

THE MECHANISM OF RETENTION OF VANADIUM OXO-SPECIES AT THE “TITANIUM OXIDE / AQUEOUS SOLUTION” INTERFACE

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ABSTRACT

The mechanism of retention of vanadium oxo-species at the “titanium oxide/aqueous solution” interface was investigated over a wide pH range (4-9) and V(V) solution concentration (10^{-5} - 2×10^{-2} M) by combining equilibrium deposition experiments, potentiometric titrations, microelectrophoresis and “proton-ion” titration curves. It was inferred that the adsorbed V(V) oxo-species are retained inside the compact layer of the interface through hydrogen/coordinative bonds forming very probably inner-sphere complexes with the titania surface groups.

KEYWORDS: Titania, vanadates, interface, adsorption, innersphere surface complex, equilibrium deposition filtration, aqueous solution, hydrogen bonds, pzc, iep.

INTRODUCTION

The presence of vanadium compounds in wastewater is a major water pollution problem. In fact, these compounds have harmful effects on the circulatory system and disturb the metabolism (Namasivayam and Sangeetha, 2006). In the case of plants, the latter causes chlorosis and limit growth (Kabata-Pendias and Pendias, 1993). Moreover, numerous reports have warned of the carcinogenic and other toxic effects of vanadium resulting from extensive industrial exposure (Abbasi, 1987). Vanadium is emitted into the environment from vanadium refineries, iron and steel industries and chemical industries (mainly phosphate industries) (Garcia-Sanchez *et al.*, 2004). Several methods can be used to remove vanadium from aqueous solutions. Adsorption is a relatively inexpensive, non-hazardous, rapid and versatile technique which allows recovery of vanadium from the solid adsorbent. Various adsorbents have been used so far including high surface area carbon cloth (Abbas and Conway, 2002), iron oxyhydroxide (Blackmore *et al.*, 1996), chitosan (Guzman *et al.*, 2002; Jansson-Charrier *et al.*, 1996), ZnCl₂ activated carbon (Namasivayam, Sangeetha, 2006), amorphous ferric oxyhydroxide (Shieh and Duedall, 1988), modified silica (Garcia-Sanchez *et al.*, 2004) as well as iron and titania based commercial adsorbents (Naeem *et al.*, 2007).

The latter work indicated that titania is a promising adsorbent for removing vanadium species from aqueous media. Moreover, impressive progress has been pointed out in the last decade towards the preparation of anatase with very high specific surface area. Thus, the additional increase of the specific capacity of this adsorbent is anticipated. In spite of the great importance of the adsorption of the vanadium (V) oxo-species at the “anatase / aqueous solution” interface, the retention mechanism remains practically unknown, though electrostatic or chemical retention has been reported (Naeem *et al.*, 2007; Bourikas *et al.*, 1997). A modern picture has been recently developed for the structure of the aforementioned interface (Panagiotou *et al.*, 2008). This indicates that two types of oxo-

groups with different charges are developed on the titanium oxide surface: the terminal oxo-groups ($\text{TiO}^{-0.35}$) and the bridging ones ($\text{Ti}_2\text{O}^{-0.57}$). Almost all terminal oxygens are non-protonated at pH values higher than pzc, but even at low pH values they are predominant. In contrast, the greater portion of the bridging oxygens is protonated even at relatively high pH values. Moreover, according to this structure, the interface is divided by three charged planes into three sub – regions (see Figure 1). The surface plane is located at the oxygen atoms of the (hydr)oxo-groups. Plane 1 (Plane 2) is located at the oxygen atoms of the first (second) layer of structured water molecules surrounding the titania surface. The distance of the plane 1 from the surface is equal to the distance of the plane 2 from the plane 1 (1.7 Å). The first two regions constitute the *compact layer* of the interface. The third sub – region, up to bulk solution, is the *diffuse layer*. The *shear plane* is situated to the solution side with respect to the plane 2. It divides the interface into two parts: the stagnant one, which “accompanies” the titania aggregates when they are moved under the influence of an electric field, and the external part which is separated from the moving aggregates. The diffuse layer is divided, thus, into the *stagnant – diffuse layer* and the *mobile – diffuse layer*. The counter ions and the co-ions are distributed among the various sub-regions. Those located inside the compact layer form ion-pairs with the opposite charged surface (hydr)oxo groups.

