EQUILIBRIUM STUDIES OF ALKYLTIN(IV) COMPLEXES WITH D-GLUCOSAMINE

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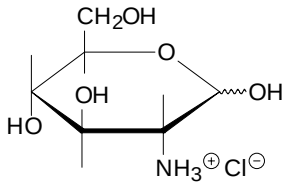
The acid-base and complex-formation equilibria involving glucosamine and its complexes with alkyltin(IV) chlorides have been studied by potentiometric technique. The results prove to a formation of 1 : 1 complex with trialkyltin(IV) and both 1 : 1 and 1 : 2 complexes with dialkyltin(IV) species. The stability constants in water were determined, the effects of temperature (from 15 to 35 °C) and ethanol (up to 88 vol.%) was studied and the speciation of the complexes was resolved.

Key words: Alkyltin(IV) chlorides; Alkyltin(IV) complexes; Glucosamine; Stability constants.

The deleterious effects of alkyltin(IV) compounds on man and environment are now well documented[1,2]. The alkyltin(IV) derivatives are highly toxic to insects and mammals[3], supposedly due to the inhibition of mitochondrial oxidative phosphorylation[4] and the ability to bind certain proteins[5]. For these reasons, significant attention is paid to environmental pollution by alkyltin compounds and to their presence in food. For example, the level of tributyltin chloride (which is highly toxic to variety of aquatic organisms[5,6]) was found to range from 5 to 188 ppb as tin in the salmon fish tissue. Investigation of the alkyltin-compounds-to-biomolecules interactions is thus of interest because it can provide an insight into behaviour of tin compounds in biological systems.



D-Glucosaminium chloride

In the present paper we report on the complexes of R_2SnCl_2 and R_3SnCl (where R is methyl, Me or butyl, Bu) with glucosamine (G). This ligand is known to be associated with humic matter[7] and to interact with trace metals in nature[7]. This work is a continuation of our earlier studies on alkyltin complexes[8–10].

EXPERIMENTAL

Materials and Reagents

Trimethyltin chloride, dimethyltin dichloride, tributyltin chloride and dibutyltin dichloride (all supplied by Merck) and G . HCl (Sigma) were used as received. Solutions of Bu_3SnCl and Bu_2SnCl_2 were prepared in ethanol. Sodium hydroxide stock solutions were prepared by diluting the content of concentrated volumetric solution vials (BDH). These solutions were systematically checked by titration with potassium hydrogen phthalate. All solutions were prepared in deionized water.

Methods and Procedures

The potentiometric titrations were performed using a Metrohm 686 titroprocessor equipped with a 665 Dosimate (Switzerland). Standardized, concentrated (≈0.1 M) NaOH solution was used as the titrant to minimize the volume added and to avoid a dilution due to volume change. The titroprocessor and electrode were calibrated with standard buffer solutions, prepared according to NBS Specifications[11]. The temperature was maintained constant by a Colora Ultrathermostate.

The dissociation constant of G . HCl was determined by titration of the mixture: G . HCl (0.01 M, 10 cm^3) + $NaNO_3$ (0.13 M, 30 cm^3) in an absence of any alkyltin compound. The stability constants of G–alkyltin chloride complexes were determined by titrations of the mixture of G . HCl (0.01 M, 10 cm^3) + $NaNO_3$ (0.20 M, 20 cm^3) to which either R_3SnCl (0.01 M, 10 cm^3) or R_2SnCl_2 (0.005 M, 10 cm^3) was added. The G/Sn mole ratios were chosen in accordance with known coordination properties of R_3SnCl (one coordination vacancy[12]) and R_2SnCl_2 (two coordination vacancies[13]). The titration data were evaluated based on equations:

$$M_mG_gH_h \rightleftharpoons m\,M + g\,G + h\,H \qquad (1)$$

$$\beta_{mgh} = \frac{[M_mG_gH_h]}{[M]^m[G]^g[H]^h} \,, \qquad (2)$$

where M stands for alkyltin compound and H for protons. In the absence of tin compound M we obtain protolytic equilibria $GH^+ \rightleftharpoons G + H^+$. If the alkyltin compound is added, it reacts with GH^+ forming a complex and releasing protons:

$$R_nSnCl_{(4-n)} + (4-n)\,GH^+ \rightleftharpoons R_nSnG_{(4-n)}Cl_{(4-n)} + (4-n)\,H^+ \,, \qquad (3)$$

where n = 2 or 3. The released protons are titrated by NaOH.

