CHELATES OF VANADIUM(V) WITH ORGANIC HYDROXY COMPOUNDS IN AQUEOUS SOLUTIONS

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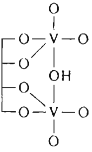
The formation of vanadium(V) complexes has been examined potentiometrically by the method of acidimetric titrations of aqueous solutions at pH 7—5. The composition has been determined and the formation constants have been calculated for the oxalate chelates $VO_2Ox_2^{3-}$ and $VO_2Ox.(OH)^{2-}$, the maltol chelate $VO_2A_2^-$, the ternary complex VO_2OxA^{2-}, and for binuclear and tetranuclear complexes with tartrate, glycolate, sorbitol, and mannitol. The structure of the complexes is discussed in terms of the consumption of protons for their formation.

In acid aqueous solutions (pH < 1), the noncomplexed vanadium(V) is present in the form of VO_2^+ cations[1]; as the acidity is decreased, yellow decavanadates $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$, and $V_{10}O_{28}^{6-}$ appear. Highly dilute solutions contain the VO_3^- (metavanadate) species at pH ≈ 8 and the HVO_4^{2-} species at pH $\geqq$ 10; at higher vanadium concentrations, these mononuclear anions are in equilibrium with the binuclear[2] $HV_2O_7^{3-}$ species in more alkaline solutions and with the trinuclear $V_3O_9^{3-}$ and the tetranuclear $V_4O_{12}^{4-}$ species in less alkaline solutions. In approximately neutral solutions the decavanadates decompose slowly[3], which hampers the study of vanadium(V) systems in weakly acid solutions and makes impossible an accurate determination of the equilibrium protolysis constant for the conversion of VO_2^+ to VO_3^-. Complex compounds of vanadium(V) are formed in highly acid solutions by substitution of the water molecules in the $VO_2(OH_2)_4^+$ species for ligands. In approximately neutral aqueous solutions, complexes arise from a condensation reaction of the solvated metavanadate with the complexing agent; molecules of water emerge as the side product of this second kind complexing reaction[4]. Acid solutions are optimal for the reduction of V(V) by some reagents such as *o*-diphenol[5]; the reduction to V(IV) is manifested by a blue colour. In nearly neutral solutions V(V) is not reduced or the reduction is very slow. Neutral or alkaline solutions are to be acidified cautiously, because the kinetically almost inert decavanadates can form even during a short-term local acidification in solutions with pH > 8.

In vanadium(V)–oxalic acid (H_2Ox) aqueous systems, the $VO_2Ox_2^{3-}$ and VO_2Ox^- complexes have been identified[6–11]. The complete X-ray structure analysis[12] of the salt $(NH_4)_3VO_2Ox_2$ points to a somewhat distorted octahedral configuration of the oxygen atoms about the central V^{5+} ion. The oxygen atoms of the VO_2^+ group are in the *cis* position and their distances from the central atom are not quite identical, nor are precisely identical the bonding distances of the oxygen atoms in the chelate ring.

The coloured compounds of vanadium(V) with maltol (3-hydroxy-2-methyl-4-pyrone, HA) have been studied photometrically[13,14]. The yellow $VO_2A_2^-$ complex appearing in neutral solutions is transformed into the violet HVO_2A_2 and the blue $H_2VO_2A_2^+$ species on acidification. The complex acid HVO_2A_2 in acid aqueous-methanolic solutions is readily transformed into the red ester $VO(OCH_3)A_2$. The results of a number of investigations of vanadium(V)–tartaric acid (H_2T) mixtures are mutually inconsistent, thus indicating a complexity of the system. In the study[15], the formation was proved of yellow-orange tartrate complexes with divanadate (*I*) and tetravanadate (*II*) in which tartrate is bonded to vanadium *via* two oxygen atoms of the hydroxy groups and two oxygen atoms of the carboxy groups. The system of vanadium(V)–glycolic acid (HG) was studied[16] by potentiometric titrations at pH 7–4; the $V_4O_{11}G_2^{4-}$ and $V_2O_5G_2^{2-}$ complexes were identified, the glycolate being supposedly bonded in them as a monodentate ligand. This assumption, however, is in contrast with the observed behaviour of glycolate in the chelation of B(III) (ref.[17]), Ge(IV), and Mo(VI) (ref.[18]). Of aliphatic α-hydroxy acids, mandelic acid was studied[19] as a chelating agent for vanadium; here, too, polynuclear complexes were found, two phenyl acetate groups being coordinated to a divanadate or a cyclic tetravanadate.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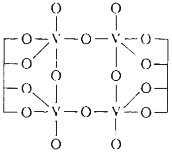
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In neutral solutions of alcoholic sugars, sorbitol or mannitol (Su), lightly yellow tetranuclear vanadium complexes are formed, two molecules of reagent being bonded to a tetravanadate[19,20]. On acidification the complex is protonated and acquires red colour. No reduction of vanadium(V) by alcoholic sugars has been observed in approximately neutral solutions.

