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Comparative IR Study of Solid Hydrate Decavanadates and Polyvanadates in Acidic Aqueous Solution

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An attempt has been made to compare i.r. spectra of polyvanadate solutions with those of solid polyvanadates, in order to solve the problem if aqueous solution decavanadate species have the same structure as reported in solid hydrate decavanadates, and if hexavanadate species are coexisting with them.

The i.r. spectra directly obtained from water solutions were unreliable; so, solution species have been extracted into a low absorbing organic phase. A previous control showed that no modifications of existing species were occurring for the phase transfer. In this way, evidence resulted for a complete identity between aqueous solution and solid decavanadate structure, and for a lack of hexavanadate species, at least within the sensitivity limits of the i.r. technique.

These findings are in agreement with a recent Raman investigation, but appear in contrast with NMR and complexation data. A new interpretation of NMR data is suggested, leading to the removal of disagreement.

Introduction

The old dispute between supporters of Düllberg's view[1] that hexavanadates are the main species present in weakly acidic vanadium(V) solutions, and those who supported Britton's view[2], concerning decavanadates as prevailing species in the same field, seemed to be solved in favour of the latter, when by emf studies Rossotti and Rossotti[3] established with fair certainty the predominant existence in solution of decavanadate species. Further support to this conclusion was reached by means of cryoscopic[4,5], emf[6–9], conductimetric[8,10], absorption[7,9], ultracentrifuge[11] and, lastly, Raman[12] measurements. However, exchange[13], emf[14] as well as NMR[15] studies again suggest an hexavanadate species coexisting with decavanadate in the higher pH range.

On the other hand, it has been found that aqueous decavanadate species are able to crystallize with specific enclosure of Na^+ [16] and to strongly interact with alkaline ions[6], bi- or trivalent cations[10] releasing protons. Jahr and coworkers have consequently depicted a kind of cage-like structure as based on tetrahedral oxygen to vanadium coordination[10]. But, a few years later, some Authors simultaneously and independently determined the structure of decavanadate ion, $V_{10}O_{28}{}^{6-}$, on $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$[17], $Ca_3V_{10}O_{28} \cdot 17H_2O$[18] and $Na_6V_{10}O_{28} \cdot 18H_2O$[19] crystals. The consistent results of these investigations indicate that ten VO_6 octahedra are linked by edge-sharing to build a compact polyanion, without any inner cavity. Jahr's structure was considered unrealistic for the observed prevalence of a higher than four coordination number at low pH values[17]. However, the proposed crystal structure did not suggest any way to the formation of cation-decavanadate inclusion complexes, and the question arose whether dissolved decavanadate could have a structure different from that related to the solid state to account for its complexing properties.

Attempts to answer this problem were recently made by NMR[20] and Raman[12] investigations. Unfortunately, the results obtained are almost entirely inconsistent with each other. Raman spectra of aqueous solution decavanadates appear to be similar and prompt to the conclusion that the structure of dissolved decavanadates is equal to that found in the solid state. On the other hand, NMR spectra show two broad and one narrow resonance, which have intensity ratios of 1:3:1 respectively, different from the expected 2:2:1 or 4:1 ratios, on the basis of crystal structure.[21,15,22]

With the purpose to clarify the above mentioned problems, and having in our mind that i.r. spectra offer an excellent technique to discern each kind of polyvanadates[23], we have sought the best way of obtaining reliable i.r. spectra of polyvanadate solutions, in order to compare them with those of the solid decavanadates.

From preliminar measurements we have ascertained that only partial and rough information could be directly obtained from aqueous solutions, even if they were vanadate oversaturated (such uncomplete i.r. data are reported by Griffith and Lesniak in their Raman study[12]). Therefore, we chose to transfer the polyanions into an inert organic solvent by rapid extraction with a liquid anion exchanger: thus, we have obtained reliable i.r. spectra, which are suitable for comparison, provided that no species modifications take place by extraction. This has been assumed to be true on the basis of the ascertained overlapping of the UV and visible spectra of polyvanadates in aqueous and organic phases.

