coordination to collagen, at higher pH. This is in agreement with the collagen distinctive conformation arising from specific aggregation and cross-linking.

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Silver–Gelatin Complex

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A new chemical process for binding silver(I) with gelatin in alkaline medium is described. The complex is susceptible to reducing substances and produces an intense red coloured, very stable silver sol. Oxygen-dependent dissolution of silver sol is discussed.

Introduction

Silver(I) complexed by ligands containing both oxygen and nitrogen donor atoms is easily reduced to metallic sol [1]; some amino acids, sodium sulphamoyl benzoate [2], albumin, and gelatin serve well for the complexation of silver(I) ion. Amongst all the reagents, an aqueous solution of gelatin and silver nitrate forms an alkali-soluble silver compound. Carbon monoxide, ascorbic acid and formaldehyde reduce the alkaline solution of silver gelatin complex, yielding a silver sol, which is intensely coloured, finely powdered, very stable, and follows Beer's law in a wide concentration range [3]. Here we report the quantitative redissolution of silver sol in the presence of oxygen and a suitable complexing ion.

Results and Discussion

Gelatin is well known but has had few analytical applications as a complexing reagent even though it has proved to be a sol stabiliser. Other protein molecules such as egg albumin or serum albumin give the same results as gelatin. Here the complexation is very effective. Even precipitated silver chloride becomes soluble in gelatin solution in 2 *M* sodium hydroxide. It is very likely that the free silver ions are reduced to metal in accordance with the formulation for the silver compound of *p*-sulphamoyl benzoic acid adopted by Cinhandu [4]:

$$2\ Ag^{+} + R + 4OH' \rightleftharpoons 2\ Ag^{\circ} + Re + 2\ H_2O$$

R = Reducing agent, Re = Reduced state of R

The reducing solute rapidly reduces the silver ions to metallic silver while the gelatin is involved in the mechanism supplying free silver ions and probably contributing to the exceptional stability of the colloidal particle. The protein molecule (0.5%) stabilizes the sol in a temperature range of 10–30 °C; indoor light causes no harm. If the temperature is high enough (above 30 °C) the decay in the absorbance value of the exposed solution indicates very slow deposition of metallic silver. The unexposed solution remains unaltered over a wider range of temperature. The reduced silver looks like a very stable colloidal solution with an intense absorption.

Hence it can be a very good selective method [5] for the determination of traces of Ag(I) in biological samples in the presence of various ions. Silver gelatin complex on exposure to carbon monoxide, formaldehyde and ascorbic acid [6] *etc.* quantitatively forms metallic sol. The colour intensity of the exposed solution depends on the solutes added to the silver gelatin complex. If the solute neutralizes the alkaline solution to a greater extent (less than 1.5 *M*) destabilisation of sol occurs. Most of the metal ions are not reduced under the same conditions. Only Hg(I) breaks into a black precipitate, thereby not hindering photometry.

Aqueous solution of cyanide reacts with the sol in the presence of oxygen according to the reaction:

$$4\ Ag + 8\ NaCN + O_2 + 2H_2O \rightleftharpoons 4\ Na[Ag(CN)_2] + 4NaOH$$

The reaction for the silver sol is instantaneous and the end point is red to colourless. Thus silver sol in gelatin is not only a very good method for determining traces of carbon monoxide, formaldehyde and ascorbic acid but is also selective for Ag(I) determination in protein solution using both photometric and volumetric procedures. The complexation of silver sol above pH 6.5 in the presence of cyanide enables one to determine dissolved oxygen in water by photometric means at pH above 6.5 using a wavelength of 410 nm. The method is comparable to that of Duncan [7].

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On the Reasons and Conditions of Occurrence of Optical Activity of Natural Compounds

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It is known that α-amino acids occurring in natural proteins–enzymes belong to the L-series; at the same time, compounds subjected to oxidation (carbohydrates, sugars, *etc.*) belong to the D-series. The origin of the optical activity of these compounds is not clear, however the difference in catalytic activity of L- and D-amino acids could permit the selection of optically active catalysts at early stages of development, since according to the theory of evolutional catalysis [1], the main criterion for selection of catalytically active systems is absolute catalytic activity.

The study of the oxidation of an optically active substrate (L-cysteine) in a static system in the presence of complexes of iron with L- and D-alanine over a wide range of pH values (6–11.5) enabled us to determine the difference in catalytic activity of the complexes under study. It was found that the catalytic activity of complexes of iron with D-alanine was higher in the 6–9.2 pH range than the respective value for complexes with L-alanine, while in the 9.2–11.5 pH range the relationship reversed (see Fig. 1). At pH = 7 the catalytic activity of the iron complex with D-alanine was 7 times higher than the catalytic activity of the complex with L-alanine.

To ascertain the composition of complex compounds taking part in the catalytic process the complex formation of Fe(II, III) with L- and D-alanine has been studied over a wide range of pH values (1–12) by the oxidative potential technique [2]. It was found that the processes of complex formation of Fe(III)–Fe(II) with L- and D-alanine in aqueous solution differ from each other and the composition of the complexes prevailing in certain pH ranges was different. Thus the difference in catalytic activity of complexes of iron with L- and D-amino acids is associated with the different composition of complexes formed at different pH values. This means that selection of optically active catalysts and substrates in the early stages of chemical evolution could be determined by the differences in complex formation between L- and D-amino acids and iron ions, leading to a different catalytic activity of the systems based on them, and the value of catalytic activity, as has been shown in [1], serves as a parameter of natural selection for self-developing catalytic systems. Such a process could occur in aqueous solution only at definite pH values, for example at pH *ca.* 6–8, where the difference in catalytic activity is sufficiently high.

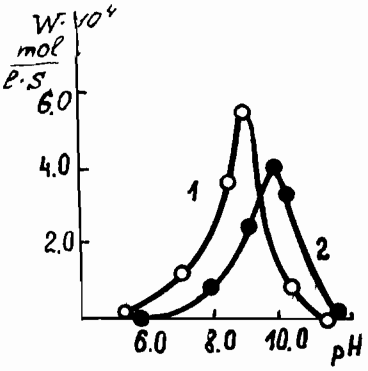

Fig. 1. Rate of oxidation of 0.2 *M* aqueous solution of L-cysteine *vs.* pH, 40 °C, $C_{Fe^{3+}} = 10^{-4}$ mol/l, $C_{ala} = 0.5$ mol/l: 1, D-Alanine; 2, L-alanine.

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