THE INTERACTION OF LINEAR POLYPHOSPHATES WITH TITANIUM DIOXIDE AND OTHER SURFACES

Andrew Michelmore, Wengi Gong, Le Huynh, Paul Jenkins and John Ralston*

Ian Wark Research Institute
University of South Australia
Mawson Lakes, SA 5095
Australia
*corresponding author email: john.ralston@unisa.edu.au

ABSTRACT

The interaction of linear polyphosphates of the general formula \([P_{n+1}O_{3n+1}]^{(2n+2)}\) with the surface of titanium dioxide and silica has been studied as a function of pH. Both equilibrium and kinetic aspects of the interaction were addressed, using in situ infrared spectroscopy, electrical double layer, ion chromatography, rheological and adsorption investigations.

Linear polyphosphates adsorb on to the titania surface over a wide pH range as two kinds of species, a bridging bidentate surface complex and an electrostatically adsorbed ion. Adsorption is driven by combined electrostatic and chemical contributions. There is no detectable interaction between the linear polyphosphates and the surface of silica at any pH investigated. Linear polyphosphates with larger \(n\) displace lower molar mass species from the titanium dioxide surface.

INTRODUCTION

The principles that underlie the adsorption of high molecular weight organic polymers and hydrolysable metal ions at solid-liquid interfaces are well defined (Stumm, 1992; Fleer et al, 1993) however this is not the case for complex inorganic species such as polyphosphates, polysilicates, polymolybdates and polytungstates (Tateyama et al, 1997). The latter are distinguished by the fact that they contain more than one P, Si, Mo or W atom (Cotton and Wilkinson, 1988). These species are very often present in detergent formulations, are used as dispersing agents in minerals processing and in the cleaning of silicon wafers in the electronics industry. Linear polyphosphates, which are the general formula \([P_{n+1}O_{3n+1}]^{(2n+2)}\) may be prepared as essentially monodisperse anions when the number of P atoms is equal to, or less than, four. The degree of polydispersity increases thereafter. Linear polyphosphates are the focus of this present study.

In this investigation we report the results of a combined in situ, attenuated total internal reflection infrared spectroscopy, electrophoretic mobility, rheological and adsorption investigation of the behaviour of linear polyphosphates at the titanium dioxide and silicaceous solution interfaces as a function of pH.

RESULTS AND DISCUSSION

Polyphosphates

No solution phase infrared spectroscopic data for polyphosphates are available, so that assignments of the bands were made with recourse to the data available for the solids (Chapman and Thirlwell, 1964; Abbas and Davidson, 1994; Ivashkevich et al, 1988; Ruimont et al, 1991). Account was also taken of the distribution of species in solution (Irani and Callis, 1961).

Based on an analysis of the IR spectra of polyphosphates and their solutions, the spectral features for linear polyphosphates adsorbed on titanium dioxide surfaces can be summarised as follows:

1 On leave from Wuhan University of Technology, Wuhan 430070, China
• a band occurs in all of the spectra in the region from 900-940 cm\(^{-1}\), shifting to lower frequency with increasing chain length. It is assigned to the antisymmetric stretching vibration of P-O-P.

• a band in the 1100-1170 cm\(^{-1}\) region is present in all of the spectra and corresponds to the antisymmetric stretching vibration of the terminal PO\(_3\).

• a band in the 1200-1270 cm\(^{-1}\) region is present in \(P_3\) and \(P_{c10}\) but not in \(P_2\); it corresponds to the antisymmetric stretching vibration of the bridging PO\(_2\). The frequency and intensity of this band increase with \(n\).

• all of the spectra of polyphosphates adsorbed on the titanium dioxide surface are characteristic of linear polyphosphates, for any cyclic polyphosphate contributions are absent (Bhatnagar et al, 1977).