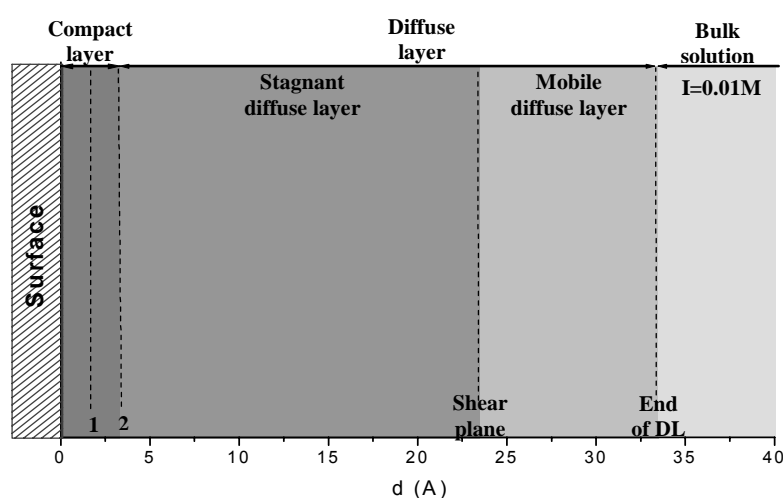


Figure 1. Structure of the “titanium oxide / aqueous solution” interface (I: ionic strength, d: distance from the surface)

The establishment of the mechanism of retention of vanadium oxo-species at the “titania / aqueous solution” interface involves the elucidation of the nature of the retention forces (electrostatic, hydrogen bonds, coordinative bonds), the plane (layer) of the interface where these species are located, the local structure of these species and the determination of the surface speciation in a wide range of pH and V(V) solution concentration. The elucidation of the first two points is the goal of the present preliminary work. This is attempted by combining equilibrium deposition experiments, potentiometric titrations, microelectrophoresis and proton-ion titration curves.

EXPERIMENTAL

Substances

NaNO_3 dissolved in triply distilled CO_2 -free water and NaVO_3 were used for the preparation, respectively, of the indifferent electrolyte and adsorbate solutions, necessary for the deposition, microelectrophoresis, proton-ion, pH-equilibrium and potentiometric titration experiments.

Industrial titania (Degussa P25) containing 80% w/w anatase and 20% w/w rutile was used for preparing the suspensions. Its surface composition is ~90% anatase and ~10% rutile (Spanos *et al.*, 1995, Contescu *et al.*, 1996) and its BET SSA equal to $50 \text{ m}^2 \text{ g}^{-1}$.

Equilibrium deposition experiments

A thermostated double walled Pyrex vessel equipped with a magnetic stirrer and a perspex lid with holes for electrodes and nitrogen gas has been used. The control (change) of the pH during the deposition (titration) experiments was carried out by an automatic microburette (Radiometer Copenhagen ABU901 Autoburette) equipped with a combination pH electrode. The experiments

were performed at $25 \pm 0.1^\circ\text{C}$ and ionic strength 0.1M adjusted with sodium nitrate. Nitrogen gas was bubbled through the titania suspensions during the experiments to prevent the dilution of the atmospheric CO_2 , which would bring about a change in the pH.

Adsorption edges were derived for three different initial V(V) concentrations (3×10^{-3} M, 6×10^{-3} M and 2×10^{-2} M) over the pH range 4-10, using a solid concentration of 20 g L^{-1} . Details concerning the experimental procedure have been reported elsewhere (Bourikas *et al.*, 2001). In all adsorption experiments the equilibrium V(V) concentration in the adsorbate solutions was determined spectrophotometrically at 392 nm (Snell, 1978).

The change of pH upon deposition was measured in each equilibrium deposition experiment. The experiments were performed at initial pH values 5 and 9 and four different values of the initial V(V) concentration.

Proton-ion titrations at constant pH

Proton-ion titrations were performed at six pH values (4, 5, 6, 7, 8, 9) under conditions favoring complete deposition of the V(V) oxo-species at the interface (low initial V(V) concentrations). Details for the experimental procedure have been reported elsewhere (Bourikas *et al.*, 2001).

