

Note

Surface ion exchange and adsorption of some dyes on α -Zr(HPO₄)₂·H₂O micro-crystals

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Electrical conductance¹ and membrane potential measurements² have shown that, at temperatures below 60°C, the ionic transport properties of α -zirconium phosphate [α -Zr(HPO₄)₂·H₂O] depend on the number and nature of counter ions present on the surface of the micro-crystals. Further, α -zirconium phosphate, both as the salt and as some organic derivatives, has already been employed in processes involving the surface such as catalysis³ and chromatography⁴⁻⁶. It was therefore of interest to investigate the chemical and physical properties of the surface of the α -zirconium phosphate micro-crystals. In previous papers^{7,8} we have reported the determination of the surface ion-exchange capacity by the Cs⁺ ion-exchange procedure, and ion exchange with alkali metal, alkaline earth metal and some transition metal ions was also investigated.

This paper reports a study on the uptake of large organic cations on the surface of α -zirconium phosphate micro-crystals. In particular, methylene blue and crystal violet were employed and the H⁺-organic cation exchange occurring at the surface of the micro-crystals was examined. The adsorption of alizarin on micro-crystals, whose surface was first loaded with a known amount of methylene blue or crystal violet, was also investigated.

EXPERIMENTAL

Chemicals

All reagents used were Carlo Erba (Milan, Italy) R.P.E. products, except ZrOCl₂·8H₂O, which was a Merck (Darmstadt, G.F.R.) pro analysi product.

Ion-exchange material

α -Zr(HPO₄)₂·H₂O was prepared by slow decomposition of zirconium fluoro complexes in the presence of phosphoric acid⁹. The crystals were washed with distilled water to pH 4.5 and stored over P₄O₁₀. The total amount of the surface exchangeable protons was obtained by the procedure described previously⁷. The surface ion-exchange capacity of the micro-crystals employed was 2.9 ± 0.1 μ equiv. per gram of exchanger.

Methylene blue and crystal violet surface ion exchange

Uptake. A 1-g amount of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was equilibrated with a $1 \cdot 10^{-4} M$ solution of methylene blue or crystal violet at $20 \pm 1^\circ\text{C}$ for 24 h. The solutions were analysed for their Cl^- , H_3O^+ , methylene blue and crystal violet contents.

Release. A 10-g amount of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was equilibrated, with stirring, with 500 ml of a $1 \cdot 10^{-4} M$ solution of methylene blue or crystal violet, then the solid was washed three times with 250 ml of acetone and dried in air. A 1-g amount of this material was equilibrated, with stirring, with 25 ml of hydrochloric acid of suitable concentration at $20 \pm 1^\circ\text{C}$ for 24 h. The solutions were analysed for their methylene blue or crystal violet content.

Alizarin adsorption

Some samples (2 g) of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, whose surface was loaded with a known amount of methylene blue or crystal violet, were equilibrated with 15 ml of $1 \cdot 10^{-4} M$ alizarin in acetone solution at $20 \pm 1^\circ\text{C}$ for 24 h. The solutions were analysed for their alizarin contents.

Analytical methods used

pH and chloride ion concentration were measured with a Beckman Research pH meter. Silver-silver chloride electrodes were prepared according to Brown's method¹⁰. Methylene blue, crystal violet and alizarin concentrations were determined with a Beckman 25 spectrophotometer at 664, 591 and 426 nm, respectively. The absorbances of methylene blue and crystal violet solutions were determined at constant pH (4.5).

RESULTS AND DISCUSSION

Methylene blue and crystal violet ion exchange

$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ has a layered structure such that, under suitable conditions (room temperature and $\text{pH} \leq 4$), only its surface protons can be replaced by cations having ionic radii greater than 1.32 \AA ^{11,12}. Hence it was interesting to study the interaction between the α -zirconium phosphate surface and large organic cations; for this purpose methylene blue and crystal violet, whose structural formulae are shown in Fig. 1, were used. Fig. 2 reports the uptake of methylene blue and crystal violet from $1 \cdot 10^{-4} M$ solutions; the added dye was completely taken up by the surface of the ion exchanger up to a level of $1.5 \mu\text{equiv./g}$; this value is about 50% of the surface ion-exchange capacity ($2.9 \mu\text{equiv./gram}$), determined by caesium ion uptake. When further dye was added, the slopes of the uptake curves decreased and vanished above $3 \mu\text{equiv./g}$.

