# Ionic liquids: Defending ships' hulls against corrosion and biofouling

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Ships' hulls are the target of two ongoing threats. On the one hand, there is corrosion, attacking the structure of the metal and shortening the active life of the ship; on the other hand, organisms attach themselves to the outer layers and form large organic conglomerates of matter (called fouing), leading to a loss of hydrodynamic shape and to a substantial increase of fuel consumption during the voyage. In recent years, an innovative class of chemical compounds, the ionic liquids, has arisen, which may act against both corrosion and fouling. These chemicals, liquid at ambient temperatures (< 100°C), consist completely of ions: usually an organic cation, such as (a derivative of) imidazolium, and an inorganic anion such as a chloride, bromide, tetrafluoroborate or hexafluorophosphate, although organic anions have been used as well. Several different types of ionic liquids (such as imidazolium derivates) have been found useful to combat metal corrosion (see e.g. Arenas and Reddy 2003, Likhanova et al. 2010) or bacterial growth (e.g. Pernak et al. 2003, Fitzpatrick et al. 2005, Ganske & Bornscheuer 2006); however, the exact mechanism is still largely unknown.

To test the anticorrosive action of different imidazole-based compounds under maritime conditions, grade A steel coupons of 2 cm by 8 cm by 6 mm were etched for 15 min in 37% HCl containing 20 g/L $Sb_2O_3$ and 60 g/L $SnCl_2$ to remove existing layers of rust. These coupons were then cleaned in running tap water and submerged overnight (20-24 h) in 1 M $H_2SO_4$ containing one of the ionic liquids at one of two concentrations: 100 mg/L or 10 mg/L $C_{16}C_1$-imidazolium bromide, 400 mg/L or 40 mg/L 1.3-dioctyl imidazolium bromide, 100 mg/L or 10 mg/L $C_{12}C_1$-imidazolium chloride, or 100 mg/L or 10 mg/L 1,6-imidazole ionene. The coupons were attached to small frames, labelled, and put in the sea for the specified amount of time. They were suspended in sea water in the Ostend harbor at a platform, designed for these experiments (Swain and Schultz 1996, Casse and Swain 2006). After one month, a series of coupons was taken out, etched again to remove all corrosion and fouling and weighed again. Significant corrosion inhibition was observed on the coupons treated with the higher concentrations of the ionic liquids. Further tests are needed, however, to elucidate whether these ionic liquids are suitable for maritime use, to protect ships.

Additionally, some coupons, having been exposed between one day and one month in the seawater, were also collected for microbiological analysis. To this end, the coupons were taken out of the sea, fixed in 3% formaldehyde, washed in tap water, dehydrated in three steps in ethanol (50% - 75% - 100%) and dried before further microscopic analysis. Coupons were stained with DAPI (visualizing the cells' DNA) to assess the spread of the microfouling, which is currently ongoing.

Lastly, toxicological testing using *Artemia* sp. as a test organism showed that the toxicity of the imidazolium derivates depends upon its substituents. The low overall toxicity of the ionic liquids supports the possible use of these components.

Keywords: corrosion; fouling; paint; ionic liquids; toxicity

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