Poster Session: Complexes of Aminoacids, Peptides and Proteins

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Comparative Studies on the Adsorption of Urease to Porous and Nonporous Aluminium Oxides

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The adsorption of enzymes and other proteins has for a long while played an important role in the field of chromatography [1]. Beyond that, the adsorption of proteins, as well as their covalent attachment to carriers is known as a method for preparing immobilized enzymes. The application of carrier bound urease in the fields of analytical chemistry and medicine [2, 3] is well known.

Most of the adsorption equilibria examined can be described quantitatively in terms of the Freundlich or Langmuir adsorption isotherm. We studied the adsorption equilibria between the enzyme urease and some aluminium oxide modifications and found that all followed the Langmuir theory with one exception: in the case of α-Al_2O_3 (corundum) the quantity of enzyme adsorbed to it as a function of enzyme supply steeply increases in the range of small enzyme concentrations and, going through a maximum again decreases to a saturation value. A plot of the activity of the adsorpt shows the same course. At unfavourable α-Al_2O_3 to enzyme ratios the activity of the adsorbed urease is low, an effect resulting from the spreading of the protein molecule on the non-porous plain surface. However, at the adsorption maximum the residual activity is nearly 100%. Accordingly, the loss of activity of urease adsorbed to porous aluminium oxide modifications (γ-Al_2O_3) is considerable. Even though these surfaces are much larger and contain a large number of hydrophilic groups the adsorbed quantity of enzyme per square metre is 5 to 6 fold smaller than when α-Al_2O_3 is applied as adsorbent.

For an explanation of this anomalous adsorption behaviour, at present two working models are discussed. If it is assumed that the structure of the urease molecule deviates from the spherical shape, the adsorption maximum could be a result of a particular orientation of the urease molecules, which is especially favourable for the conservation of catalytic activity and is dependent on enzyme concentration in solution [4]. A second proposal for interpretation is based on investigations concerning the association of urease molecules in solutions of different concentrations [5] as well as the dissociation of an urease monomer in several active subunits [6], and on calculations about the thickness of the adsorbed protein layer. Assuming that in the range of the adsorption maximum coverage of the surface is 100%, the thickness of the layer is identical with that of a 4 n subunit of urease. Therefore, a kind of 'dissociative adsorption' of the enzyme to plain α-Al_2O_3 surfaces cannot be excluded.

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Coordination Catalysis: the Oxidation of Amino Acids and Peptides by Dioxygen in the Presence of Transition Metal Ions

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The modification of ligand reactivity which occurs when amino acids and related ligands are coordinated to certain transition metal ions is now well known [1]. Increased reactivity is demonstrated both by the base catalysed racemisation of amino acids and by the oxidation of the amino acid to a keto acid with dioxygen as oxidant [2]. In the case of labile complexes, *e.g.* with Cu^{2+} or Zn^{2+}, oxidation serves to increase racemisation *via* the formation of a coordinated Schiff base which can undergo subsequent reactions [2, 3].

Although such oxidation has been reported [2] for the Cu^{2+}–L-alanine system certain mechanistic details remained unclear. This system has been re-investigated and the role of oxygen (and the intermediary of superoxide and peroxide intermediates) re-examined. The role of peroxide derived from oxygen is related to the effect of hydrogen peroxide added separately to the system and the general nature of the oxidation for aliphatic amino acids has been demonstrated.