EXPERIMENTAL

A quantity of $NaVO_3.2\,H_2O$ (Reakhim, USSR) was dissolved in water and the content of vanadium(V) was determined by titration with a ferrous salt using potentiometric indication. Sodium oxalate, sodium potassium D-tartrate, and potassium nitrate *p.a.* (Lachema, Brno) were used with no pretreatment. Maltol *p.a.* (Merck, Darmstadt), D-sorbitol, and D-mannitol of pharmacopoeial purity *pro infusi* were dried over silica gel in a vacuum dessicator prior to use. A solution of sodium glycolate was prepared by neutralization of glycolic acid (pure grade, Lachema, Brno) with sodium hydroxide using phenophthalein as indicator. The 0·1M-HNO_3 titrant solution was adjusted to $I = 0{\cdot}5$ using potassium nitrate.

The potentiometric titration curves were recorded on an apparatus of Radiometer, Copenhagen, comprising ABU-12, PHM 26, TTT 11, and SBR-2c instruments; the electrode system consisted of a G 202 B glass electrode and a K 401 calomel electrode. The pH-meter was standardized by means of a phosphate buffer, pH 6·50 ± 0·02, and a phthalate buffer, pH 4·00 ± 0·02 (in the conventional activity pH scale). The solutions were made up at least 24 h before the measurement; the ionic strength of the solutions was adjusted to $I = 0{\cdot}5$ by using KNO_3. The temperature was held at 20 ± 1°C during the titrations. The equilibrium was regarded as established when on interrupting the titration the pH remained constant for a minimum of 10 min. The titration curves served for the calculation of the $\bar{z}$ function, representing the average number of moles of hydrogen ions taken up in the reaction with one mole of vanadium as VO_3^- or $(VO_3^-)_n$. The equilibrium constants were calculated in terms of the activity of hydrogen ions and concentrations of the remaining components.

The calculations of the equilibrium constants were performed by employing the POT-LETAG program[21] modified for a faster performance. The minimization procedure LETAG seeks for the "optimum" values of the equilibrium constants yielding the best fit of the calculated $\bar{z}$ values ($\bar{z}_{calc}$) to the observed data ($\bar{z}_{obs}$). The fit was estimated in terms of the quantity $U = \sum(\bar{z}_{obs} - \bar{z}_{calc})^2$, the minimum value of which was sought. The program then calculates the S quantity referring to the standard deviation of $\bar{z}$ (see Table I caption) and the expression $s \log K = \frac{1}{2} \,.\, \log (K + s) - \frac{1}{2} \log (K - s)$, where K is the average equilibrium constant and s is its standard deviation[22].

RESULTS

Solutions of the reagents, *viz.* NaG, Na_2T, Na_2Ox, and CH_3COONa, in a concentration of 0·15 mol l^{-1}, and similar solutions containing, in addition, $NaVO_3$ in a concentration of 0·02 mol l^{-1}, were titrated with acid in the region of pH 9–5. The titration curves of vanadium(V) alone and in a mixture with acetate are identical in shape, the solution turns yellow and protons are taken up at pH < 8·5. In nonchelating media the kinetically nearly inert decavanadate is formed; the solutions remain yellow even several hours after their alkalization. In this respect they differ from the yellow chelates of vanadium(V) with tartrate, maltol, or alcoholic sugars, which decompose on alkalization and the colour disappears. Consumption of acid for the titration of solutions of the reagents alone takes place at pH < 6; the titration curves of solutions containing V(V) and a chelating agent are identical in shape at pH 9–8; consumption of protons is observed in oxalate solutions at pH < 8 and in tartrate and glycolate solutions at pH < 7·5. At pH < 6 the titration curves exhibit an ill-developed potential jump, from which the number of protons consumed per vanadium(V) atom in metavanadate can be estimated to be two in oxalate, one in tartrate, and 0·85 in glycolate solutions. Reduction of V(V) by tartrate or glycolate at room temperature could be observed after 24 h only at pH < 3; the reaction was accompanied by a blue colouration of the solution.