Although the spectra of the linear polyphosphate solutions varied markedly with pH, the spectra of polyphosphates adsorbed on to titania surfaces showed little change with pH. The number of bands and the contours of the spectra remained essentially the same as the pH varied. This indicates that the type of adsorbed species and their symmetry remains the same. The frequency of some of the bands changed however, suggesting that the interaction strength between the polyphosphate species and titania surface changes with pH. A marked shift of the 1169 cm\(^{-1}\) band in the spectra of \(P_2\) adsorbed on to the titanium dioxide surface (Figure 1(i)) to lower frequencies was observed as the pH increases. This indicates that the interaction between the terminal PO\(_3\) groups of the \(P_2\) species and the titanium dioxide surface becomes stronger with increasing pH. In the spectra of \(P_3\) adsorbed on to the titanium dioxide surface (Figure 1(ii)), a significant shift of the bands at 1171 cm\(^{-1}\) towards lower frequencies is evident, whilst there is a smaller shift of the band at 1226 cm\(^{-1}\). This reveals that terminal PO\(_3\) of \(P_3\) interacts with the titanium dioxide surface quite strongly, whilst the bridging PO\(_2\) interaction is rather weak. The strength of both interactions increases with pH. In the spectra of adsorbed \(P_{c10}\) on the titanium dioxide surface (Figure 1(iii)), the band at 1159 cm\(^{-1}\), due to the anti-symmetric stretching vibration of the terminal PO\(_3\), remains at almost the same frequency. It is entirely absent in the solution spectra shown, for clarity sake in Figure 1 (iv), testifying to the specific nature of the adsorption process. Therefore, either this group in \(P_{c10}\) is not attached to the titanium dioxide surface or the interaction between the group and the surface remains unchanged as the pH varies. The modest decrease in frequency of the band at 1262 cm\(^{-1}\) with increasing pH means that the anti-symmetric stretching frequency of the bridging PO\(_2\) of \(P_{c10}\) becomes slightly stronger with pH, presumably due to a change in solution speciation. There is certainly no interaction between the bridging PO\(_2\) groups and the TiO\(_2\) surface, for the peak does not shift upon adsorption (Figure (1(iv))).

**Figure 1**

ATR-FTIR spectra of species adsorbed on titanium dioxide from \(P_2\) solution of 0.05 M PO\(_4\), I = 0.1 M KBr at pH (a) 3.7, (b) 6.5 and (c) 9.1 after 10 min interaction; (ii)
ATR-FTIR spectra of species adsorbed on titanium dioxide surface from $P_3$ solution of 0.05 M PO₄, $I = 0.1$ M KBr, at pH (a) 3.7, (b) 6.5 and (c) 9.1 after 10 min interaction; (iii) ATR-FTIR spectra of species adsorbed on titanium dioxide surface from $P_{<10>}$ solution of 0.05 M PO₄, $I = 0.1$ M KBr, at pH (a) 3.7, (b) 6.5 and (c) 9.1 after 10 min interaction; (iv) ATR-FTIR spectra of solution and adsorbed forms of $P_3$ and $P_{<10>}$ solution = 0.05 M PO₄, $I = 0.1$ M KBr. 

(a) $P_3$ in solution; (b) $P_3$ adsorbed on TiO₂; (c) $P_{<10>}$ in solution; (d) $P_{<10>}$ adsorbed at pH 3.7 on TiO₂.

The general trend of increase in the strength of interaction between the linear polyphosphate species and the titanium dioxide surface leads to the following suggestions:

- Linear polyphosphate species interact with the titanium dioxide surface through ionized terminal P-O groups, an interaction which increases with pH.
- The terminal ionized P-O groups in the linear polyphosphate species interact with the titanium ions on the titanium dioxide surface to form a P-O-Ti bond.