Electrochemical techniques

Potentiometric titrations were used for determining the point of zero charge of the suspensions, both in the absence and presence and of the V(V) oxo-species. They were performed, under N_2 atmosphere, at three different values of the ionic strength (0.1, 0.01 and 0.001 N) and constant temperature ($25.0 \pm 0.1^\circ\text{C}$). Details about the experimental procedure and the derivation of "surface charge density vs pH" curves have been reported elsewhere (Bourikas *et al.*, 2003; Bourikas *et al.*, 2005). The potentiometric titrations in the presence of the V(V) oxo-species were performed at a V(V) concentration equal to 5×10^{-5} M where the whole amount of the V(V) oxo-species is practically deposited at the interface. It should be mentioned that after each addition of the titrant the pH stabilized quickly ($\Delta\text{pH}/\text{min} < 0.01$) and the solubility of the titania was negligible over the entire pH studied, even in the presence of the V(V) oxo-species.

The ζ potential of the suspensions was determined in the pH range 2 – 8, both in the absence and presence of the V(V) oxo-species, at four initial V(V) concentrations (6×10^{-6} M, 10^{-5} M, 5×10^{-5} M and 10^{-4} M), using a Zetasizer 5000 (Malvern Instruments Ltd) microelectrophoresis apparatus. Details for the experimental procedure have been reported elsewhere (Bourikas *et al.*, 2003).

Simulations

The V(V) speciation in the solution was carried out under conditions similar to those of the deposition experiments using Visual MINTEQ, a computer code for calculating chemical equilibria in aqueous media (Gustafsson, 2005).

RESULTS AND DISCUSSION

The V(V) oxo-species in the adsorbate solution

Two monomer (HVO_4^{2-} , H_2VO_4^-), one dimer ($\text{H}_2\text{V}_2\text{O}_7^{2-}$), one quadramer ($\text{V}_4\text{O}_{12}^{4-}$), one quintamer ($\text{V}_5\text{O}_{15}^{5-}$) and one decamer ($\text{NaHV}_{10}\text{O}_{28}^{4-}$) V(V) oxo-species are present in the vanadate solutions. The distribution of vanadium in the various V(V) oxo-species depends on both the solution pH and the V(V) total concentration (see Figure 2).

Vanadium is present almost exclusively in the form of the H_2VO_4^- at too low vanadium total concentration (3×10^{-5} M) and in the whole pH range studied (4-9). Vanadium is mainly present in the form of the monomer H_2VO_4^- species at relatively low V(V) total concentration (3×10^{-4} M) whereas a smaller amount of vanadium is present in the form of the $\text{H}_2\text{V}_2\text{O}_7^{2-}$ and $\text{V}_4\text{O}_{12}^{4-}$ species. A significant portion of the V(V) is present as $\text{NaHV}_{10}\text{O}_{28}^{4-}$ species at pH lower than 5.5. This portion increases as pH decreases.

The speciation is more complicated at an intermediate V(V) total concentration (3×10^{-3} M). Vanadium is mainly present as the monomer oxo-species at pH greater than 8.5, whereas it is mainly distributed among the monomers (HVO_4^{2-} , H_2VO_4^-), the dimer, $\text{H}_2\text{V}_2\text{O}_7^{2-}$ and the quadramer $\text{V}_4\text{O}_{12}^{4-}$ in the pH range 8.5-5.5. Vanadium is mainly present in the form of the decamer $\text{NaHV}_{10}\text{O}_{28}^{4-}$ at pH lower than 5.