The dye uptakes corresponding to the plateau is $2 \mu\text{equiv./g}$ for methylene blue and $1.8 \mu\text{equiv./gram}$ for crystal violet; these values are about 70% and 60% of the total surface ion-exchange capacities, respectively. The strong affinity of the two dyes for the α -zirconium phosphate surface seems to indicate that the surface protons are exchanged by the cationic dyes. In agreement with this hypothesis, the uptake occurs at various pH values, but pH measurements do not often permit a careful discrimination between exchange and adsorption. However, it can be pointed out that proton exchange does not alter the chloride ion concentration, whereas adsorption necessarily involves ion pairs (organic cation + chloride ion) because of the electroneutrality of

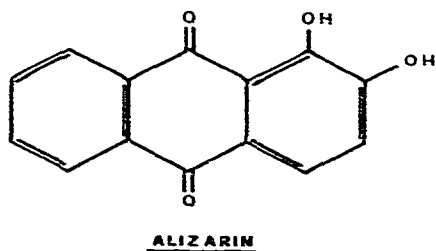
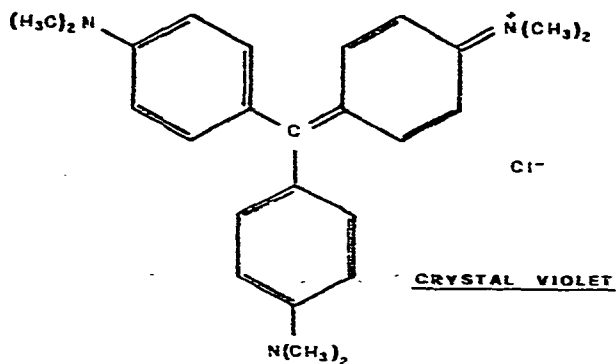
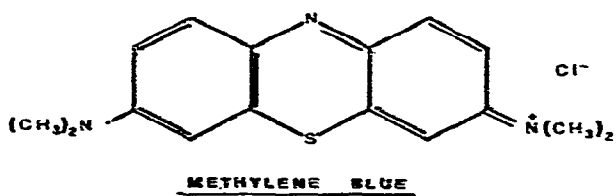


Fig. 1. Structural formulae of methylene blue, crystal violet and alizarin.

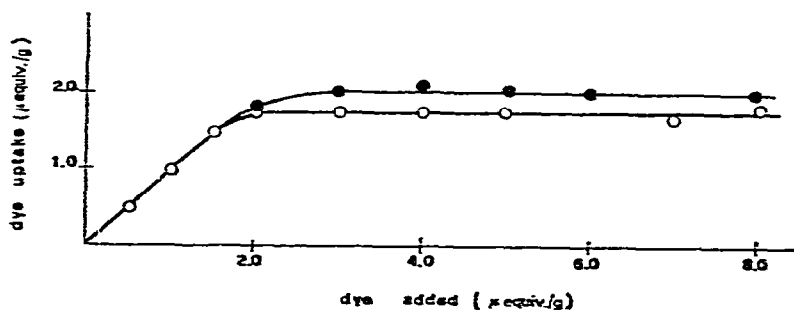


Fig. 2. Methylene blue (●) and crystal violet (○) uptake on the surface of α -Zr $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ micro-crystals, from $1 \cdot 10^{-4}$ M solutions of dye at 20°C .

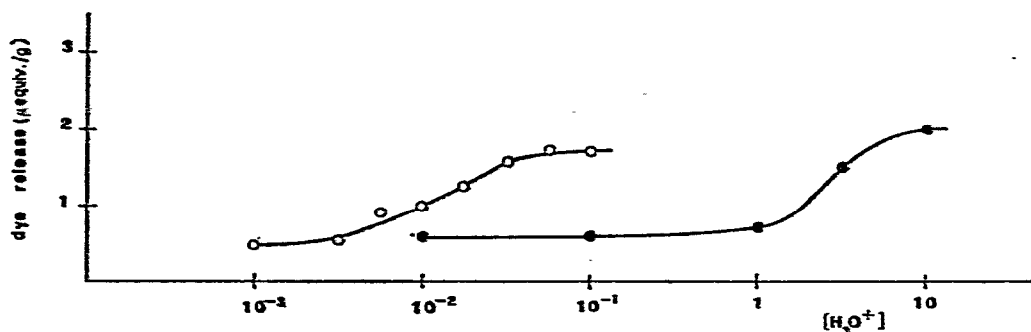


Fig. 3. Methylene blue (●) and crystal violet (○) release for samples whose surface was saturated by the dye, as a function of H_3O^+ concentration. Conditions: 1 g of exchanger equilibrated with 25 ml of HCl of suitable concentration.

the exchanger. Potentiometric determinations with the silver-silver chloride electrode have shown that the chloride concentration is constant and equal to $1 \cdot 10^{-4} M$ for all the uptake curve points, so confirming the ion-exchange hypothesis.

