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Decavanadate Protonation Degrees in Aqueous Solution

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Aqueous solutions of vanadium(V) have been prepared at different OH^- vs. vanadium concentrations from both decavanadic acid and metavanadate solutions. These solutions have been extracted with an excess of tetraheptylammonium bromide in benzene. The bromide displaced has been determined in order to gain information on the average charge of the extracting species already known to be variously protonated decavanadate anions. The addition of a constant excess of supporting electrolytes has been avoided, as it is known it could affect the position of equilibria.

Besides the already well known $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$ species, strong evidence has also been obtained for the existence of $H_3V_{10}O_{28}^{3-}$.

Moreover, a slow disproportionation of $V_{10}O_{28}^{6-}$ into $HV_{10}O_{28}^{5-}$ and $V_2O_7^{4-}$ (or HVO_4^{2-}) during a first stage, and then into metavanadate, resulted.

Therefore, $H_6V_{10}O_{28}$ proves a strong acid as triprotic instead of tetraprotic, as reported in the literature. Inconsistent results are almost certainly due to the high ionic media usually employed.

Introduction

In 1956 Rossotti and Rossotti reported that aqueous solutions of vanadium(V) in the pH range from 2 to 7 contain bi-, mono- and unprotonated decavanadate species, on the basis of emf measurements in an 1*M* $NaClO_4$ medium at 25°C.[1] Though some later papers provided confirmations to the existence of these three species,[2–5] two more recent emf studies[6,7] have cast some doubt on $V_{10}O_{28}^{6-}$ existence. In the first paper[6] experiments have been performed in a rapid flow apparatus. It was shown that, by adding an equivalent amount of NaOH to $HV_{10}O_{28}^{5-}$, the $V_{10}O_{28}^{6-}$ unprotonated species may only fugaciously be obtained, as it extensively, though slowly, reequilibrates to the monoprotonated species and, perhaps, metavanadate. The second work[7] has been accomplished at 40°C to accelerate equilibration on going from metavanadates to more acidic species, *i.e.* in a reverse sense as before. It suggested a lack of the unprotonated $V_{10}O_{28}^{6-}$ species, so a better fit with experimental data could be obtained. Furthermore, in this system, it seems very remarkable that all known exchange studies[8–10] have indicated even an $H_3V_{10}O_{28}^{3-}$ species present at lower pH's, whereas emf and conductimetric studies can hardly be precise.

Nevertheless, all the more recent papers[11–14] still include $V_{10}O_{28}^{6-}$ in the equilibrium scheme on polyvanadates, and do not take into account $H_3V_{10}O_{28}^{3-}$. We used an extractive method with an anionic liquid exchanger to obtain informations about the average charge for each decavanadate group (E/V_{10}) of the extracted species from aqueous solutions, having a known OH^- *vs.* vanadium ratio. Tetraheptylammonium bromide, $(C_7H_{15})_4NBr$, in benzene has been used as extractant for its fair specificity to decavanadate polyanions, while it is unable to extract OH^-, meta-, pyro- and ortovanadates.

Experimental Section

Chemicals

Sodium metavanadate or decavanadic acid solutions, assumed having respectively 6.0 and 5.0 $[OH^-]/[V]$ values, have been converted into decavanadate solutions at intermediate $[OH^-]/[V]$ ratios either by $NaVO_3$ acidification, or by $H_6V_{10}O_{28}$ alkalinization.[15]

Vanadium has been standardized by complexometric[16], gravimetric[17] and spectrophotometric (aliquots have been diluted to 2.5–10 m*M*, acidified to pH 3.5–4 and measured at 480 nm) methods, 60 m*M* NaOH and 30 m*M* HBr solutions against high grade Na_2CO_3, cation exchanger according to ref. 18.

As even alkaline metal cations are known to interact with decavanadates splitting out protons[6], an excess of supporting electrolyte has been avoided. Therefore, a small addition of NaBr has only been made, when necessary, to keep the ionic strength constant at a 0.08*M* level.

