ADSORPTION MECHANISM OF ORGANIC SULFONATED COMPOUND, PONCEAU R, TO HYDROXYAPATITE IN AN AQUEOUS PHASE — EFFECT OF SODIUM CHLORIDE ON THE ADSORPTION AMOUNT —

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Abstract: Adsorption mechanisms of Ponceau R (PR) by hydroxyapatite (HAP) in an aqueous phase were discussed. PR was adsorbed mainly through isomorpous substitution of phosphate ion on the surface of HAP with terminal sulfonate group of PR and through electrostatic attractive force between calcium ion on the surface and the sulfonate group of PR. Added NaCl interfered the adsorption of PR when the concentration of PR was low. This was explained in terms of ionic strength effect, that is, electrostatic attractive force between PR and HAP was weakened by the NaCl added. On the other hand, added NaCl accelerated the adsorption when a concentration of PR was high. This was due to the fact that the added salt dehydrated the PR ions which are adsorbed and/or located close to the surface of HAP, resulting in acceleration of hydrogen bonding between –OH groups and of the hydrophobic interaction between dimethyl benzene groups of PR ions on the surface of HAP, that is, lateral interaction of PR on the surface became significant.

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INTRODUCTION

Binding mechanism of methyl orange (MO) and Ponceau R (PR) to hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂) was discussed in the previous paper¹. These dyes have one or two sulfonated groups in each chemical structure (see FIGURE 1) and the size of sulfonated group is quite similar to that of orthophosphate ion. It was concluded that these dyes were easily adsorbed after an ion exchange or isomorphous substitution between sulfonate group of the dyes and phosphate group of HAP in an aqueous phase ². The effect of added NaCl on the adsorption was, however, too complicated to explain in the previous paper¹.

MO was not adsorbed by HAP at its low concentrations but adsorbed at rather higher concentrations (0.3 – 0.5mM) in the absence of NaCl. However, the adsorption could be hardly detected in the presence of 50 or 100 mM NaCl, that is, NaCl inhibited the adsorption. It was concluded in the previous paper¹ that binding of MO to HAP was dominantly electrostatic and, therefore, the adsorption amount decreases with an ionic strength prepared by
NaCl. Unfortunately, studies on the adsorption of MO at concentrations higher than 0.5 mM were unable to develop and extend due to its low solubility.

The binding behavior of PR was more complicated than that of MO. The adsorption amount of PR at concentrations less than 0.15 mM decreased with a concentration of added NaCl. It, however, increased with a concentration of added NaCl when the concentrations of PR were higher than 0.2 mM. The effect of added NaCl on the adsorption amount of PR was, thus, reversed with a concentration of the adsorption amount of PR.

The effect and behavior of NaCl on the adsorption amount of PR will be discussed in the present paper. To study the interaction between HAP and organic compounds is important for understanding the mechanism of formation of biological hard tissues, such as teeth and bones, which are composites of inorganic and organic compounds.

MATERIALS AND METHODS

HAP was the same sample as that used in the previous papers \(^1\)-\(^5\). It was a product of Nacalai Tesque Co. (Kyoto), of which specific surface area was 50 m\(^2\)/g. Chemical structures of dyes, PR and MO, used in the present paper are shown in FIGURE 1. These compounds are azo dyes and have one or two sulfonated groups in their chemical structures. These dyes as well as other reagents were purchased from Tokyo Kasei Co. (Tokyo) and Nacalai Tesque Co. (Kyoto). These were used without further purification.

Adsorption amount of dye was calculated from the difference in concentrations before and after the adsorption by HAP (= 2.5 g/dl) at 30 °C. It was confirmed that the adsorption equilibrium was attained within 3 days after the preparation of the sample solution mixed with the HAP powder. The concentration of PR was determined by colorimetry at 502 nm after separation of the supernatant from the HAP particles by means of centrifugation.