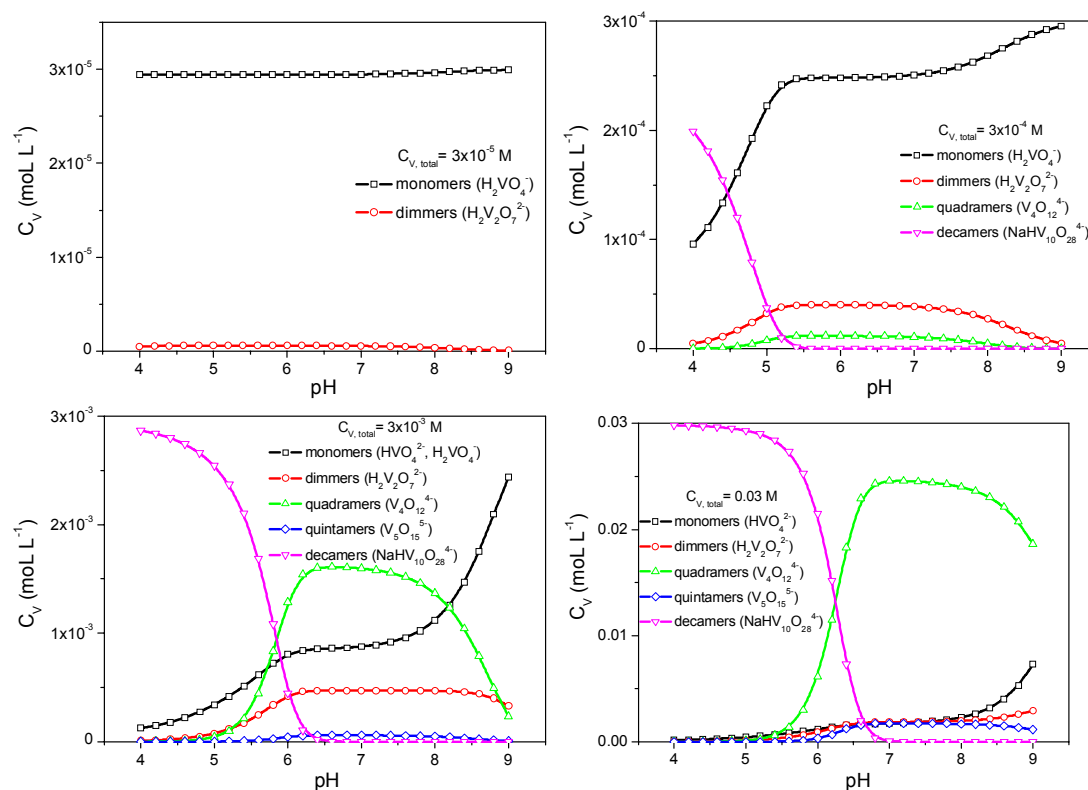


Figure 2. Distribution of V(V) (expressed as vanadium concentration, C_V) among the various V(V) oxo-species over the pH range 4-9, for four different V(V) total concentrations ($C_{V, \text{total}}$) of an aqueous solution with $I=0.1 \text{ M NaNO}_3$

Finally, vanadium is mainly distributed between the $V_4O_{12}^{4-}$ and $NaHV_{10}O_{28}^{4-}$ species at relatively high V(V) total concentration ($3 \times 10^{-2} \text{ M}$). The former prevails at pH values higher than 7 whereas the latter at pH values lower than 5.5.

Overall, decrease of pH and increase of the total vanadium concentration favor the vanadium distribution in the polymer species. This is the normal behavior encountered in the oxo-species of the transition metals.

Retention of V(V) oxo-species at the “titanium oxide / aqueous solution” interface

Figure 3 shows the variation of the V(V) surface concentration with the pH of the adsorbate solution for three initial V(V) solution concentrations.

It is observed that the surface V(V) concentration is maximized at $\text{pH}=4$ and initial solution concentration equal to $2 \times 10^{-2} \text{ M}$. Comparison of this value with the maximum values obtained for other transition metal ionic species on the same adsorbent (see Table 1) confirms that titanium oxide is an excellent adsorbent of the V(V) oxo-species. This finding in conjunction with the impressive progresses of the last decade with respect to the preparation of titanias with very high specific surface areas renders this oxide a quite promising material for removing these species from aqueous solutions.

Investigating the retention mode of V(V) oxo-species at the “titanium oxide / aqueous solution” interface by deposition experiments

Figure 3 shows that the surface V(V) concentration increases as pH decreases. Taking into account the negative charge of the retained V(V) oxo-species and the fact that the surface charge of the support becomes positive below pzc (6.4) and then increases as pH decreases, we might propose that the deposition takes place through simple electrostatic accumulation of the V(V) oxo-species in the diffuse part of the interface (see Figure 1). But this retention mode cannot explain the observation that considerable deposition takes place even at pH higher than or equal to pzc of the support, where its surface was initially neutral or negatively charged. This observation strongly

suggests some kind of specific interactions of the V(V) oxo-species with the surface (hydr)oxo-groups and presumably formation of inner sphere surface complexes (Bourikas *et al.*, 2006a; Panagiotou *et al.*, 2006; Bourikas *et al.*, 2006b).

