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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

Full Text

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STUDY OF THE COMPOSITION AND PROPERTIES OF VANADYLVANADATES BY SPECTROPHOTOMETRY

The existence of vanadylvanadates (v.v.), chemical compounds between V^{IV} and V^{V}, was noted already by Berzelius (^{1}). Cannery (^{2}) obtained v.v. by fusing V_2O_5 with oxides of alkali metals. Goncharenko and Suvorova (^{3}) obtained v.v. by electrolysis of alkaline solutions of Na_3VO_4 or

Fig. 1. Absorption spectra of mixtures $V^{IV}+V^{V}$ at various pH. $[V^{V}]/[V^{IV}] = 4:1$; $[V^{IV}] = 5 \cdot 10^{-3}\ M:$ 1—pH 4.5 and 5.5; $l = 3$ mm; 2—pH 7.1, $l = 10$ mm; 3—pH 8.3, $l = 10$ mm; 4—pH 9.2, $l = 10$ mm; 5—pH 9.8, $l = 10$ mm; 6—pH 10.3, $l = 10$ mm.

Fig. 2. Dependence of the optical density of mixtures $V^{IV}+V^{V}$ on pH: $\lambda = 520$ mμ, $l = 10$ mm, $[V^{V}]/[V^{IV}] = 4:1$, $[V^{IV}] = 5 \cdot 10^{-3}\ M$.

K_3VO_4. We obtained v.v. in the case of electrolytic oxidation of V^{IV} at pH 3.0-3.5 on a platinum electrode (^{4}). Ducret (^{5}) suggested a variable composition of v.v. with a ratio $V^{V} : V^{IV}$ from 3 to 4. We found no other data on the composition of v.v. in the literature.

We determined the ratio $V^{IV} : V^{V}$ and the approximate instability constants of v.v. ions as a function of pH by the spectrophotometric method, and also their charge from the direction of their migration under the action of an electric field. Spectrophotometric measurements were carried out with an SF-4 instrument. For the study we used NH_4VO_3 of chemically pure grade and $VOSO_4 \cdot 2H_2O$,

recrystallized in an atmosphere of SO_2 from a technical salt. The remaining reagents were of chemically pure grade and were not subjected to additional purification. To create a constant ionic strength, spectrophotometric measurements were carried out with solutions containing 0.5 N NaCl. For measurements at pH 7.1-10.3, borate buffer solutions were used, since neither V^IV nor V^V forms compounds with $B_4O_7^{2-}$ (5) under these conditions. At pH 4.5-5.5, the

Fig. 3. Determination of the composition and instability constants of vanadyl vanadates by the logarithmic method. Series at pH 4.5: I $-[V^{IV}] = 5 \cdot 10^{-3}$ M; II $-[V^{IV}] = 2.5 \cdot 10^{-3}$ M; III $-[V^{IV}] = 1 \cdot 10^{-3}$ M

Figure 2: Fig. 3. Determination of the composition and instability constants of vanadyl vanadates by the logarithmic method. Series at pH 4.5: I $-[V^{IV}] = 5 \cdot 10^{-3}$ M; II $-[V^{IV}] = 2.5 \cdot 10^{-3}$ M; III $-[V^{IV}] = 1 \cdot 10^{-3}$ M

pH of each mixture was brought to the required value with a small amount of HCl or NaOH. The initial V^IV solution was prepared in 0.5 N NaCl. The V^V solution was also prepared in 0.5 N NaCl; in the case of measurements at pH 7.1-8.3, concentrated NH_4OH was added to this solution up to the corresponding pH value.

Fig. 3. Determination of the composition and instability constants of v.v. by the logarithmic method. Series at pH 4.5: I $-[V^{IV}] = 5 \cdot 10^{-3}$ M; II $-[V^{IV}] = 2.5 \cdot 10^{-3}$ M; III $-[V^{IV}] = 1 \cdot 10^{-3}$ M

The initial solutions of V^IV and V^V were mixed in the required ratio; then either buffer solution, or HCl or NaOH, was added to a definite pH, the latter being monitored with a pH meter with a glass electrode. In studying the electromigration of v.v. ions, the V^IV and V^V solutions were prepared without NaCl, since otherwise electromigration would have occurred at the expense of the background ions. Spectrophotometric measurements were carried out for series with variable V^V concentration, since the cation VO^{2+} is the coordinating group (V^V is in an anionic form throughout the investigated pH range) and, in addition, the region in which V^IV, precipitating upon an increase in pH, is present in excess occupies only a small part of the curve. At all pH values, mixtures with the ratio $[V^V] : [V^{IV}] \geq 0.4$ were transparent and did not give a precipitate on standing. The course of the curves at lower V^V concentrations was interpolated between the last value of the optical density (D) and the origin. Measurements were made two hours after mixing the solutions. Water was used as the reference solution.