A quaternary ammonium salt exchanger in an inert solvent was required in order to avoid proton interaction with alkali in the aqueous phase and with the extracted polyanions. Tetraheptylammonium bromide, $(C_7H_{15})_4NBr$, in benzene has been found suitable as low absorbing in the water (3600–3100 and 1600–1700 cm^{-1}) and polyvanadate (1000–700 cm^{-1}) absorption ranges.

Occasional carbon disulphide substitution for benzene has been found to have no relevant effect.

Experimental Section

Chemicals

$K_2Zn_2V_{10}O_{28} \cdot 16\,H_2O$, $Ca_3V_{10}O_{28} \cdot 17\,H_2O$ and $Na_6V_{10}O_{28} \cdot 18\,H_2O$ have been prepared according to the literature[17–19]; $(\text{acridineH})_5HV_{10}O_{28} \cdot 4\,H_2O$, $(\text{quinolineH})_4H_2V_{10}O_{28} \cdot 4\,H_2O$ and $(\text{tetraphenylphosphonium})_3H_3V_{10}O_{28} \cdot 2\,H_2O$ have been prepared according to ref. 24.

30 to 80 m*M* vanadium(V) aqueous solutions at pH from 2.5 to 7 have been prepared either by acidification of sodium metavanadate solutions with a solid strong cation exchanger in an acid form, or by adding NaOH to a fresh polyvanadic acid solution obtained according to ref. 10 (*i.e.* by dissolving V_2O_5 in H_2O_2, oxygen evolution being complete after 2 days).

Merck $(C_7H_{15})_4NBr$ has been weighed to prepare a 0.1*M* benzene solution, which has been washed before use with a 20 to 40 m*M* NaBr aqueous solution, prepared with freshly boiled distilled water.

Procedure and Instruments

10 ml aliquots of the extracting phase have been equilibrated with 10 ml of vanadate solutions in ground glass stoppered centrifuge tubes, by hand shaking for a minute or less. Immediate and complete extraction was achieved under pH 5.50, while at upper pH's the extraction was found immediate but not higher than 93%.

The pH has been checked by glass and calomel electrodes connected to a PHM4c Radiometer pHmeter, standardized with a pH 4.00 buffer.

I.r. spectra of solids have been obtained in nujol mulls, between NaCl disks. The solution spectra have been recorded in 0.1 mm cells with NaCl windows *versus* the $(C_7H_{15})_4NBr$ solution, presaturated as before. The instrument was a Perkin–Elmer mod. 257 spectrophotometer. The investigated range was 4000–625 cm^{-1}.

Results and Discussion

Duplicate runs with both vanadium solutions gave identical results through the entire concentration range.

From the data reported in Table 1, there appears evident a strict spectral similarity both of solid neutral decavanadates with the extracts from higher pH solutions, and of solid protic decavanadates with the extracts from lower pH solutions.

Deprotonation effect on i.r. spectra substantially consists of an about 30 cm^{-1} band shift towards lower frequencies, both in aqueous solution and solid decavanadates (with the exception of the 815 cm^{-1} band, where only an increase of intensity is found). The same effect has been observed in the Raman study[12], and it has been attributed to a slight increase of the bond order of the remaining VO groups due to protonation of some of them.

In the water absorbing ranges two broad stretching bands at 3480 and 3250 cm^{-1} and a weak deformation band at 1640 cm^{-1} appear. The first stretching band strongly increases with deprotonation, indicating that decavanadate polyanion coordinates much more water if its charge increases. At higher pH's, the band extensively widens to lower frequencies obscuring the so far unchanged 3250 cm^{-1} band. In the hydrate solids a very broad band is present, going from 3100 up to 3600 cm^{-1} and a broad weak deformation band occurs at 1640–1600 cm^{-1}.