The calculations were performed using the program[14] MINIQUAD-75 which minimizes the sum of squares of weighed residuals in the analytical hydrogen ion concentration by successively varying the set of formation constants. The stoichiometry and stability constants of the complexes formed were

ascertained by trying various possible composition models for the system studied, as: MG, (MG + MG_2), (MG + MG_2 + MG_3), (MG + [MG(OH)]) and (MG + MG_2 + [MG(OH)]). The model selected was that which gave the best statistical fit and which was chemically consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals as described elsewhere[14].

RESULTS AND DISCUSSION

The addition of organotin compound to G . HCl results in presence and absence of Me_3SnCl in a decrease in pH value of the solution due to protons released in the complex formation. The titration curves of R_3SnCl complexes are consistent with a formation of 1 : 1 (Sn : G) species, whereas those for R_2SnCl_2 corresponds to a consecutive formation of 1 : 1 and 1 : 2 species, as expected according to the literature[12,13]. The obtained values of stability constants at 25 °C are listed in Table I. From the temperature dependence of β_{mgh}, Fig. 1, the values of enthalpy (ΔH^0_{298}) and entropy (ΔS^0_{298}) of complex formation were calculated (see values in Table I).

It is seen that the stability constants of the methyltin derivatives are higher than those of the butyl counterparts (see Table I). In addition, the G–R_3SnCl complex formation is exothermic for R = Me but endothermic for R = Bu (see Table I) for which also entropy of formation is higher. This reveals an increased disordering of the system due to poor interactions of butyl groups with hydroxyls of G and molecules of water. Thus the lower stability of Bu complexes in water can be mainly attributed to the higher hydrophobicity and bulkiness of butyl compared to methyl groups.

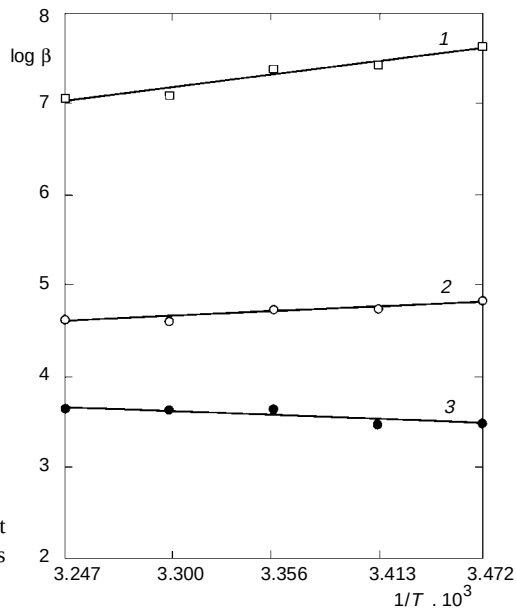
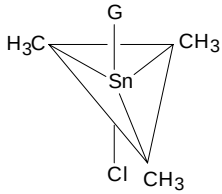


FIG. 1
Effect of temperature on the stability constant β (log β) of glucosamine (*1*) constants of its complexes with Me_3SnCl (*2*) and Bu_3SnCl (*3*)

D-Glucosamine is known to bind the transition metal ions[15,16] *via* the amino and deprotonated hydroxyl groups (NH_2, O^-, donor set). The potentiometric data are fitted assuming that glucosamine is bound to alkyltin(IV) by the amino group only. The formation constants of trialkyltin complexes with glucosamine are compared favourably with those of the monodentate imidazole[10]. This reveals that glucosamine binds with



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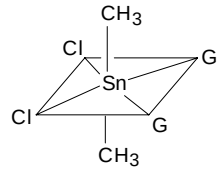

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trialkyltin by the amino group. The log β values for the dialkyltin complexes with glucosamine are about three orders lower than those of the bidentate amino acids (NH_2, O^-, donor set)[17]. This is taken as an evidence for the involvement of the amino group only in the dialkyltin(IV) complexes with glucosamine. The structure of the complex species as suggested on the basis of the literature data on analogous pyridine complexes[12,13] are shown in structures **1** and **2**. In $G–R_3SnCl$ species G is supposed to be bound as axial ligand together with Cl atom. Similarly, in $G_2–R_2SnCl_2$, two axis should be occupied each by G–Cl couple (thus being both in *cis*-configuration) leaving the alkyls in *trans*-configuration.