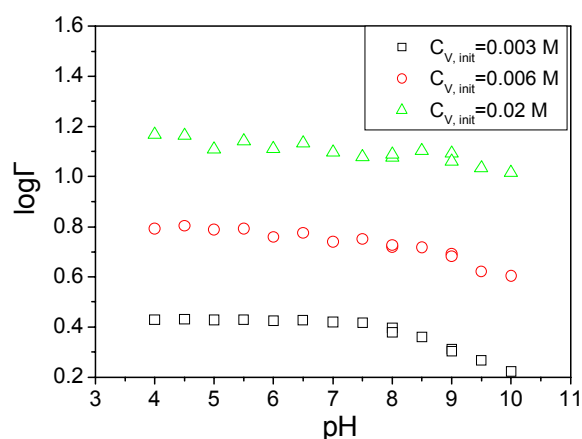


Figure 3. Variation of the V(V) surface concentration (Γ : $\mu\text{mol m}^{-2}$) with the pH of the adsorbate solution (adsorption edge) obtained in the pH range 4-10, for three initial V(V) concentrations ($C_{V,\text{init}}$) in the solution

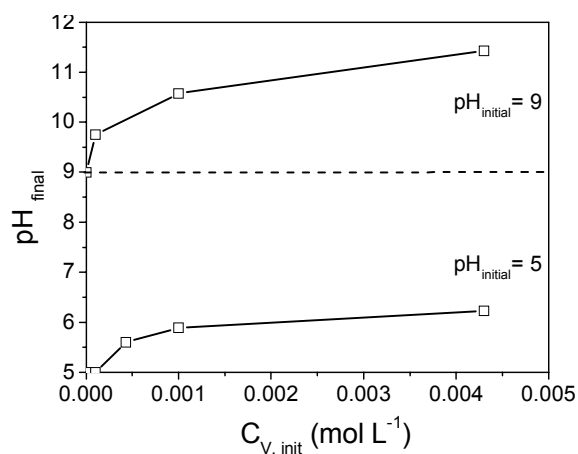


Figure 4. Increase of pH upon the deposition of the V(V) oxo-species at the "titanium oxide / adsorbate solution" interface for various initial V(V) solution concentrations ($C_{V,\text{init}}$) and two values of initial pH

Table 1. Maximum values of the surface concentration of various transition metal ionic species adsorbed on the titania surface

Species	Initial concentration	Optimum pH	Surface density $\mu\text{mol m}^{-2}$	Reference
V(V) oxo-species	2×10^{-2} M	4.0	15	This work
Cr(VI) oxo-species	2.5×10^{-2} M	4.5	4	Petsi (2006)
Mo(VI) oxo-species	1.5×10^{-2} M	4.0	6	Panagiotou <i>et al.</i> (2010)
W(VI) oxo-species	3×10^{-2} M	4.0	11	Panagiotou <i>et al.</i> (2009)
Co(II) aqua complex	2×10^{-2} M	7.5	7	Petsi <i>et al.</i> (2009)
Ni(II) aqua complex	2×10^{-2} M	7.5	8	Stavropoulos (2010)

The mode of interfacial deposition may be further investigated by studying the change of pH upon the deposition of the V(V)-oxo species. This change is illustrated in Figure 4.

It is clear that the deposition of the V(V) oxo-species causes a considerable increase of pH. The magnitude of the effect increases with the initial V(V) solution concentration and thus, with the surface V(V) concentration. The observed increase of pH upon deposition corroborates the development of specific interactions and presumably the formation of inner sphere complexes, at least for some of the deposited V(V) oxo-species. In fact, following this retention mode some of the V(V) oxo-species are located inside the compact layer of the interface (see Figure 1). Negative charge is, thus, accumulated in this region of the interface. The adsorption of hydrogen ions into one or more of the charged planes of the compact layer (surface plane, plane 1 or plane 2) is therefore expected to compensate the increase in the negative charge.