![FIGURE 1. Chemical structures of methyl orange (MO) and Ponceau R (PR)](image)

RESULTS AND DISCUSSION

1) Buffer Function of HAP against Solution pH

HAP particles (2.5 g/dl) showed a buffering action toward various pHs of an aqueous solution containing 0.2 mM PR. Some results are shown in FIGURE 2. An initial pH, \(pH_{init}\), was adjusted by combination of NaOH and water (closed diamond) or of NaOH and 100 mM NaCl (open square). An equilibrium pH, \(pH_{eq}\), after 3 days at 30 °C was almost constant over a wide range of \(pH_{init}\) irrespective of the concentration of NaCl added. Diagonal straight line in FIGURE 2 is showing the relationship of \(pH_{init} = pH_{eq}\), on which line the experimental points should be plotted if OH\(^-\) or H\(^+\) ion was not consumed by HAP at all.
The results in FIGURE 2 are showing that the OH⁻ ion was consumed by HAP and the surface concentration of OH⁻ becomes denser after the adsorption than that before the adsorption, when pH_{init} is higher than ca. 7.4 - 7.5 where pH_{eq} < pH_{init}. This fact is significant to explain the result shown in FIGURE 5, which will be discussed later. Some of OH⁻ might be consumed by hydrogen ions of the surface phosphates (HPO₄²⁻ and H₂PO₄⁻). However, this consumption mechanism should be negligible, because an equilibrium pH, pH_{eq}, remains between 7 and 8, where orthophosphate ion might be re-protonated to HPO₄²⁻ and/or H₂PO₄⁻.

The constancy of pH_{eq} over a wide range of pH_{init} is convenient to discuss the adsorption amount of PR. Spectra of PR are different, depending on the medium pH. In this study, however, pH_{eq} was located between 7 - 8 after attaining the adsorption equilibrium and the spectra were almost the same irrespective of the pH_{init}. Therefore, the concentration and adsorption amount of PR after attaining the adsorption equilibrium were easily determined by means of colorimetry.

(2) Effect of Added NaCl on the Adsorption Amount of PR

Adsorption isotherms of PR by HAP at various concentrations of NaCl are shown in FIGURE 3. The isotherms were not of the Langmuir type but rather of the cooperative. The adsorption amount was low at the concentrations of PR less than 0.05 mM, but it increased steeply with a concentration of PR in particular in the presence of 50 and 100 mM NaCl.

The amount of adsorption of PR decreased with a concentration of added NaCl in the concentration range lower than 0.1 mM PR, while it increased in the concentration range higher than 0.2 mM PR. The effect of NaCl on the adsorption amount of PR was reversed at the concentrations around 0.12 - 0.20 mM PR. We have to consider the reason why the duplicity of NaCl was exhibited on the adsorption amount of PR.

The adsorption amount of PR as a function of a concentration of added NaCl was studied in order to confirm the fact mentioned above. The results are shown in FIGURE 4, where the concentrations of the added PR were kept constant at 0.1 mM (open diamond) and 0.5 mM (open square). The adsorption amount of PR from 0.1 mM PR decreased with a concentration of added NaCl, while that from 0.5 mM increased. Thus, the tendency observed in FIGURE 3 was confirmed again.

The PR molecules were separately adsorbed one by one on the surface, that is, without
lateral interaction between PR ions on the surface when the concentration and adsorption amount of PR was low. The driving force for the adsorption might be just electrostatic attractive force between adsorbate PR and Ca$^{2+}$ on the surface and between PR and vacant site for phosphate ion on the surface of HAP. These adsorption sites are positively charged and the vertical interaction between adsorbent and adsorbate species is dominant driving force for the adsorption. NaCl added to the solution showed the shielding effect against electrostatic attractive force (i.e., the ionic strength effect) and, therefore, the adsorption amount decreased with a concentration of added NaCl, as shown by a symbol of open diamond in FIGURE 4.

