred to reaction

$$GeO_2 + H_4Y = Ge(OH)HY + H_2O ; \quad K_J \qquad (J)$$

because the measurements have been carried out with solutions in which $[H_3Y^-] > > [H_4Y]$.

When characterizing the equilibrium by the constant of a chemical reaction chosen according to the above rules, a comparatively simply formulated equilibrium is obtained, for the evaluation of which a minimal number of low precision data is used. If the chemical equation concerned is given in addition, there is no problem in transforming this constant into other equilibrium or stability constants, provided that sufficiently accurate data concerning the dissociation of the components involved are known.

A survey of the complex equilibria studied in this work, characterized taking into account the rules suggested, is given in Table II. Our data are in a good agreement with published values.

REFERENCES

1. Ingri N.: Acta Chem. Scand. *17*, 597 (1963).
2. Nazarenko V. A., Flyantikova G. V.: Zh. Neorg. Khim. *13*, 1855 (1968).
3. Bartušek M.: Chem. Listy *73*, 1036 (1979).
4. Konopik N., Meszaros P.: Monatsh. Chem. *100*, 649 (1969).
5. Konopik N., Meszaros P.: Monatsh. Chem. *99*, 902 (1968).
6. Nazarenko V. A., Vinarova L. L., Lebedeva N. V.: Zh. Neorg. Khim. *14*, 700 (1969).
7. Lebedeva N. V., Egorova A. L.: Zh. Neorg. Khim. *14*, 706 (1969).
8. Nazarenko V. A., Lebedeva N. V., Vinarova L. I.: Zh. Anal. Khim. *19*, 87 (1964).
9. Piryutko M., M., Benediktova I. V.: Zh. Anal. Khim. *29*, 922 (1974).
10. Šprta F., Bartušek M.: M.: This Journal *39*, 2023 (1974).
11. Votava J., Bartušek M.: This Journal *40*, 2050 (1975).
12. Mikanová E., Bartušek M., Havel J.: Scripta Fac. Sci. Nat. Univ. J. E. Purkyně Brně, Chemia *10*, 3 (1980).
13. Mikešová M., Bartušek M.: This Journal *44*, 3256 (1979).

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