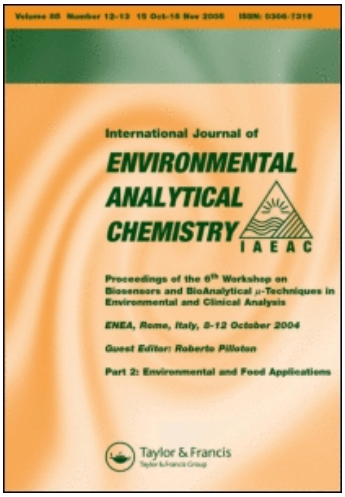

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The Interaction of Mercury (II) Ions with Sugars and Amino Acids

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Formation constants of mercury (II) complexes with several sugars and amino acids have been investigated by applying Schubert's method and using ^{203}Hg as the radioactive tracer. Experiments were performed at pH 7.8, which was adjusted by the addition of barbital buffered solutions. Experiments were carried out at constant ionic strength ($I = 0.375$), $T = 298$ K and all systems were 0.125 M Na_2SO_4 solutions. All the complex ions formed were of the 1:1 type.

The effect of $-OH$, $-NH_2$, $-COOH$, configuration and chelate ring size on stability complex formation was obtained by comparison of the formation constants of 4 amino acids and 5 sugars. Formation constants ($\log K_f$ in brackets) were determined for: galactose (5.02), sorbose (4.67), xylose (4.26), glucose (5.18) and sucrose (4.87), glycine (4.57), alanine (4.47), serine (4.53), aspartic acid (4.27), methionine (3.37), arginine (3.65) and proline (3.55).

KEY WORDS: Formation constants, mercury complexes, radioactive tracer, ionic strength.

INTRODUCTION

The physical chemistry of sugar and amino acid compounds containing mercury has not been thoroughly investigated. Therefore, data on the formation of such compounds, their stability and structure are of general interest.

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The pollution of the environment with mercury seems to be a serious problem in certain areas.[1–3] The behaviour of mercury in the aquatic environment, however, is not well understood and our knowledge of the interaction of mercury with dissolved organic matter is rather scarce.[4,5] It is well known that dissolved animal and plant organic matter is always present in the aquatic environment.[6] Amino acids and sugars, as disintegration products of biological matter, are therefore common compounds found in continental and oceanic waters. On the other hand, the interaction of mercury with sugars and amino acids is of special interest from toxicological and physiological aspects.

The aim of this work is to study for the stability of amino acid and sugar compounds containing mercury since these data could be an important contribution to understanding mercury behaviour in the aquatic environment. Literature contains limited information on the stability constants of mercury chelates with amino acids,[7–14] but there are no reports on the stability constants of mercury chelates with sugars.

EXPERIMENTAL

High activity ^{203}Hg was obtained from the Vinča reactor at the Boris Kidrič Institute, Belgrade. All reagents were analytical grade. The solution of the ligand was prepared just before use by dissolving weighed amounts of either the sodium salts, acid or base, and diluting them to a known volume after adjustment to pH 7.8 with dilute NaOH.

The universal veronal buffer, devised by Michaelis was employed.[15] The buffer is essentially a 0.125 M solution of sodium sulphate and contains a mixture of acetate and diethyl barbiturate ions, each at a concentration of 0.02856 M.

The synthetic organic cation exchanger, Dowex-50, was used particularly because its capacity is independent of pH over a wide pH range; the air-dried resin was classified by means of U.S. standard sieves to 100–150 mesh particle size. The Dowex-50 resin used for exchange experiments was rendered iron-free by percolation with 6 M HCl at room temperature.

The resin was put through several alternate Na^+–H^+ cycles with 5% solutions of Na_2SO_4 and HCl. After saturation with excess

Na_2SO_4 the resin was equilibrated with excess 0.125 M Na_2SO_4 solution and the supernatant solution in contact with the resin was adjusted to pH 7.8 with dilute NaOH solution. After the mixture was stirred 1 h the pH of the supernatant was tested and readjusted, until no change in pH took place after stirring. The resin was filtered through a Büchner funnel, and rapidly washed free of adhering salt solution with distilled water. The washed resin was spread in a thin layer on a tray and air-dried.

To each of ten flasks containing 100 mg of the sodium form of Dowex-50 were added 25 ml of veronal buffer at pH 7.8 and 0.125 M of Na_2SO_4. To each flask was added a predetermined volume of a given ligand. The ligand-containing solution was adjusted to a pH 7.8 and to 0.250 M in Na^+ with Na_2SO_4. Finally, the volume in each flask was brought to 100 ml with 0.125 M Na_2SO_4 solution. Generally, four to eight different concentrations of the ligand were employed; the concentration range chosen depended on the ligand's affinity for Hg(II). Two of the ten flasks contained zero concentration of the given ligand, and an additional two flasks containing only buffer plus Na_2SO_4 were run as blanks. After shaking the flask mechanically for 3 h, an aliquot of the supernatant from each was removed for the radiochemical assay. Subsequently, in some cases, 1 ml of a 0.125 M Na_2SO_4 solution containing carrier-free ^{203}Hg was added to each flask. After an additional 3-h shaking period, aliquots were removed for the ^{203}Hg assay. In other runs the ^{203}Hg was already present in the buffer. This method has been described in more detail by Schubert *et al.*,[16–18] and Huljev.[19] Radioactivity was measured by a 2×1.5 inch NaI (T1) well type scintillation counter attached to an automatic present time counter.

