Determination of contaminated estrogen and heavy metals in canal of Thailand with their biological effects on human and the environment

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The objectives of this study are to determine the contamination of 17β-estradiol (E2) and heavy metals in water samples from the Saen Seep canal to health and environmental problems[1]. A pre-treatment methodology of analysis based on High-Performance Liquid Chromatography with ultraviolet absorption detection (HPLC-UV) and Flame atomic absorption spectrophotometry (Flame AAS) were developed for the determination of E2 and heavy metals trace elements, respectively.[2] Then, mutagenic and estrogenic activities of the water samples were investigated with an Ames test and Yeast estrogen screen assay (YES assay), respectively. The determination of the E2 content with HPLC-UV indicated that concentrations of E2 in the water samples collected from Saen Saep canal were in the range of 0.63-11.89 mg/L. Heavy metals (Cd, Cu, Fe, Ni, Pb, and Zn) were determined by Flame AAS. There was contamination of Cd, Cu, Fe, and Zn in all sampling areas, while the quantities of Ni and Pb could not be detected. The results of the Ames test demonstrated that E2 in the concentration levels found in the Saen Saep canal did not induce the frame-shift mutations and base-pair substitutions in Salmonella typhimurium TA98 and TA100, respectively. For the YES bioassay, the water extracts containing E2 in the concentration range of 4.22-13,347.6 ng/L and raw water in the concentration of 67 ng/L were used for estrogenic activity tests. The results revealed that the estradiol equivalent (EEQ) of E2 extract equals to 4.12 ng/L while the EEQ of the raw water could not be determined. The bioassays demonstrated that the E2 level found in the water collected from the Saen Saep canal did not express the mutagenic and estrogenic activities.

[1] Tang, Z., Liu, Z.H., Wang, H., Dang, Z., Yin, H., Zhou, Y., et al. *Water Research*, **2020**, Vol. 1(182), pp. 115976.

2 Aydoğmuş, Z., Yılmaz, E.M., Yörüsün, S., Akpınar, S. *International scholarly research notices*, **2015,** Vol. 2015(3), pp. 1-7.

Biodegradable Silicone Polymers and their Perfumes

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Long lasting fragrance on fabrics after a wash cycle is an important aim of many detergent manufacturers. However, currently large amounts of perfumes are added to the formulations as very little adheres to clothing consequently, most ends up down the drain and therefore large amounts of these chemicals are ending up in the environment, with potential impact to the biosphere. This can have wide reaching impacts from foaming in the treatment plant to toxicity to aquatic life, so increasing the efficiency of the detergents and perfumes so that less is needed to be used is a key target for many manufacturers.
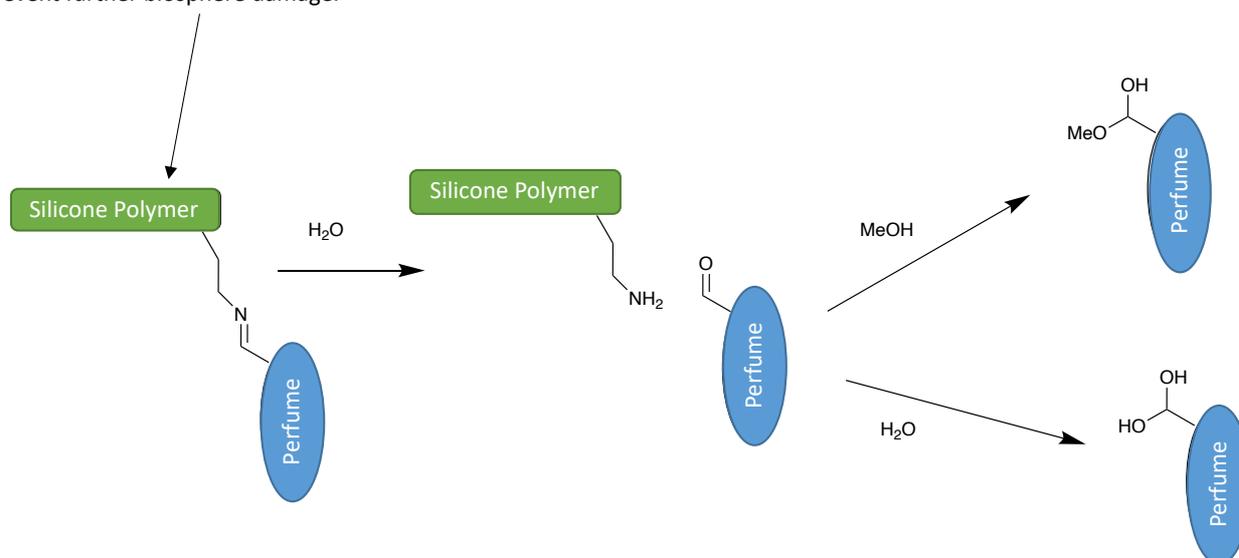

*Figure 1- a cartoon of the reaction scheme studied.*

Working in collaboration with Proctor and Gamble, we present an investigation in a silicone polymer–linker–perfume based system (Figure 1). In this system, the perfume is attached to a silicone polymer via a chemical linker with the polymer reversibly adhering to clothing, then the chemical linker will slowly break over time to release the perfume. The aim of this project is to understand the factors that affect the rate of perfume release, initially focusing on silicone biopolymer and imine hydrolysis as the method of perfume release. Using UV-vis studies it has become clear that the hydrolysis isn't the only reaction occurring in the model system and NMR and HPLC have been utilised to gain insight into the reactions and release occurring.