Vanadium(V)–Oxalate System

The titration curves were recorded for solutions whose composition is given in Table I. The solutions remain nearly colourless, the complex formed has a yellow-green

TABLE I

Parameters of the reaction $h\,H^+ + m\,VO_3^- + x\,X + y\,Y = \text{product} + w\,H_2O$ conducted at 20 ± 1°C, $I = 0{\cdot}5\,(KNO_3)$. The products are formulated conventionally without the molecules of bonded solvent; for the complexes with alcoholic sugars, the SuH_{-2}^{2-} ligand is considered

Parameters $h\ m\ x\ y$	Product of the reaction	Labelling reaction	log $K \pm s$. (log K)[a]	a[b] %	Parameters of calculation[c]
	Binary system with oxalate (Ox^{2-}); c_V = 5 and 20 mmol l^{-1}, c_X/c_V = 2·5, 5·0, 7·5[d], $\bar{z}$ = 0·2–1·8, pH 7·6–6·0				
1 0 1 –	HOx^-	–	3·56		$U = 4{\cdot}3 \cdot 10^{-2}$
0 3 0 –	$V_3O_9^{3-}$	*A*	7·20	50–4	$S = 0{\cdot}028$
0 4 0 –	$V_4O_{12}^{4-}$	*B*	10·15	35–1	$p = 54$
2 1 2 –	$VO_2Ox_2^{3-}$	*C*	17·42 ± 0·002	8–58	
1 1 1 –	$VO_2Ox(OH)^{2-}$	*D*	8·58 ± 0·03	3–12	
	Binary system with tartrate (T^{2-}); c_V = 5 and 20 mmol l^{-1}, c_X/c_V = 2·5, 5·0, 7·5[d], $\bar{z}$ = 0·1–0·8, pH 7·3–6·1				
1 0 1 –	HT^-	–	3·68		$U = 8{\cdot}6 \cdot 10^{-3}$
0 3 0 –	$V_3O_9^{3-}$	*A*	7·20	52–6	$S = 0{\cdot}014$
0 4 0 –	$V_4O_{12}^{4-}$	*B*	10·15	35–2	$p = 44$
4 4 2 –	$V_4O_8(TH_{-2})_2^{4-}$	*E*	39·75 ± 0·008	2–68	
1 2 1 –	$HV_2O_5(TH_{-2})^{3-}$	*F*	11·82 ± 0·02	10–27	
	Binary system with glycolate (G^-); c_V = 5 and 20 mmol l^{-1}, c_X/c_V = 4·4 and 6·6[d], $\bar{z}$ = 0·1–0·9, pH 6·9–5·2				
1 0 1 –	HG	–	3·52		$U = 9{\cdot}6 \cdot 10^{-3}$
0 3 0 –	$V_3O_9^{3-}$	*A*	7·20	54–2	$S = 0{\cdot}015$
0 4 0 –	$V_4O_{12}^{4-}$	*B*	10·15	35–0·3	$p = 46$
2 4 2 –	$V_4O_{10}(GH_{-1})_2^{4-}$	*G*	25·42 ± 0·002	8–49	
2 2 2 –	$V_2O_4(GH_{-1})_2^{2-}$	*H*	18·66 ± 0·007	2–79	
	Ternary system with oxalate ($X = Ox^{2-}$) and maltol (Y = HA) c_V = 5 mmol l^{-1}, c_X/c_V = 7·5, c_Y/c_V = 2·5 and 5·0[d], $\bar{z}$ = 0·2–1·9, pH 6·9–4·8				
1 0 1 0	HOx^-	–	3·56		$U = 3{\cdot}7 \cdot 10^{-3}$
2 1 2 0	$VO_2Ox_2^{3-}$	*C*	17·42	1–63	$S = 0{\cdot}016$
1 1 1 0	$VO_2Ox(OH)^{2-}$	*D*	8·46	0·1–0·5	$p = 17$
0 1 0 2	$VO_2A_2^-$	*I*	7·31 ± 0·01	80–4	
1 1 1 1	VO_2OxA^{2-}	*J*	12·67 ± 0·02	18–50	