Therefore, washing of the micro-crystals with an aprotic solvent should not alter the amount of dye present on the surface and it should be possible to elute all of the dye with an electrolyte solution of suitable concentration. To confirm this experimentally, a large amount of α -zirconium phosphate was equilibrated with an aqueous solution of dye, in order to saturate the micro-crystal surfaces with methylene blue or crystal violet. After washing with acetone (for further details, see under Experimental) some samples of this material (1 g) were equilibrated with 25 ml of hydrochloric acid of suitable concentration. The results are shown in Fig. 3: in both instances the maximal release value is equal to that of the maximal uptake. Further, it is clear that the affinity of methylene blue for the zirconium phosphate surface is greater than that of crystal violet, probably because of its smaller steric hindrance, higher charge density on the nitrogen atoms and its ability to make dimers on the micro-crystal surfaces¹³ and in solution. Finally, let us consider the possible positions of these two organic cations on the zirconium phosphate surface. Methylene blue and crystal violet are planar cations: if they were lying parallel to the surface (Fig. 4), they would be able to cover three or four fixed charges, so that dye uptake would not be greater than 25 or 33% of the surface ion-exchange capacity. As the ion-exchange percentages are greater than these values, it seems to indicate that the dye molecules are lying perpendicularly or obliquely to the surface plane.

Alizarin adsorption

Alizarin is a neutral molecule whose structure is similar to that of methylene blue (Fig. 1). Preliminary experiments have shown that alizarin adsorption on α -Zr(HPO₄)₂·H₂O micro-crystals is negligible (about 1% of the surface ion-exchange capacity). Thus, it was interesting to investigate if alizarin adsorption was increased by the presence of organic cations on the zirconium phosphate surface. For this purpose, 2 g of α -Zr(HPO₄)₂·H₂O, whose surface was previously loaded with a known amount of methylene blue or crystal violet, were equilibrated with 15 ml of $1 \cdot 10^{-4} M$ alizarin in acetone solution. Fig. 5 shows the results of these experiments. Alizarin