TABLE I
The formation constants and thermodynamic parameters of D-glucosaminium and alkyltin (IV) complexes with glucosamine in pure water at 25 °C

System	log β	ΔH^0, kJ/mol	ΔS^0, J/deg mol
Glucosamine (G)	7.369 (0.004)	–47.11 (7.37)	–7.94
Me_3SnCl–G	4.737 (0.035)	–17.99 (4.70)	+12.93
Bu_3SnCl–G	3.636 (0.053)	+16.43 (5.78)	+22.33
Me_2SnCl_2–G	6.780 (0.019) 13.287 (0.007)[a]	–	–
Bu_2SnCl_2–G	5.286 (0.114) 9.474 (0.108)[a]	–	–

[a] 1 : 2 complex.

In order to examine effect of organic compounds upon the G–Me_3SnCl complex formation the corresponding stability constants were also determined in various water/ethanol mixed solvents. As a reference, also the dissociation of GH^+ in the same solvents was studied. It is namely known that the properties of water closed in the active site cavities of enzymes considerably differ from those measured in liquid water[18–20] and, it was suggested that these properties approximately correspond to those (or can be simulated by those) existing in the water/alcohol mixtures[21].

As it is seen from Fig. 2, the stability constant of GH^+ increases, whereas that of G–Me_3SnCl complex decreases as the ethanol fraction increases. This can be explained by a better solvation of virtually hydrophobic species R_3Sn^+/R_3SnCl by ethanol resulting in lowering the complex stability[22,23].

Estimation of equilibrium concentrations of alkyltin(IV) chlorides and their complexes as a function of pH provides a useful picture for alkyltin binding towards glucosamine. In all the species distributions the concentration of the complex increases with increasing pH, thus favouring the alkyltin complex formation in the physiological pH range. Under the selected experimental conditions, the magnitude of the stability constants controls the concentration distribution of the different species. For the R_2SnCl_2–G_n complexes, the maximum proportion of 1 : 1 complexes is 41.2% at pH 5.0 and 65.0% at pH 7.0 for the dimethyl and dibutyl derivatives of tin, respectively. The 1 : 2 species predominates with a maximum percentage of 90.6% at pH 8.5 for Me_2SnCl_2 and of 31% at pH 8.8 for Bu_2SnCl_2. The differences in concentration maxima of methyltin and butyltin complexes are an additional illustration of the above mentioned higher stability of methyltin complexes.

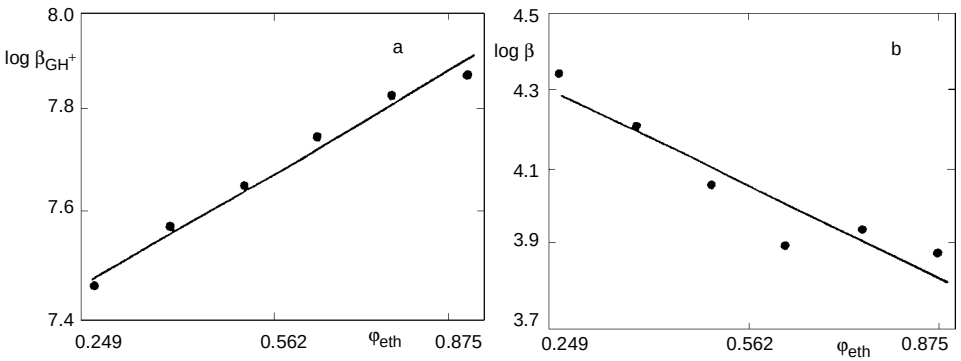

FIG. 2

Effect of the solvent composition on stability of glucosaminium (a) and Me_3SnCl–glucosamine complex (b) in ethanol/water mixtures; φ_{eth} volume fraction of ethanol

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