TABLE 1. Infrared Spectral Data (cm^{-1}) for Aqueous Solution and Solid Hydrate Decavanadates.

pH 2.5–3.5 solutions	3480w, 3250m, 1635vw, 988s,sh, 971vs, 940w,sh, 840s, 815m, 768w,br
$([C_6H_5]_4P)_3H_3V_{10}O_{28} \cdot 3\,H_2O$	3500–3100vw,br, 1640vw,br, 987s,sh, 968vs, 850s, 818m, 760w,br
pH4.5 solution	3480m, 3250m, 1635w, 988m,sh, 972vs, 945s,sh, 840s, 815s, 750m,br
$(\text{quinolineH})_4H_2V_{10}O_{28} \cdot 3\,H_2O$	3500–3100vw,br, 1640vw,br, 988m,sh, 973vs, 945s,sh, 840s, 815m, 750w,br
pH 5.5 solution	3480s, 3250m, 1635w, 988m,sh, 980–945vs,br, 840s, 820s, 750m,br
$(\text{acridineH})_5HV_{10}O_{28} \cdot 4\,H_2O$	3500–3100vw,br, 1640vw,br, 990w,sh, 979s, 960–945vs,br, 840s, 820s, 750w,br
pH 6.0–7.0 solutions	3570–3200s,vbr, 1635m,br, 988w,sh, 978s, 960–945vs,br, 840–815s, 750m,br
$K_2Zn_2V_{10}O_{28} \cdot 16\,H_2O$	3580–3100m,vbr, 1630m,br, 982s,sh, 970–950vs,br, 840s, 808s, 730w,br
$Ca_3V_{10}O_{28} \cdot 17\,H_2O$	3580–3100m,vbr, 1630m,br, 987s, 968–940vs,br, 840–815s, 740m
$Na_6V_{10}O_{28} \cdot 18\,H_2O$	3580–3100m,vbr, 1630m,br, 992s, 960–940vs,br, 840s, 810s, 740s
$CaV_6O_{16} \cdot 3\,H_2O$[23]	1009s, 970vs, 733vs

Hexavanadate species are known to exhibit in their solid salts an i.r. spectrum[23] no traces of which could be found in our solution spectra. Even if they were somewhat differently structured, when dissolved, from those in their solid salts[25], they would be unlikely to howe the same i.r. spectrum as decavanadates. Therefore, their existence can be excluded, at least within the sensitivity limits of the i.r. technique.

Our results are entirely consistent with those obtained in the Raman investigation[12]. Both lead to the conclusion that decavanadates are not only the species merely existing in an aqueous solution at pH 2–7, but also they have the same structure as described for their solid hydrate salts.

On the other hand, NMR data[15] have been considered inconsistent with this conclusion. However, we propose a different interpretation, which seems to be more plausible, being capable of correlating the 1:3:1 intensity ratios with the decavanadate structure.

In the $V_{10}O_{28}^{6-}$ ion structure (described as consisting of a group of six VO_6 octahedra arranged in a 2 × 3 rectangular array by sharing edges, with two VO_6 octahedra joined from above and two more from below, sharing the equatorial oxygens with those at the apices of the octahedra in the rectangule) two fundamentally different kinds of VO_6 octahedra are present. The two central octahedra have the six oxygen atoms all shared with neighbouring octahedra and the vanadium atom displaced towards an edge (pseudo-tetrahedral configuration); the eight external ones have the vanadium atom displaced towards an apex (pseudo-square-pyramidal configuration), one of the six oxygens being unshared. On this basis, only two resonances with an 8:2 intensity ratio should be expected, according to ref. 15. But polyanion mono- or biprotonation, which surely occurs at the working pH's, may introduce further dissymmetry. A third resonance of low intensity may then appear.

If our interpretation of NMR data is reliable, all contrasting views on this matter can be considered as removed.

However, the problem concerning the above mentioned complexing properties of decavanadate ion remains to be explained. Indeed, the inner cavity which has been invoked to account for them, is almost certainly not existing. This topic will be more extensively developed in a further paper.

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