

tric data collection and analyses enable precise, accurate formation constants to be routinely measured. These constants, together with sophisticated computer modelling techniques, allow one to compute metal-ligand species distributions in complex systems [2]. Such techniques have been used successfully to elucidate the principles governing the efficacy of copper salicylate, for example [3]. We are currently interested in the mode of action of active agents present in dentifrices, for example, zinc salts in the reduction of the growth of plaque [4]. As these agents exhibit their biological activity in the oral environment, their interaction with the components of saliva is of prime importance. As a first step in establishing the factors which determine the clinical efficacy of these agents, we have used the computer modelling technique to determine the distribution of trace metals amongst the organic ligands in saliva. The poster will present details of this model together with a collation of data concerning the composition of saliva and relevant binding equilibria. Concentration effects for the various components will be demonstrated and the "important" endogenous ligands will, thus, be identified.

REFERENCES

- [1] B.M. SUTTON, D.L. BRYAN, J.C. HEMPEL, G.R. GIRARD, D.T. HULL, «Proc. 23rd International Conference on Coordination Chemistry», Boulder, Colorado, 1984, p. 310.
- [2] J.C. WESTALL, J.L. ZACHARY, F.M.M. MOREL, «MINEQL, A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems», Tech. Note No. 18, Dept. Civil Eng., Mass. Inst. Tech., Cambridge, MA, 1976.
- [3] G.E. JACKSON, P.M. MAY, D.R. WILLIAMS, *J. Inorg. Nucl. Chem.*, **43**, 825-9 (1981), and references therein.
- [4] G.J. HARRAP, C.A. SAXTON, J.S. BEST, *J. Periodont. Res.*, **18**, 634 (1983).



PS7.9 — TU

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STUDIES ON THE BIOCHEMICAL ACTIVITY OF SELENOCARRAGEENAN

The preparation and biochemical activity of selenocarrageenan are described. The results indicate that, for male mice, the supplementation of the diet with kappa-selenocarrageenan results in significantly higher biological availability and physiological effects than the supplementation with Na_2SeO_3 . The concentration of Se in whole blood, the glutathione peroxidase enzyme activity and the hemoglobin content increase by 23%, 13% and 22%, respectively with kappa-selenocarrageenan. The ability to prevent H_2O_2 and free radicals attack to the red cells also increases by 50% and 55% respectively.



PS7.10 — TH

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**THE FORMATION AND DISSOLUTION
OF CALCIUM BILIRUBINATE.
A CHEMICAL MODEL SYSTEM
SIMULATING THE FORMATION
AND DISSOLUTION
OF CALCIUM-CONTAINING PIGMENT
GALLSTONES**

The nature of the formation of calcium-containing gallstones is the formation of a specially constructed solid phase of calcium bilirubinate in the presence of bile acids and mucoproteins. As a model, the kinetic and thermodynamic behaviors of the Ca-Bilirubin-Taurocholate-Chondroitin sulphate system were studied by monitoring the variations of the concentrations of calcium and bilirubin with time. The solid phase separated was studied by means of X-ray diffraction, SEM, IR etc. In the absence of bile acids and mucoprotein, calcium ions react instantly with bilirubin (pH 7.9) giving aggregates of fine particles. No further growth or aggregation is observed. Taurocholate (TC) inhibits the reaction to some extent depending on the concentration of TC. The initial reaction stage is of first order, with $\log k = a - bC_{TC}$ ($r = 0.9934$). The conditional solubility products of calcium bilirubinate decrease with the increasing of the concentration of TC. SEM shows that, differing from the case without TC, the primary aggregates may aggregate further to clusters of various shapes. The addition of chondroitin sulphate compensates the inhibitory effect of TC and a number of particular shaped particles were obser-

ved, which support the idea that the calcium bilirubinate binds to the polysaccharide.

The differential UV spectra of the solutions containing TC and bilirubin and the potentiometric studies of the solutions containing calcium and TC show that both Ca and bilirubin tend to bind to TC micelles. Thus, it is proposed that the reactions of calcium ion and bilirubin proceed in a special mode in the micellar background. The TC micelles, with the bilirubin molecules in their hydrophobic cores, catch calcium ions rapidly from the solution. The calcium ions are likely to be bound to the negative charged micellar surface. And then, calcium ions react with bilirubin in the micelle. Fluorescence studies give some evidence supporting this proposal.

The dissolution of calcium bilirubinate pellets with some chelating agents were studied by monitoring the concentration of calcium and bilirubin at different time intervals in the presence or absence of bile acids. The calcium and bilirubin dissolve nonsynchronously. Thus a two step process is suggested. This process includes a rapid dissolution of calcium leaving the sparingly soluble, polymerized bilirubin in the solid. As the second step, bilirubin dissolves slowly and to a much smaller extent than calcium. A significant cooperative dissolving effect was observed between the chelating agents and the bile acids. For different chelating agents, the limits of dissolution (Ca concentration) are parallel with the conditional stability constants of the calcium chelates.