TABLE I

(*Continued*)

Parameters h m x y	Product of the reaction	Labelling reaction	$\log K \pm s$. $(\log K)^a$	a^b %	Parameters of calculation^c
Ternary system with tratrate ($X = T^{2-}$) and alcoholic sugar ($Y = Su$)^e $c_V = 10$ mmol l^{-1}, $c_X/c_V = 5^d$, $c_Y/c_X = 2·5$, 5·0, 10·0 (sorbitol), 6·25, 12·5, 25·0 (mannitol), $\bar{z} = 0·1-0·9$, pH 6·9—5·6					
1 0 1 0	HT^-	—	3·68		$U = 7·6 . 10^{-3}$
0 3 0 0	$V_3O_9^{3-}$	*A*	7·20	14—0	$4·2 . 10^{-3}$
0 4 0 0	$V_4O_{12}^{4-}$	*B*	10·15	5—0	$S = 0·017$
				2—0	0·013
4 4 2 0	$V_4O_8(TH_{-2})_2^{4-}$	*E*	39·79 ± 0·02	1—83	$p = 27$
			39·81 ± 0·02	2—83	
1 2 1 0	$HV_2O_5(TH_{-2})^{3-}$	*F*	11·62 ± 0·18	2—8	25
			11·64 ± 0·31	1—4	
0 4 0 2	$V_4O_{10}(SuH_{-2})_2^{2-}$	*K*	14·47 ± 0·02	59—1	
			13·87 ± 0·03	37—0	
0 2 0 2	$V_2O_4(SuH_{-2})_2^{2-}$	*L*	6·86 ± 0·04	28—1	
			6·87 ± 0·01	53—3	
2 4 1 1	$V_4O_9(TH_{-2})(SuH_{-2})^{4-}$	*M*	27·29 ± 0·03	10—34	
			27·11 ± 0·03	9—33	

[a] K is the mixed constant; the $s(\log K)$ value is given only for those constants that were optimized for the system in question; [b] $a = 100m\,[\text{product}]/c_V$; the higher a value is given first for those complexes only that are present in neutral solutions at the beginning of the titration and whose concentration diminishes on acidification; [c] $U = \sum_{i=1}^{p} (\bar{z}_{obs} - \bar{z}_{calc})^2$, $S = [U/(p-q)]^{1/2}$, where p is the number of experimental points and q is the number of optimized equilibrium constants; [d] all the possible combinations of the c_V, c_X/c_V, and c_Y/c_V values were used; [e] where a pair of data is given, the first value pertains to sorbitol, the second to mannitol.

tint. Solutions containing oxalate in lower concentrations ($c_{Ox}/c_V = 1·5$ or $1·0$) turned yellow on account of the forming decavanadate; the titration curves were not evaluated.

Assuming that the reaction taking place in the solution is

$$M + n\,L + h\,H^+ = ML_n + w\,H_2O \qquad (N)$$

with the equilibrium constant K_N, and defining the $\bar{z}$ quantity as

$$\bar{z} = h[ML_n]/c_M = h[ML_n]/([M] + [ML_n])\,, \qquad (1)$$

we have

$$\mathrm{pH} = (n/h)\log[\mathrm{L}] + (1/h)\log K_\mathrm{N} + (1/h)\log[(h - \bar{z})/\bar{z}]\,. \tag{2}$$

In the form

$$\mathrm{pH} = \mathrm{f}(\log \mathrm{L})_{\bar{z}=\mathrm{const}}\,, \tag{3}$$

the plot of Eq. (*2*) is linear and its slope is n/h. In the presence of polynuclear complexes, function (*3*) is to be evaluated only for a constant c_M. An approximate value of the constant K_N, suitable for entering as input data for the calculation, is obtained from Eq. (*4*) which is valid for $\bar{z} = h/2$,

$$\log K_\mathrm{N} = h\,\mathrm{pH} - n\log(c_\mathrm{L} - nc_\mathrm{M}/2)\,. \tag{4}$$