In order to test this mechanism of interaction between phosphate ions and metal ions on surface, the spectra of linear polyphosphates adsorbed on SiO₂ surfaces were determined using the same IR technique. A low pH of 1.5 was selected instead of 3.7 since SiO₂ has a pHₚₑₚ of about 2 (Vansant et al., 1995). SiO₂ has a very strong infrared absorption band due to Si-O-Si stretching vibration in the region 1000-1100 cm⁻¹ (Vansant et al., 1995). The spectra of SiO₂ were obtained from the spectra of the relevant phosphate solutions plus a SiO₂ coating, from which the spectra of the phosphate solution were subtracted. Useful information regarding the possible adsorption of phosphate on SiO₂ surface can be obtained from the subtraction spectra in the region outside 1000-1100 cm⁻¹. Since no significant absorption bands were observed in the region outside 1000-1100 cm⁻¹, $P_1$ does not apparently form a P-O-Si bond with the SiO₂ surface. There were no bands observed in the region 1200-1300 cm⁻¹ due to the antisymmetric stretching vibration of the bridging PO₂, hence $P_{<10>}$ also does not adsorb on SiO₂ surface. The absence of a detectable P-O-Si bond on the SiO₂ surface indicates that the presence of surface metal atoms is a prerequisite for the formation of P-O-metal surface bond.

**Phosphate Adsorption: Equilibrium Electrical Double Layer and Adsorption Considerations**

(a) **Zeta Potential**

The zeta potential of titanium dioxide particles was determined at pH 4 ($I = 10^{-3}$ M KNO₃) as a function of both phosphate concentration and $n$. The results in Figure 2 show that the addition of polyphosphate to titanium dioxide decreases the magnitude of the zeta potential of the particles and reverses the potential in all cases. There is a clear dependence on $n$, with larger species reversing the zeta potential at lower concentrations. As phosphates in solution are anionic, there is an electrostatic attraction between the titanium dioxide surface and the linear polyphosphates at pH 4. However, reversal of the zeta potential indicates that the interaction is not governed by electrostatic forces alone - there is clear evidence of specific adsorption, in direct agreement with the FTIR data.

![Figure 2](image)

The zeta potential of titanium dioxide particles as a function of polyphosphate concentration (pH 4, $I = 10^{-3}$ M KNO₃).

(b) **Adsorption Isotherms**

The adsorption of phosphates onto titanium dioxide was studied at two pH values. Of particular interest was the effect of $n$ on the maximum adsorbed amount and the affinity of the polymer for the surface. The adsorption isotherm results are presented in Figure 3.
The adsorption isotherm data were fitted to the Langmuir adsorption isotherm \((\text{Hunter, 1989})\). The chemical free energy of adsorption, \(\Delta G_{\text{chem}}^0\) was then calculated as\(^1\)

\[
\Delta G_{\text{chem}}^0 = \Delta G_{\text{ads}}^0 - z e \xi
\]

where \(\Delta G_{\text{ads}}^0\) is the total free energy of adsorption, \(z\) is the ionic charge of the polyphosphate, \(e\) is the electronic charge and \(\xi\) is the zeta potential of the titanium dioxide. The chemical free energy as a function of chain length relationship is presented in Figure 4.

Surfactant adsorption behaviour has been studied previously (Somasundaran et al., 1988). The total energy of adsorption required to bring a surfactant molecule to a surface is given by the sum of a number of contributing forces, reflecting in part contributions from each individual component of the surfactant molecule. Hence the dependence of the total energy of adsorption on the chain length of the adsorbate can be used to extract the energy of adsorption specific to each component of the molecule. If we consider a polyphosphate molecule with \(n\) phosphorus atoms, two will be present as terminal PO\(_3\)
groups, while the other (n-2) will be bridging PO₂ groups. Hence:

$$\Delta G_{n}^{\circ} = 2\Delta G_{P_{2}}^{\circ} + (n - 2) \Delta G_{P_{2}}^{\circ} \quad (5)$$

The gradient of the chemical free energy(n) relationship for n greater than or equal to 2 repeat units should yield the chemical free energy of adsorption of the linking PO₂ groups (Figure 4). At pH 4 this is +1.8 kJ/mol. The positive free energy indicates that the PO₂ / titanium dioxide chemical interaction is slightly unfavourable at pH 4. Hence it is concluded that the PO₂ groups do not interact with the surface. This is confirmed by the FTIR spectra where the peak at 1260 cm⁻¹ for P₄ Po₄ is assigned to the antisymmetric vibration of the PO₂ group. This peak is not shifted when the P₄ Po₄ is adsorbed onto titanium dioxide when the “solution” and “adsorbed form” spectra are compared (Michelmore et al, 1999).