Resulting aqueous solutions have been diluted in order for the vanadium(V) concentration to range from 5 to 50 m*M*, and shaken with 10 ml of a 0.1*M* extractant phase.

Procedure

Extractant solutions, extraction runnings, pH measurements and i.r. spectra have been made according to ref. 15. Absorbance measurements have been done on a Beckman DU spectrophotometer.

Aliquots of the aqueous phase were centrifugated and analyzed by Mohr's method for the bromide content resulting from its displacement out of the ammonium salt by decavanadate, according to the following exchange reaction:

$$\times\ (C_7H_{15})_4NBr(org) + H_{6-x}V_{10}O_{28}{}^{x-}(aq) \rightarrow ((C_7H_{15})_4N)_xH_{6-x}V_{10}O_{28}(org) + \times\ Br^-(aq)$$

Completeness of this reaction has been tested in the aqueous phase with H_2O_2. When it has been found not to occur, aliquots of both phases have been spectrophotometrically determined for vanadium content. The bromide *vs.* decavanadate molar ratio represents the average negative charge of the polyanions existing in each aqueous phase. It will be reported as E/V_{10} and compared with the established $[OH^-]/[V]$ ratios.

Results and Discussion

Results are reported in Table I; all of them have been reproduced with at least three replicates at different aqueous vanadium concentrations, ranging within 5–50 m*M*.

At $[OH^-]/[V]$ ratios ranging from 5.00 to 5.30, the same value of E/V_{10} has always been obtained, *i.e.* 3.1 ± 0.1. In the runs with $[OH^-]/[V] = 5.00$ (*i.e.*, $H_6V_{10}O_{28}$ solutions without any addition of NaOH) the determination of the $[H^+]/V_{10}$ ratio gave a value of 3.1 as well. Furthermore, i.r. spectra have been found identical through the whole range.

At $[OH^-]/[V]$ ratios going from 5.30 up to 5.50, E/V_{10} values of 3.1 ± 0.1 to 5.0 ± 0.1 were respectively found.

For $[OH^-]/[V]$ ratios higher than 5.50, the E/V_{10} ratios have no longer been found corresponding. All were sensibly smaller as those expected if a further deprotonation would occur. Extraction was uncomplete only in this range. Vanadium unextracted has been

TABLE I. Extraction Data of 5 to 50 m*M* Vanadium(V) Solutions.[a]

Extracted vanadium mmoles	Unextracted vanadium mmoles	Displaced Br^- mmoles	$[OH^-]/[V]$	E/V_{10}
0.797	–	0.248	5.00	3.1
0.557	–	0.169	5.20	3.0
0.557	–	0.174	5.225	3.1
0.557	–	0.178	5.25	3.2
0.578	–	0.176	5.30	3.1
0.578	–	0.193	5.33	3.3
0.540	–	0.216	5.40	4.0
0.522	–	0.236	5.45	4.5
0.540	–	0.272	5.50	5.0
0.522	–	0.273	5.55	5.2
0.527	0.013	0.295	5.60	5.6
0.517	0.023	0.278	5.60	5.4*
0.551	0.026	0.307	5.60	5.5*
0.540	0.037	0.307	5.67	5.7
0.483	0.039	0.271	5.67	5.6*

[a] Extraction runnings have usually been made 5 min after the preparation of the solutions; those signed with an asterisk have been made the day after.

TABLE II. Time Dependence of 510 nm Absorbance and pH of 30 m*M* Vanadium(V) Solutions at Different $[OH^-]/[V]$ Ratios.