The titration curves in oxalate solutions display a jump at $\bar{z} \approx 2$, indicating that $h = 2$, and function (*3*) leads to $n/h. = 1$ The K_N values calculated from the experimental points inserting $n = h = 2$ were different for the two c_M values, hence, polynuclear species are involved in the equilibrium. Data of the formation of trivanadates and tetravanadates (reactions (*A*) and (*B*), Table I) were taken from ref.[23] The processed data for the assumed reactions (*A*), (*B*), and (*C*) give a reasonably small value of $S = 0{\cdot}042$; thus the principal product of the chelating process is $\mathrm{VO_2Ox_2^{3-}}$. By taking into account reaction (*D*) as a supplementary process, a considerable decrease was obtained of the differences between the observed and the calculated $\bar{z}$ values, and the S value dropped down to 0·028. Hence, the $\mathrm{VO_2Ox(OH)^{2-}}$ species appears to a lesser extent as well. We failed to detect the $\mathrm{VO_2Ox^-}$ complex whose formation in acid solutions has been reported[7]; presumably, it arises from a protonation of the $\mathrm{VO_2Ox(OH)^{2-}}$ complex in more acid solutions. The constants listed in Table I characterize the equilibrium of formation of products from the starting mononuclear components. In the solutions studied, trinuclear and tetranuclear complexes predominate at the beginning of the titration, and are transformed into oxalate complexes on acidification. The transformation of the oligovanadate into the mononuclear complex is a real equilibrium characterizing the situation in the solution. The value of the constant for this real equilibrium can be calculated from the equilibrium constants given in Table I.

Vanadate(V)*–Tartrate System*

Tartrate solutions ($I = 0{\cdot}5$, $\mathrm{NaNO_3}$) were titrated at pH 4·7–3·2 in the absence of vanadium to afford the dissociation constants of tartaric acid, $\mathrm{p}K_{\mathrm{a}1} = 2{\cdot}675 \pm \pm 0{\cdot}02$, $\mathrm{pK_{a2}} = 3{\cdot}685 \pm 0{\cdot}001$ ($S = 0{\cdot}001$, 13 points). Colourless solutions of Na.$\mathrm{.VO_3}$ with NaKT (for details see Table I) turn yellow to red on acidification. The shape of the curves $\bar{z}(\mathrm{pH})_{c_\mathrm{M},c_\mathrm{T}=\mathrm{const.}}$ depends considerably on the concentrations of both tartrate and vanadium, thus indicating the presence of polynuclear species. The plot (*3*) for a constant c_M is linear and its slope gives the value of n/h, 0·51 to 0·58. The inexpressive potential jump on the titration curve indicates the consumption of one mole of hydrogen ions per mole of metavanadate, hence, the components react in the ratio $VO_3^- : T^{2-} : H^+ = 2 : 1 : 2$. The predominating formation of such a binuclear complex was not confirmed by the POT-LETAG analysis; a better fit was obtained for the tetranuclear complex, the *S* value for reactions (*A*), (*B*), (*E*) is 0·056. A number of other equilibria were also tested and the optimum was reached if the binuclear complex (reaction (*F*)) was assumed to be also formed in a small amount; this complex appears mainly at higher pH values.

Vanadium(V) – *Glycolate System*

The dissociation constant of glycolic acid, as obtained from a set of 9 points of the titration curve of sodium glycolate in the region of pH 4·6–3·1, is $pK_{a1} = 3{\cdot}520 \pm \pm 0{\cdot}001$ ($S = 0{\cdot}001$). The colourless solutions of vanadium(V) and glycolate titrated with acid acquite a slight yellow-green tint if glycolate is present in a sufficient excess. Solutions with the c_G/c_M ratio of 2·5 turned yellow on account of decanadate formed; their titration curves were note valuated. The plot (*3*) for a constant c_M gives the n/h ratio in the region of 0·76 to 1·01. This, along with the inexpressive jump on the titration curve at $\bar{z} \approx 0{\cdot}85$, indicates roughly the proportion $VO_3^- : G^- : H^+ = = 1 : 1 : 1$. The POT-LETAG program gave an unsatisfactory fit to the experiment for the mononuclear complex ($S = 0{\cdot}096$) and a slightly better fit for the binuclear complex ($S = 0{\cdot}083$). The minimum deviations of the calculations from the experimental data were obtained with a model involving equilibria (*A*), (*B*), (*G*), and (*H*) (Table I). The distribution diagram shows that at the beginning of the titration, the tetranuclear complex with two glycolates is predominantly formed, turning into the binuclear chelate, also with two glycolates, on acidification.