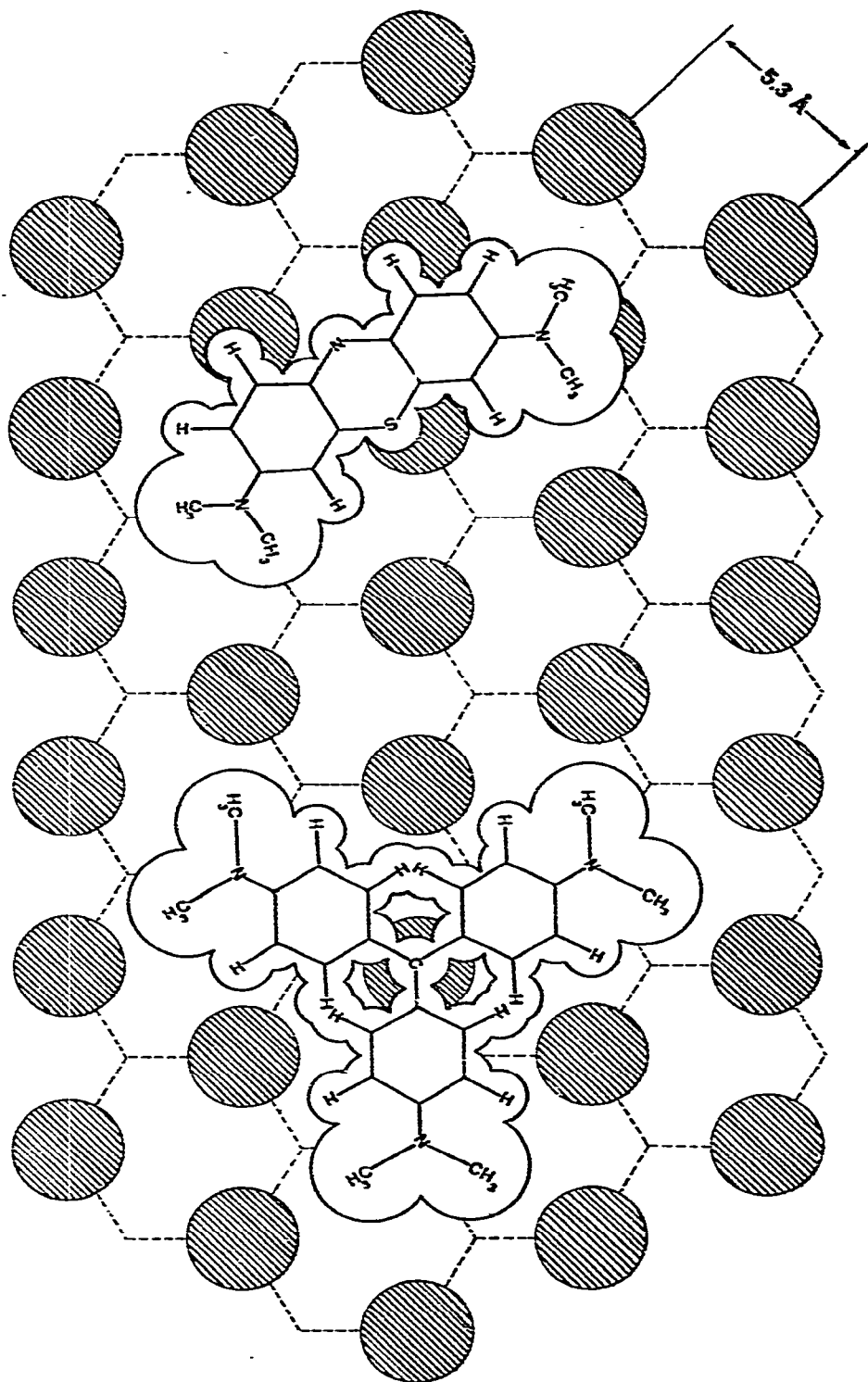


Fig. 4. Possible positions of methylene blue and crystal violet lying parallel to the α -zirconium phosphate surface. Circles represent surface fixed charges.

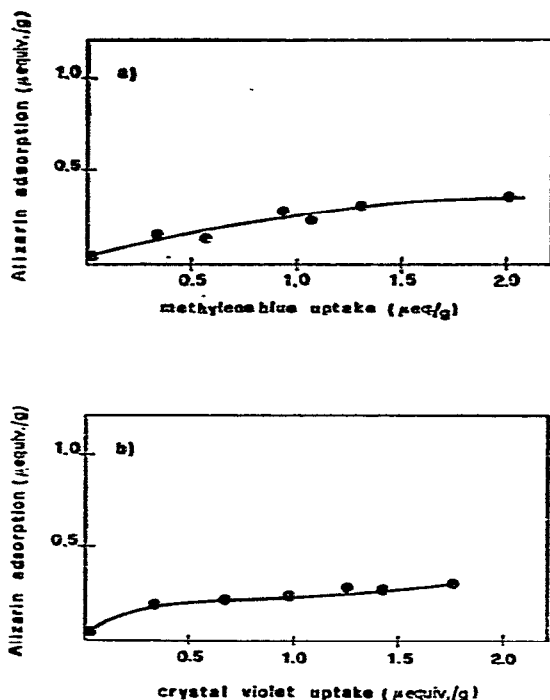


Fig. 5. Alizarin adsorption as a function of (a) methylene blue and (b) crystal violet uptake on the surface of α -Zr $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ micro-crystals. Conditions: 2 g of α -Zr $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ equilibrated with 15 ml of a $1 \cdot 10^{-4}$ M alizarin in acetone solution at 20°C .

adsorption increases with dye uptake from 0.04 to 0.3–0.4 $\mu\text{equiv./g}$; further, the slopes of the adsorption curves decrease with increasing dye uptake, showing that the interaction of alizarin with each organic cation is greater when the alizarin adsorption is smaller.

CONCLUSION

Large monovalent, organic cations, such as methylene blue and crystal violet, are able to exchange reversibly the protons present on the surface of α -Zr $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ micro-crystals. For conversions of less than 50% their affinity for surface fixed charges is greater than that for protons, probably owing to their smaller hydration energy. Further, surface replacement of protons with methylene blue or crystal violet increases alizarin adsorption from acetone solutions. From a practical point of view, these results show that it is possible to change reversibly the adsorption properties of α -Zr $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ micro-crystals, replacing surface protons by different organic cations, and so to employ the same material for different kinds of separations. Other than as a solid support in gas chromatography^{4–6}, the utilization of α -zirconium phosphate micro-crystals (with their surface hydrogens or in a suitable organic cationic form), in thin-layer or high-performance liquid chromatographic separations can thus be envisaged.

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