The slight increase in free energy is possibly due to unfavourable entropic considerations, for the PO₂ groups are forced to assume a “flat” conformation on the surface by the chemically adsorbed terminal PO₃ groups.

(c) Effect on Particle Interactions

The effect of polyphosphate and silica addition on the interactions between titanium dioxide particles was studied using rheology. The effect of P₃ is shown in Figure 6. A maximum yield stress value was determined at very low polyphosphate concentrations, followed by a substantial decrease at higher concentrations. In contrast, silica particles did not cause a marked decrease in the yield stress of the titanium dioxide dispersion at high concentrations.

The rheological data were combined with zeta potential measurements and the yield stress was plotted against the square of the zeta potential. For silica, the relationship was linear, indicating that electrostatic interactions dominate the interparticle forces. For the linear polyphosphates, there was a significant deviation from linearity at low polyphosphate concentrations, indicating that interactions apart from simple electrostatic may be operative. We have demonstrated elsewhere, through colloid probe microscopy, that a short range steric barrier arises in the presence of adsorbed polyphosphates and dominates the interactions at small interparticle separation distances. At higher polyphosphate concentrations, when the zeta potential is negative, electrostatic interactions are dominant.

Phosphate Adsorption: Competitive and Kinetic Considerations

The ATR-FTIR spectra indicate that only the bridging bidentate surface complex (TiO₂)P₂ (bands at 11 15 and 915 cm⁻¹) was detected initially on the titania surface in contact with the sodium orthophosphate solution. After about three minutes, the electrostatically adsorbed PO₄²⁻ ion (bands at 1008 cm⁻¹) was detected. The ATR-FTIR spectra of species adsorbed from a mixed solution of P₁ and P₄ Po₄ showed that the bridging bidentate surface complex (TiO₂)P₂ (bands at 1114, 1056 and 915 cm⁻¹) is dominant initially. The bands shifted during the first five minutes and the spectra gradually changed into that of adsorbed P₄ Po₄ (bands at 1265, 1158, 1087 and 900 cm⁻¹). After five minutes the position of the bands remained constant. This behaviour is mirrored in rheological data, where a large decrease in the yield stress occurs over the same time period.

The displacement of small n linear phosphates from the surface of titanium dioxide by their larger n relatives was followed as a function of time by ion chromatography. P₃ was preadsorbed onto the surface of titanium dioxide followed by the addition of P₂, P₁ and P₄ Po₄. In all cases, the larger linear polyphosphate displaces the smaller species, perhaps shown most clearly evident in the case of P₄ Po₄.

CONCLUSIONS

Linear polyphosphates specifically adsorb onto titanium dioxide surfaces over a wide range of pH values. The proposed mechanism involves terminal PO₂ groups chemically adsorbing to the titanium dioxide surface, with a bidentate complex forming in the case of orthophosphate. Linking PO₂ groups interact very weakly, if at all, with the surface. Electrostatic attraction is also involved when the polyphosphate and titanium dioxide surfaces are oppositely charged. There was no detectable adsorption onto silica substrates at any pH examined. The type of surface metal atom involved plays a key role in controlling polyphosphate adsorption.

Both silica and polyphosphate addition were shown to have a marked influence on the rheological properties of titanium dioxide slurries, producing a maximum yield stress value at low concentrations. The yield stress was very sensitive to polyphosphate concentration, behaviour attributed to the introduction of a short range steric barrier.
Competitive adsorption between different adsorbates showed that higher n linear polyphosphates can displace lower n species from the surface.

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REFERENCES