Vanadium(V)-*Maltol System*

If neutral solutions of vanadium(V) and of maltol are mixed together, yellow colour appears, while the acidity remains unchanged. This implies that hydrogen ions do not take part in the reaction of maltol with metavanadate, and such reactions do not lend themselves to study by neutralization titrations. For an indirect investigation, two solutions of maltol ($c = 0{\cdot}025 \text{ mol l}^{-1}$), one free of vanadium, the other containing V(V) in a concentration of $0{\cdot}01 \text{ mol l}^{-1}$, were titrated with 0·1M-NaOH, and the neutralization of maltol as a weak acid was followed ($pK_a = 8{\cdot}59$ for $I = 0{\cdot}5$ and $t = 20°C$). The consumption of the base necessary for attaining a pH value in the former solution was five times that necessary for attaining the same pH in the latter solution; this ratio was constant at pH $< 8{\cdot}5$. It can be inferred that a complex was formed with the V : A ratio of 1 : 2 and that only the excess maltol not bonded in this complex was titrated. The complex is highly stable; otherwise an enhanced consumption of base would be observed on account on its reaction with both maltol and metavanadate if these were released from the complex on its decomposition.

A solution with $c_V = 0{\cdot}01 \text{ mol l}^{-1}$ and $c_A = 0{\cdot}03 \text{ mol l}^{-1}$ was titrated by acid; values of $\bar{z} = 0{\cdot}18 - 1{\cdot}10$ were obtained in the region of pH 3·7–2·0. The computer analysis of a set of 8 points of the titration curve pointed to a two-stage protonation of the mononuclear complex,

$$VO_2A_2^- + H^+ \rightleftarrows VO(OH)A_2 \qquad (O)$$

$$VO_2A_2^- + 2\,H^+ \rightleftarrows V(OH)_2A_2^+ \;; \qquad (P)$$

values of $\log K_O = 3{\cdot}07 \pm 0{\cdot}007$ and $\log K_P = 4{\cdot}49 \pm 0{\cdot}016$ $(S = 0{\cdot}007)$ were calculated. The electroneutral $VO(OH)A_2$ species is violet in colour, the $V(OH)_2A_2^+$ cation is blue.

Oxalate was employed as a competitive ligand for the determination of the stability of the $VO_2A_2^-$ complex. When the neutral solutions whose composition is given in Table I are titrated with acid, the maltol ligand is replaced gradually with oxalate.

Since there are no oligonuclear vanadates present in solutions with excess maltol, the equilibria (*A*) and (*B*) were omitted from the evaluation. Virtually no $VO_2Ox.(OH)^{2-}$ was found to be present in the solutions under study, the gradual coordination of oxalate gave to the ternary complex VO_2OxA^{2-}, forming primarily at the beginning of the titration and at higher pH values.

Vanadium(V)–Alcoholic Sugar Systems

Yellow colour appears in neutral solutions of vanadium(V) on the addition of sorbitol or mannitol, the pH remaining constant. The yellow colour changes to red on acidification. The red solutions lose their colour very slowly on alkalization; the presence of decavanadate is here conceivable. These red solutions were not subject to a detailed investigation. The titration curves of the vanadium(V)–oxalate system are very slightly affected by alcoholic sugars, hence, oxalate does not constitute a suitable competitive ligand for systems with alcoholic sugars. Tartrate, on the other hand, proved to act as a competitive ligand, the shape of the titration curve for the vanadium(V)–tartrate system being affected by additions of the oligoalcohols. The solutions contained "noncomplexed" oligovanadates, binuclear and tetranuclear tartrate and oligoalcohol chelates, and a tetranuclear chelate involving both tartrate and the alcoholic sugar. The optimum agreement between the calculation and the experiment was attained for the model given in Table I. For this ternary system the equilibrium constants of reactions (*E*) and (*F*) were also optimized. The equilibrium constants found in the vanadium(V)-tatrate binaty system and in the vanadium-tartrate-sorbitol and vanadium-tartrate-mannitol ternary systems are mutually fairly consistent.