Investigating the retention mode of V(V) oxo-species at the "titanium oxide / aqueous solution" interface by potentiometric titrations and microelectrophoresis.

The "surface charge density vs pH" curves are given in Figure 5. These are recorded at three values of ionic strength in the presence of the V(V) oxo-species in the adsorbate solution. It is well known that the pzc is identified by the common intersection point of these curves. A considerable increase in the pzc value from 6.4 into 8.4 is observed. This increase strongly suggests the development of specific interactions and presumably formation of inner sphere complexes (Bourikas *et al.*, 2006a; Panagiotou *et al.*, 2006; Bourikas *et al.*, 2006b). In fact, as already mentioned, the deposition of the

V(V) oxo-species inside the compact layer is accompanied by H^+ adsorption. This takes place at all pH values including $pH=pzc$, where the surface was neutral before deposition. Thus, in the presence of the deposited V(V) oxo-species, we need more hydroxyls in the solution in order to deprotonate surface groups and restore a zero proton charge at the surface.

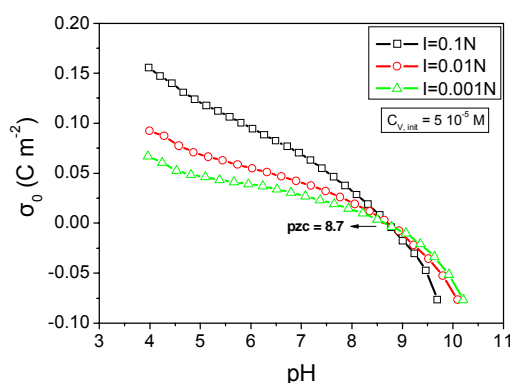


Figure 5. “Surface charge density (σ_0) vs pH” curves in the presence of an initial V(V) concentration in the adsorbate solution ($C_{V,init}$) for 3 different values of the ionic strength

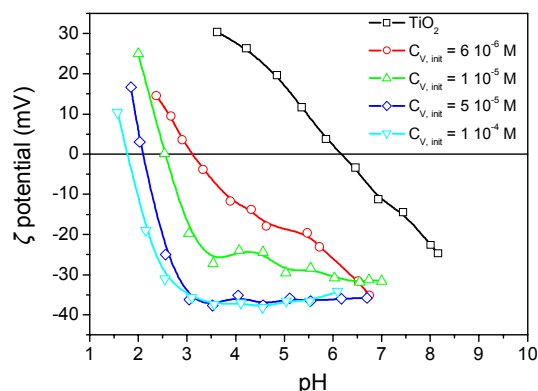


Figure 6. “ ζ potential vs pH” curves obtained both in the absence and presence of the V(V) oxo-species in the adsorbate suspension, at various initial V(V) solution concentrations ($C_{V,init}$) and ionic strength equal to 0.01 M

It is well known that the isoelectric point (iep) is the pH value where the ζ potential takes a zero value. The ζ potential is the potential at the shear plane of the interface (see Figure 1). Figure 6 shows that the ζ potential decreases and the iep shifts to lower values due to the presence of the V(V) oxo-species in the adsorbate solution. The effects become more and more pronounced increasing the initial V(V) concentration in the solution and thus, the amount of the V(V) adsorbed. These effects indicate accumulation of the negatively charged V(V) oxo-species at the compact and/or stagnant–diffuse part of the interface (Bourikas *et al.*, 2006a; Panagiotou *et al.*, 2006; Bourikas *et al.*, 2006b). In fact, in such a case the values of the ζ potential should decrease over the whole pH range studied. Moreover, the iep should be shifted to a lower value because a surface protonation is required to restore the electrokinetic charge, and thus, the ζ potential at zero value. The high intensity of the effects suggests accumulation of the aforementioned species at the compact rather than at the stagnant–diffuse part of the interface. This is related to the development of specific interactions and presumably to the formation of inner sphere complexes located inside the compact layer. Overall, the microelectrophoresis results corroborate the potentiometric titration results, the deposition data and the change of pH suggesting specific interactions of the V(V) species and presumably formation of inner sphere complexes.