When the added concentration of PR was increased up to 0.5 mM (open square in FIGURE 4), the adsorption amount of PR increased with a concentration of added NaCl. In contrast with the case of 0.1 mM PR, the intermolecular interaction between PR ions increased on the surface or in the vicinity of the surface. That is, lateral interaction between the adsorbate molecules increased by virtue of high adsorption amount and high concentration of PR and also due to dehydrating and/or salting-out effect of NaCl. These effects result in strengthening of hydrogen bonding between -OH groups of PR ions and between –OH groups of PR and OH$^{-}$ ions on the surface of HAP. Hydrophobic interaction between dimethylbenzene groups of PR ion adsorbed on the surface also might accelerate the adsorption of PR to the surface of HAP.

It was concluded that the addition of a simple salt, NaCl, showed two different effects; one is the adsorption decreasing effect (i.e., ionic strength...
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effect) and the other the adsorption increasing effect (i.e., salting-out effect, or effect of promoting dehydration and hydrophobic interaction). As for MO, electrostatic shielding effect by NaCl was observed, as mentioned in the previous paper. However, the salting-out effect was not observed due to its low solubility and lacking in the –OH groups in its chemical structure.

(3) Comparison of Effects of Added Electrolytes between 0.5 mM NaCl and 0.5 mM NaOH

The effect of NaCl was compared with that of NaOH at the same concentration of 0.5 mM. The result was shown in FIGURE 5. Although the effect of 0.5 mM NaCl on the adsorption amount of PR was little (i.e., the symbol of open circle is very close to that of closed diamond in the figure), 0.5 mM NaOH strongly decreased the adsorption amount of PR. According to the results shown in FIGURE 2, the equilibrium pH was almost the same irrespective of the initial pH, while OH⁻ concentration on the surface should increase after the treatment with an aqueous solution of NaOH. These phenomena were explained as follows; the anion OH⁻ was consumed from the mother solution after the adsorption to the HAP surface, therefore, the solution pH was kept constant (i.e., buffer function by HAP), while the surface charge of HAP became more negative after the adsorption of OH⁻ (i.e., the accumulation of OH⁻ ions on the surface). This fact is suggesting that electrostatic repulsion between PR anion in the mother solution and OH⁻ anion on the surface increases, resulting in a decrease in the adsorption amount of PR. It was concluded that NaOH competes with an anionic PR for the adsorption sites on HAP, even though 0.5 mM NaCl, the same concentration as that of NaOH, hardly shows the competitive effect like this on the adsorption amount of PR. The OH⁻ anion is one of the component ions for HAP, therefore, it shows high affinity for the surface of HAP. On the other hand, the anion Cl⁻ is not a component ion for HAP. Therefore, it shows little affinity for HAP, resulting in a low adsorption amount to the surface of HAP. This is the reason why OH⁻ is repulsive while Cl⁻ hardly repulsive against PR anion.

FIGURE 5. Effect of an added electrolyte on the adsorption amount of PR by HAP, where the added electrolyte was 0.5 mM NaCl (open circle), 100 mM NaCl (open triangle), 0.5 mM NaOH (open square), and none (= just pure water, closed diamond). Although an initial pH, pH_{init}, in the presence of 0.5 mM NaOH was 10.55, it decreased to an equilibrium pH, pH_{eq}, of 7.60 after 3 days at 30 °C. See also the pHs shown in FIGURE 2.
吸附机理的PR和添加电解质的影响讨论，并得出以下结论。

1. PR主要通过HAP中PO₄³⁻和PR中末端-SO₃⁻之间的等同晶取代和静电吸引力，以及Ca²⁺在表面和-SO₃⁻之间的静电吸引作用来吸附。
2. PR和HAP之间的静电吸引力（即垂直互动）在低浓度NaCl存在时被减弱。这是由NaCl或离子强度效应引起的屏蔽作用。
3. 加入NaCl加速了PR的吸附，当PR浓度高时。这是由于NaCl的脱水作用，加速了PR分子间的氢键和疏水性相互作用。这是横向互动的增强。
4. 尽管0.5 mM NaCl几乎没有影响吸附，但在0.5 mM NaOH存在时，吸附量减少。这是因为OH⁻吸附在表面，通过静电排斥作用抑制了PR的吸附（即，竞争吸附）。