Fixation and Activation of Carbon Dioxide via Crypate Cascade Reactions

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Carbon dioxide is an abundant and readily accessible atmospheric gas and may be regarded as a useful synthetic source for organic compounds, including fuels. The thermodynamic stability and kinetic inertness of the molecule offers a significant challenge however, with significant efforts employed into its activation and functionalisation.[1] In recent years, there has been increasing interest in the development of synthetic analogues which mimic the function of ribulose-1,5-bisphosphate carboxylase oxygenase (Rubisco). Rubisco catalyzes the first major step of carbon dioxide fixation in nature, a conversion process to form energy-rich molecules, such as glucose.[2] Nelson and co-workers observed that the reaction of M^{2+} ions with a m-benzene-based cryptand (L^1) in water, and either methanol or acetonitrile, produces dinuclear carbonato-cryptates $[M_2L1(\mu\text{-}CO_3)]^{2+}$ and dinuclear methoxycarbonate-cryptates $[M_2L^1(\mu\text{-}MeCO_3)]^{3+}$, respectively.[3] The work described here goes on to look at the attempted isolation of methylcarbonate bridged complexes from the reaction of L^1, transition metal salts and dry ice in methanol and other higher alkyl chain alcohols. It has been observed that the attempted synthesis of higher alkyl carbonate bridged dinuclear complexes leads to the isolation of methyl carbonate instead of expected ethylcarbonate, propylcarbonate, isopropylcarbonate and butylcarbonate, even upon purification of the solvents. It has been proposed that this occurs due to a possible solvent rearrangement to give the methylcarbonate bridged complex.

L^1
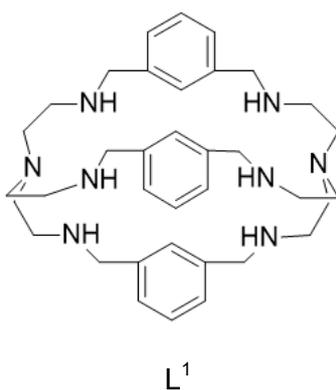
1.   M. M. El-Hendawy, N. J. English, D. A. Mooney, *J. Mol. Model.* **2011**, *17*, 3151-3162.

2.   N. Kitajima, S. Hikichi, M. Tanaka, Y. Morooka, *J. Am. Chem. Soc.* **1993**, *115*, 5496-5508.

3.   Y. Dussart, C. Harding, P. Dalgaard, C. McKenzie, R. Kadirvelraj, V. McKee, J. Nelson, *J. Chem. Soc., Dalton Trans.* **2002**, 1704-1713.

Redox and Spin State Preferences in Manganese Model Complexes

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Manganese is an important and biologically active element involved in a number of redox enzymes (e.g., catalase, peroxidase, superoxide dismutase)[1] and in the oxygen-evolving center (OEC) of photosystem II.[2] This has stimulated interest in its properties and reactivity, especially in oxidation states II, III, and IV. Lord et al.[3] raised the question of electron transfer between the Mn(II) and Mn(IV) redox states via either the spin quintet or spin triplet forms of the intermediate Mn(III), Fig. 1. Studying some uncommon low-spin Mn(III) compounds, with the help of X-ray crystallography and electrochemical, spectroscopic, and magnetic methods, they suggest a greater component of reaction pathway via a high-spin intermediate.

Our group has been interested in the spin states and oxidation states of manganese in hexadentate chelates with an N4O2 donor set embedded in chelates with different numbers and positions of connecting methylene groups, Fig. 2. Our results show that the Mn(III) redox form is preferred and that spin crossover is sometimes possible in the solid state. The data also show that many examples can also be stabilized in the Mn(II) and Mn(IV) forms under ambient conditions. An important question is: does compression in the Jahn-Teller orbital direction of the high spin state have a role in determining access to more than one spin state and does this affect the redox window? This will be explored and compared among more constrained and elastic frameworks with smaller or greater number of carbons in the tetraamine backbones.
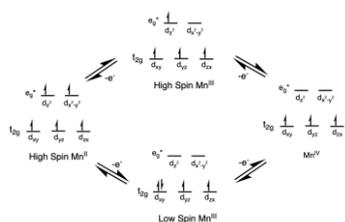

Figure 1 – Proposed electron transfer steps for oxidation/reduction reactions going from Mn(II) to Mn(IV) through Mn(III).
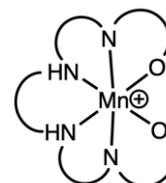

Figure 2 – General structure of studied manganese hexadentate ligands.

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[1] N. A. Law, M. T. Claude and V. L. Pecoraro, *Adv. Inorg. Chem.*, **1998**, 46, 305-440.

[2] S. Mukhopadhyay, S. K. Mandal, S. Bhaduri and W.H. Armstrong, *Chem. Rev.*, **2004**, 104, 3981-4026.

[3]F. Hossain, M. A. Rigsby, C. T. Duncan, P.L. Milligan, Jr., R. L. Lord, M. H. Baik and F. A. Schultz, *Inorg. Chem.*, **2007**, 46, 2596–2603.