RESULTS AND DISCUSSION

Formation constants, K_f, were calculated from the equation:

$$K_f = \frac{(K_d^0/K_d) - 1}{[A]^n} \tag{1}$$

where K_d^0 and K_d are distribution coefficients obtained in the absence and presence, respectively, of the ligand A, and n is the number of moles of A relative to the metal ion M. The distribution

coefficient for the cation M is defined as

$$K_d = \frac{\%\,\text{M in exchanger}}{\%\,\text{M in solution}} \times \frac{\text{volume of solution (ml)}}{\text{mass of exchanger (mg)}} \tag{2}$$

The term K_d^0 can be obtained directly or from K_d by graphical or analytical means. It is convenient to plot $1/K_d$ versus $[A]^n$ and to extrapolate the straight line for proper n values to zero concentration of A, as indicated by the relation

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{[A]^n \cdot K_f}{K_d^0} \tag{3}$$

Equation (1) can be rewritten:

$$\text{Log}\left(\frac{K_d^0}{K_d} - 1\right) = n \log [A] + \log K_f \tag{4}$$

A plot of $\log(K_d^0/K_d - 1)$ versus $\log [A]$ should be straight with slope n. The value of $\log K_f$ is the intercept of the straight line. Plots of $1/K_d$ vs. $[A]$ were linear, indicating that all the complexes were of the 1:1 type, i.e., $n = 1$.

The following conditions must be fulfilled for the method described:

1) Formation of anionic or neutral complexes which do not exchange on the cation exchanger,

2) Use of a very low concentration of metal ions (less than 10^{-8} M).

3) Use of an excess concentration of the ligands (sugars and amino acids).

4) Measurements made at high and constant ion strength.

5) No significant interaction between Hg(II) and the buffer components.

Conditions 1–4 must be fulfilled for Eqs. 1 and 2 to hold. Indeed it was found that:

a) Most of the mercury was bound to the resin.

b) Adsorption of a complex ion on the ion exchanger was not significant,

c) Control experiments without buffer showed that barbiturate buffers only form a weak complex with Hg(II) that has little effect on the stability of the investigated complex ions.

The results are summarized in Tables I and II.

TABLE I

Formation constants of some Hg(II)-sugar chelates

Sugar	Investigated concen. range of sugar ($\times 10^{+5}$ M)	$\log K_f$	Relative error (%)
D(+) glucose	below 2.9	5.18	2
D(+) galactose	below 2.9	5.02	2
L(−) sorbose	below 3.3	4.67	3
D(+) xylose	below 3.3	4.26	3
Sucrose	below 3.3	4.87	10

TABLE II

Formation constants of some Hg(II)-amino acid chelates

Amino acid	Investigated concen. range of amino acid ($\times 10^{+5}$ M)	$\log K_f$	Relative error (%)
Glycine	1–6	4.57	5
Alanine	0.1–0.3	4.47	7
Serine	0.1–0.5	4.53	7
Aspartic acid	1.5–4.0	4.27	5
Methionine	1.0–6.0	3.37	5
Arginine	1.0–3.0	3.65	8
Proline	0.2–0.6	3.55	5

Table I lists the formation constants for complexes of five sugars with Hg(II). Experiments were performed in low concentration of sugars which in all cases was not higher than ca. 10^{-2} milimoles per liter where the molar ratio of sugar to Hg(II) in the complex is always 1:1.

Results presented in Table II indicate that $\log K_f$ values for most of the investigated Hg-amino acids systems are close to four. The only exception is the Hg-methionine complex with a somewhat lower value of 3.37 because of the methionine structure.

Due to the high and constant ionic strength, it is possible that mercury has to compete with the excess of sodium ions in complex formation. For this reason the results for the formation constant are significantly lower than in literature.

The value of $\log K_f$ for sodium diethyl barbiturate at pH 7.8 is only approximately 0.1 so that this buffer component exerts little, if any complexing action. In tests without the barbiturate buffer, using only 0.1 M HCl, NaOH for adjusting pH, we calculated the formation constant K_f for the complex compounds. Data show that the main components of the buffer do not significantly affect the stability of the amino acids and sugars.

Literature mentions the stability of mercury acetate ($\log K_f = 5.81$) and chloride ($\log K_f = 6.7$) but for other values of pH, I and temperature. There are also data about $\log K_f$ for the complex compounds of Hg with amino acids,[7-14,18-19] but the constants cannot be compared because experiments were performed with other methods (glass electrode, solvent extraction) and under different experimental conditions. We worked with a proportionally high ionic strength so that it is difficult to compare these results with those in the literature. In recent reports, there are no data about the formation constants of complex compounds of mercury and sugars.

The positively charged $-NH_3^+$ group in the aspartic acid molecule can be expected to repel a positively charged ion from the adjacent carboxyl anion. Under experimental conditions, aspartic acid as far as its complexing action is concerned, is the equivalent of a monocarboxylic acid anion.

In actuality, there is not one form of a complex or chelate but a mixture in which the relative proportions of the different forms are a function of the respective formation constants. It is obvious, when relative K_f values are examined, that in aspartic acid, for example, the predominant form involves a combination of the mercury cation with both carboxyl groups. In an equilibrium mixture, however, small fractions must be present in which the mercury cation is combined with only a carboxyl group and an amino group, with a carboxyl group only, and with an amino group only.

The presence of these compounds in an aquatic system can influence the fresh oceanic water cycle of trace elements. The formation of certain complexes with amino acids and sugars can particularly be responsible for the uptake of certain trace metals by some biota, detritus and sediments.

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