The absorption spectra of mixtures of V^IV + V^V are shown in Fig. 1. At pH 4.5–5.5 the spectra are identical; the color intensity is maximal (curve 1 was recorded in a cuvette with $l = 3$ mm), and the minimum of D occurs at 550 mμ. At pH 7.1–8.3 the color intensity of the solution decreases, the minimum shifts to longer wavelengths and becomes flat, and absorption in the red region of the spectrum decreases. At pH 9.2 and 9.8 the spectra are almost identical; absorption in the red region decreases in comparison with solutions at pH 8.3. At

pH 10.3, a decrease of D at $\lambda 500–600$ mμ begins, probably explained by the onset of decomposition of v.v.

On the curve of the dependence of D on pH (Fig. 2), characteristic regions can be distinguished, corresponding to changes in the absorption spectra, since they

Table 1

Results of determining the composition and instability constants of vanadyl-vanadate ions as a function of pH

pH	$[V^{IV}]\cdot 10^3$	$n = V^V : V^{IV}$ in the complex ion, by the method of straight lines, n	$n = V^V : V^{IV}$ in the complex ion, by the logarithmization method, $\operatorname{tg}\alpha$	$n = V^V : V^{IV}$ in the complex ion, by the logarithmization method, n	Instability constants K_{inst}, calculated by the method of straight lines	Instability constants K_{inst}, calculated by the logarithmization method	Instability constants K_{inst}, by the calculation method of A. K. Babko, number of determinations	Instability constants K_{inst}, by the calculation method of A. K. Babko, $K_{\text{inst,av}}$	Charge of the complex ion according to electromigration data
4.5	5.0	1	1.16	1*	$4.0\cdot 10^{-4}$	$1.1\cdot 10^{-3}$	6	$3.0\cdot 10^{-3}$	Negative
4.5	1.0	1	1.03	1*	$9.8\cdot 10^{-4}$	$4.2\cdot 10^{-4}$	8	$4.0\cdot 10^{-4}$	Negative
4.5	1.0	1	0.95	1*	$6.3\cdot 10^{-4}$	$5.9\cdot 10^{-4}$	6	$3.1\cdot 10^{-4}$	Negative
5.5	5.0	1	1.18	1*	$2.2\cdot 10^{-4}$	$1.3\cdot 10^{-3}$	6	$3.2\cdot 10^{-3}$	Negative
5.5	1.0	1	1.12	1*	$4.0\cdot 10^{-4}$	$1.4\cdot 10^{-4}$	4	$1.3\cdot 10^{-4}$	Negative
7.1	5.0	?	1.66	2	–	$5.3\cdot 10^{-5}$	3	$1.7\cdot 10^{-6}$	Negative
7.1	2.5	?	1.80	2	–	$5.6\cdot 10^{-6}$	6	$4.5\cdot 10^{-7}$	Negative
7.1	1.0	?	2.06	2	–	$1.4\cdot 10^{-7}$	6	$6.3\cdot 10^{-7}$	Negative
8.3	5.0	2	1.95	2	–	$8.9\cdot 10^{-6}$	4	$6.4\cdot 10^{-7}$	Negative
8.3	2.5	?	1.93	2	–	$4.1\cdot 10^{-6}$	5	$5.5\cdot 10^{-7}$	Negative
8.3	1.0	?	1.76	2	–	$6.0\cdot 10^{-6}$	6	$4.2\cdot 10^{-7}$	Negative

