The Role of Iron in Oxidation of Phospholipids in Liposomes

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Phospholipids from fish have a high content of polyunsaturated fatty acids and are therefore susceptible to oxidation. When dispersed in water, phospholipids spontaneously form bilayer vesicles, called liposomes. Liposomes have commonly been used as model systems for oxidation of meat and fish products, as well as cell membranes, with the ambiguities that are introduced when more complex biological systems are used. Heavy metals, particularly those processing two or more valency states, increase the rate of lipid oxidation. Increased knowledge of the role of iron could help to find better ways to protect food from lipid oxidation.

The rate of lipid oxidation was measured by the consumption of dissolved oxygen by liposomes in a closed vessel. The concentration of dissolved oxygen was measured continuously by a polarographic oxygen electrode. Phospholipids, extracted from cod roe using acetone precipitation method, were used for liposome preparation. Liposomes in 5mM MES buffer, pH 5.5, were made by sonication.

Both Fe^{2+} and Fe^{3+} catalyzed lipid oxidation. When Fe^{3+} was used as a prooxidants in liposomes, a linear uptake of oxygen was observed. However when Fe^{2+} was added to liposomes a fast initial drop in dissolved oxygen, followed by a slower linear oxygen uptake was observed. The fast initial drop in dissolved oxygen was found to be due to Fe^{2+} oxidation by lipid peroxides to Fe^{3+}. The rate of reduction of Fe^{3+} by peroxides was measured and occurred at a slower rate than Fe^{2+}oxidation, showing that Fe^{3+} became a limiting factor for the red/ox cycling between Fe^{2+} to Fe^{3+}. When the equilibrium between Fe^{2+} and Fe^{3+} was achieved a linear oxygen uptake was observed. Both alkoxy and peroxy radicals form by breakdown of peroxides by Fe^{2+} and Fe^{3+} respectively reacted with fatty acid giving a lipid radical reacting with oxygen producing lipid peroxides The net results are production of lipid peroxides accompanied by oxygen consumption.

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