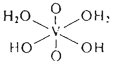
DISCUSSION

Vanadium(V) forms readily complexes in which the coordination number of the central atom is six[12]. It can be thus assumed that in aqueous solutions of metavanadate (which is a mononuclear uninegative vanadate, usually written as VO_3^-) the central atom is in a bonding relation with six donor atoms. The great majority of vanadium(V) complexes involve the VO_2^+ group. Assuming that this group remains also in the hydrated metavanadate, its formula is $VO_2(OH)_2(OH_2)_2^-$ (formula *III*). The reactions of metavanadate with the reagents under study are second order chelating reactions[4], water being produced by condensation during the chelate formation. The way of coordination of a molecule of maltol to metavanadate is depicted in formula *IV*. The reacting partners possess just the number of potentially acid hydrogen ions that is required for the formation of water molecules when two coordination sites are made free for the bonding of the ligand to the central atom; therefore the reaction proceeds with no participation of hydrogen ions. The binegative oxalate anion Ox^{2-} has one acid hydrogen less than maltol, therefore the coordination of an oxalate anion as shown in formula *V* requires an "external" proton, not delivered by the reacting metavanadate or oxalate (shown in circle in the formula). The coordination of maltol or oxalate represented by formulae *IV* and *V*, respectively, takes place both during the formation of binary complexes and during the formation of the ternary chelate of vanadium with maltol and oxalate. Maltol as well as oxalate forms highly stable chelates with vanadium(V). The bonding of the ligand to the central atom is here strong enough to bring about a breakdown of the oligovanadates; thus only mononuclear complexes are formed in the presence of a sufficient excess of reagent. The remaining reagents under study, being bonded less strongly to vanadium(V) in approximately neutral solutions, are unable to disturb the oligovanadates even if present in a high excess, and the complexes are oligonuclear.

In general, there are three possibilities of how the glycolate ligand can bond to the central atom. The coordination *via* the oxygen of the carboxy group solely gives complexes analogous to acetate complexes. Stable glycolate complexes of this type can be assumed to occur only where the analogous acetate complexes are known to exist, which is not the case with vanadium(V) in nearly neutral aqueous solutions. The second possibility of coordination of glycolate is *via* the oxygen of the hydroxy group solely. In fact, esters have been reported[13] to form in aqueous solutions, but these only exist in acid media, whereas the reaction with glycolate takes place even at pH ≈ 7. The third possibility of coordination involves both functional groups[17,18]. Chelates of this kind, which are fairly stable, have been identified[24,25] by structure analysis of tartrate complexes. In polynuclear complexes, glycolate can form a bridge connecting two central atoms. The coordination of glycolate to one central atom results in a stable five-membered chelate ring, and this way of bonding seems to be the most likely also in oligonuclear complexes.

The chelating agents: maltol (HA) and glycolate (G^-) are alike in that both of them contain a donating oxygen substituted with a potentially acid hydrogen, while the second donating oxygen is free and can be bonded directly to the central ion. Such reagents can react in the absence of hydrogen ions (formula *IV*), or also with a consumption or liberation of protons (formulae *VI* and *VII*, respectively). The experiments show that the reaction of metavanadate with maltol does not involve hydrogen ions (formula *IV*), whereas in the chelation of glycolate to oligovanadate $(VO_3^-)_n$, one proton is taken up by each glycolate, indicating that the reaction is of the type characterized by formula *VI*. In oligovanadates of the $(VO_3^-)_n$ type the metavanadate units are joined *via* V–O–V or V–(OH)–V bridges. The bridge formation was associated with the consumption of two hydroxy ligands in the former case (formula *VIII*) or of an OH ligand and an OH_2 ligand in the latter case (formula *IX*). In the oligovanadates joined exclusively by V–O–V bridges the number of OH_2 ligands is identical with that in the metavanadate by condensation of which they were formed. In linear oligocondensates with V–O–V bridges, each of the terminal members of the chain contains one OH group, while cyclic oligomers contain no OH groups at all. Such oligocondensates can react with glycolate in the way shown in formula *VII*, and only vanadium at the end of the linear chain can take part in the reaction represented by formula *IV*. If the $(VO_3^-)_n$ oligovanadates are joined by V–(OH)–V bridges solely, then the ratio of number of nonbridged OH ligands and of OH_2 ligands in them is the same as in the metavanadate. Such oligovanadates can react with glycolate according to formula *IV*, and only vanadium at the end of the linear chain, also according to formulae *VI* or *VII*. The VO_2^+ group, typical of mononuclear vanadium(V) complexes, is not always preserved in the oligonuclear, complexes, such as represented by formulae *I* and *II* taken from ref.[15]. If two hydroxy ligands arise from the interaction of a molecule of coordinated water with the oxide ligand in the VO_2^+ group, the oligovanadates characterized by structures *X* and *XI* result. Here the reaction of glycolate can be assumed to correspond to formula *VI* only; for the terminal member of the linear chain the reaction according to formula *IV* is also conceivable.