Investigation of the mode of interfacial deposition and the structure of the deposited species by studying “proton–ion” curves

The deposition of the V(V) oxo-species and the hydrogen ion adsorption may be combined quantitatively in the context of a methodology based on the so called “proton–ion” titration curves (Bourikas *et al.*, 2006a; Panagiotou *et al.*, 2006; Bourikas *et al.*, 2006b). These are linear plots of the “amount of the H^+ ions adsorbed versus the amount of the deposited V(V)”. Each of the aforementioned plots is determined at a fixed pH and under conditions favoring complete deposition of the V(V) oxo-species at the interface (low V(V) initial concentration). The ratio “amount of the H^+ ions adsorbed versus the amount of the deposited V(V)” can be determined from the slope of each curve. These plots were derived at various pH values in the pH range 9–4 (Figure 7). The experimentally determined amounts of the adsorbed protons were properly corrected to take into account changes in pH caused due to dilution of the solution disturbing the equilibria between the V(V) oxo-species. A similar procedure has been reported elsewhere (Petsi, 2006; Panagiotou *et al.*, 2010; Panagiotou *et al.*, 2009).

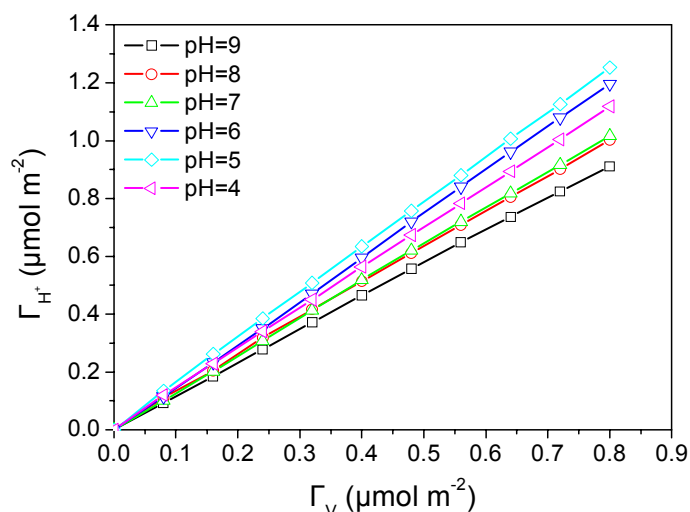


Figure 7. "Amount of the H^+ ions adsorbed (Γ_{H^+}) vs the amount of the deposited V(V) (Γ_V)". Each curve corresponds to a given pH value.

The values for the aforementioned ratio determined at pH 4, 5, 6, 7, 8 and 9 are respectively equal to 1.4, 1.6, 1.5, 1.3, 1.3 and 1.2. These were derived for initial solution V(V) concentration in the range ($8 \times 10^{-5} - 8 \times 10^{-4}$ M). The monomers $H_2VO_4^-$ are actually present in the solution in this range. Therefore, the mode of interfacial deposition investigated in this sub-section is related only to these species. The values obtained for the ratio are relatively large indicating location of the deposited $H_2VO_4^-$ species very close to the surface and thus, deposition through hydrogen bonds or formation of inner sphere complexes (Bourikas *et al.*, 2006a; Panagiotou *et al.*, 2006; Bourikas *et al.*, 2006b). The increase of this ratio as pH decreases presumably indicates increasing contribution of the inner sphere complexes at expense of the hydrogen bonding species. Alternatively, this may reflect increasing formation of a di-substituted at expense of a mono-substituted inner sphere complex.

CONCLUSIONS

Titanium oxide is an excellent adsorbent of the V(V) oxo-species. The amount of the vanadium adsorbed on TiO_2 surface increases with decreasing pH and it is maximized at pH=4 and initial solution concentration equal to 2×10^{-2} M. The joint use of V(V) equilibrium adsorption experiments, change of pH upon V(V) adsorption, potentiometric titrations and microelectrophoresis in the presence of V(V) oxo-species in the solution, as well as "proton-ion" titration curves suggested that the adsorbed V(V) oxo-species are retained inside the compact layer of the " TiO_2 / aqueous solution" interface through hydrogen/coordinative bonds.

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