pH	$[V^{IV}]\cdot 10^3$	$n = V^V : V^{IV}$ in the complex ion, by the method of straight lines, n	$n = V^V : V^{IV}$ in the complex ion, by the logarithmization method, $\operatorname{tg}\alpha$	$n = V^V : V^{IV}$ in the complex ion, by the logarithmization method, n	Instability constants K_{inst}, calculated by the method of straight lines	Instability constants K_{inst}, calculated by the logarithmization method	Instability constants K_{inst}, by the calculation method of A. K. Babko, number of determinations	Instability constants K_{inst}, by the calculation method of A. K. Babko, $K_{\text{inst,av}}$	Charge of the complex ion according to electromigration data
9.2	5.0	1	1.43	1	$6.2\cdot 10^{-4}$	$1.7\cdot 10^{-4}$	4	$4.8\cdot 10^{-8}$	Negative
9.2	2.5	1	1.16	1	$5.0\cdot 10^{-4}$	$6.6\cdot 10^{-4}$	6	$1.3\cdot 10^{-3}$	Negative
9.2	1.0	1	1.38	1	$7.2\cdot 10^{-4}$	$3.2\cdot 10^{-4}$	6	$3.2\cdot 10^{-4}$	Negative
9.8	5.0	1	1.16	1	$3.7\cdot 10^{-3}$	$1.3\cdot 10^{-3}$	4	$2.9\cdot 10^{-3}$	Negative
9.8	2.5	1	0.96	1	$1.6\cdot 10^{-3}$	$3.6\cdot 10^{-3}$	4	$2.6\cdot 10^{-3}$	Negative
9.8	1.0	1	1.24	1	$9.0\cdot 10^{-4}$	$1.1\cdot 10^{-4}$	4	$2.1\cdot 10^{-3}$	Negative
10.3	5.0	1	–	–	$6.5\cdot 10^{-4}$	–	6	$7.4\cdot 10^{-4}$	Negative
10.3	2.5	1	–	–	$1.3\cdot 10^{-3}$	–	6	$1.2\cdot 10^{-3}$	Negative

* The form of the graph indicates the presence of complex compounds with a higher n.

occur at the same pH values: a constant value of D at pH 3.0–6.0, a region with a gradual decrease of D at pH 6.0–9.0, and a sharp drop of D at pH 9.2–11.5.

Fig. 4. State diagram of vanadate ions according to Schiller and Thilo. The region of concentrations and pH investigated by us is indicated by lines parallel

to the coordinate axes. The numbers correspond to the pH values at which series of mixtures with variable concentrations of V^V were studied.

The results of calculations of the compositions and approximate instability constants of v.v. ions are given in Table 1. The composition of the ions was determined by the methods of straight lines (6) and limiting logarithmization (7). The instability constants were determined by the above-mentioned methods and by the calculation methods proposed by A. K. Babko (7). The method of straight lines, developed for the study of strongly disso-

of the cited complex compounds, did not give definite results for the compositions of the ions formed in the case of K_{unst} of the order of 10^{-6}–10^{-7}, since, when the results were processed for three values of n, we obtained graphs close to straight lines. The method of limiting logarithmization for the series with pH 4.5 and 5.5 indicates the formation of a v.v. ion with a ratio $V^V : V^{IV}$ greater than $1 : 1$ (Fig. 3).

From a comparison of the form of the absorption spectra of v.v. and the D–pH curve with the calculated data, it may be concluded that the composition of v.v. ions changes regularly with pH: V^{IV} forms compounds with ortho- (pH 10.3–9.2), pyro- (pH 8.3–7.1), and metavanadates (pH 5.5–4.5) in the form of simple and condensed ions ($V_3O_9^{3-}$). With isopolyvanadates ($V_{10}O_{28}^{5-}$), analogous compounds are not formed, since on the curves D–$[V^V]/[V^{IV}]$, D does not change when $[V^V] : [V^{IV}]$ is above 4.0.

Our assumptions regarding the interaction of V^{IV} at different pH values with various forms of vanadate ions are confirmed by literature data: Fig. 4 is a state diagram of vanadate ions according to Schiller and Thilo ([8]), on which the concentration and pH regions covered by our measurements are plotted. At pH 9.2–10.3 our series lie in the orthovanadate field (composition of the v.v. ion $1 : 1$); the series at pH 7.1–8.3 lie at the junction of three fields, including that of pyrovanadate (composition of the v.v. ion $1 : 2$). The series at pH 5.5 is located at the point of contact of the fields of metavanadate, its trimer, and decavanadate (compositions of the v.v. ion $1 : 1$ and $1 : 3$). The series at pH 4.5 lies in the decavanadate field, but since V^{IV} does not form v.v. with this ion, the appearance of v.v. in solution may cause a shift of the equilibrium toward the formation of meta-ions.

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