The structures of the binuclear and tetranuclear complexes with glycolate, whose composition is given in Table I, can be derived from formulae *X* and *XI* so that two GH_{-1}^{2-} glycolate ligands are bonded to them in the manner indicated in formula *VI*. A tartrate anion, T^{2-}, contains two —CH(OH)—COO$^-$ groups, and so the coordination of a T^{2-} ion during the formation of the tetranuclear complex is associated with the takeup of two protons; the way of coordination is shown in formula *VI*, and the tartrate is bonded to two adjacent central atoms (formula *XIII*). In the formation of the binuclear tartrate (formula *XII*) one proton is used for the coordination of a T^{2-} anion. In this case a half of the tartrate is bonded to one V(V) as shows formula *IV*, the other half is bonded to the other V(V) as corresponds to formula *VI*. Our formulae *XII* and *XIII* differ from the formulae *I* and *II* taken from ref.[15] only by two or four molecules of bonded water.



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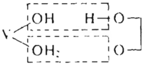
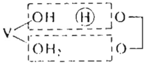


IV



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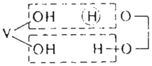

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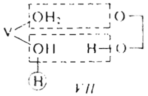

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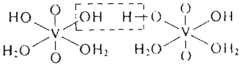
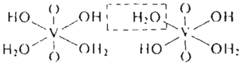
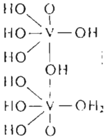


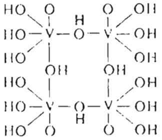
VIII



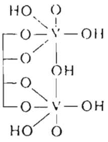
IX



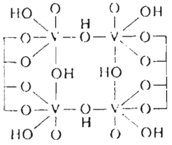
X



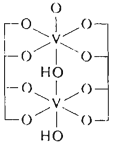
XI



XII



XIII



XIV

While in neutral tartrate or glycolate solutions the carboxy groups are dissociated, the hydroxy groups of sorbitol or mannitol remain undissociated, and so their coordination to oligovanadate $(VO_3^-)_n$ occurs with no consumption of protons. Sorbitol and mannitol contain six alcoholic groups, so the possibilities of their bonding to the central atom are manifold. Our experimental data are insufficient for a formulation of the structure of the complexes of vanadium with the oligoalcohols. It can only be assumed that a molecule of the alcoholic sugar (Su) bonds as a bidentate ligand, the bonding being to one central atom only; such complexes are known to exist for B(III), Ge(IV), As(III), or As(V) (ref.[26]). The complexes of vanadium with glycolate and with alcoholic sugars will be quite analogous, only the GH^{2-}_{-1} ligand will be replaced by the SuH^{2-}_{-2} ligand. As has been demonstrated[27,28] for compounds of alcoholic sugars with Mo(VI) and W(VI), alcohols containing a minimum of four alcoholic groups can bond as tetradentate ligands to two central atoms in a way similar to that shown in formula *XII*. Formula *XIII* portrays the structure of tetravanadate with molecules of oligoalcohol bonded in this manner, and also the structure of a ternary complex involving one tartrate TH^{4-}_{-2} ligand and one oligoalcoholate SuH^{4-}_{-4} ligand. The binuclear vanadate, similarly as the tetravanadate, bond two molecules of alcoholic sugar; formula *XIV* represents one of the possible structures of this chelate with SuH^{4-}_{-4} ligands.

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