Time	$[OH^-]/[V] = 5.33$		5.40		5.50		5.60		5.67	
	pH	absorb.	pH	absorb.	pH	absorb.	pH	absorb.	pH	absorb.
5 min	2.65	0.480	3.30	0.540	5.11	0.640	7.40	0.730	8.80	0.790
15 min	2.65	0.485	3.30	0.535	5.03	0.640	7.05	0.691	7.83	0.720
30 min	2.65	0.480	3.30	0.540	5.00	0.630	6.80	0.650	7.43	0.655
1 hr	2.65	0.490	3.30	0.540	5.03	0.640	6.55	0.628	7.10	0.625
17 hr	2.65	0.485	3.30	0.545	5.05	0.635	6.05	0.590	6.20	0.580
24 hr	2.65	0.480	3.30	0.545	5.08	0.630	5.89	0.565	6.05	0.560

found to be a small fraction (less than 10%) of the total amount, although increasing with the $[OH^-]/[V]$ ratio. As previously reported[6,7] we thought a low hydrolysis reaction was occurring. Evidence has been sought by following the absorbance in the visible and the pH of aqueous solutions, prepared at different $[OH^-]/[V]$ ratios, *vs.* time. From the data reported in Table II, it can be seen that, at $[OH^-]/[V] \leqq 5.50$, both absorbance and pH are constant with time, while at higher ratios they slowly shift to low values. An evaluation of the OH^- fraction which did not react with the extracted decavanadates could also be obtained ($[OH^-]_{aq}$) by balance with the established value of $[OH]_{tot}$. The $([OH^-]/[V])_{aq}$ indicated that unextracted vanadium was in form of HVO_4^{2-} or $V_2O_7^{4-}$.

According to the most recent works[14,15] some conclusions can be taken assuming that only decavanadate species exist in all these ranges.

In the first interval, the data suggest the existence of an $H_3V_{10}O_{28}^{3-}$ species as the more protonated weak acid species of decanavadic acid, which will be strong until the third deprotonation:

$$H_6V_{10}O_{28} \rightarrow 3\ H^+ + H_3V_{10}O_{28}^{3-}$$

On the basis of our findings, the second range includes all decavanadate species which behave as thermodinamically weak, although rapidly deprotonating acids, according to the following equilibria:

$$H_3V_{10}O_{28}^{3-} \underset{+H^+}{\overset{+OH^-}{\rightleftarrows}} H_2V_{10}O_{28}^{4-} \underset{+H^+}{\overset{+OH^-}{\rightleftarrows}} HV_{10}O_{28}^{5-}$$

In the last interval, slow acid–base reactions take place. They are evidently caused by decavanadate structure demolition which, at room temperature, comes to an end in 6 months ("true equilibrium"), when full conversion to metavanadate is eventually achieved[6,7]:

$$HV_{10}O_{28}^{5-} + OH^- \underset{\longleftarrow}{\overset{\longrightarrow}{\underline{\text{v.fast}}}} V_{10}O_{28}^{6-} \underset{\longleftarrow}{\overset{\longrightarrow}{\underline{\text{v.slow}}}}$$
$$\frac{2}{3}V_3O_9^{3-}\ (\text{or}\ \frac{1}{2}V_4O_{12}^{4-}) + \frac{8}{10}HV_{10}O_{28}^{5-}$$

Within the first 24 hours, evidence has been obtained for intermediate species such as $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$, as well as one more, having an OH/V ratio 7 (either $V_2O_7^{4-}$ or HVO_4^{2-} or both). The latter species seems to be one of the first disproportionation products of $V_{10}O_{28}^{6-}$, but it does not appear among the equilibrium products, because perhaps the average $[OH^-]/[V]$ values of solutions are too low (5.60 or 5.67) compared with its one (7.0). Consequently, a conversion to the less hydrolyzed metavanadate species takes place very slowly. Further studies are needed to clarify the mechanism.

It seems useful to point out that results and conclusions reported in this work are valid only within the limits of the chosen experimental conditions. Probably, at an higher ionic strength (where activity coefficients will be lower), the strong acid field widens including $H_3V_{10}O_{28}^{3-}$ species, as well as it is possible for the $V_{10}O_{28}^{6-}$ species to be stabilized by complexing effects, in agreement with findings of the AA., who used high ionic strengths.

Many papers, in fact, report strong evidence for a surprisingly high supporting electrolyte effect, depending not only on the concentration, but on the nature of cations as well.

Complete knowledge about this matter is highly desirable in order to account for many unusual effects which are involved. We are pursuing an interpretation of these problems.

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