

**o.m9.o5** Structural and thermal properties of carboxylates protecting metals against aqueous corrosion.

F. Lacouture, J. Peultier, M. François, J. Steinmetz, *Laboratoire de Chimie du Solide Minéral UMR 7555, BP 239, F54506 Vandoeuvre-les-Nancy Cedex.*

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Notes

Previous studies have shown that saturated straight chain aliphatic monocarboxylates of general formula  $\text{CH}_3(\text{CH}_2)_{n-2}\text{COO}^-$  with  $7 \leq n \leq 11$  (noted  $\text{C}_n^-$ ) are aqueous corrosion inhibitors for Fe, Cu, Zn, Pb, Mg as well as for their alloys<sup>1</sup>. It is well worth noting these inhibitors are safely handled, with lower environmental impact than the conventional ones. The protection of metal surfaces is due, as demonstrated by RX, IR and XPS techniques, to the growth of a thin coating constituted by a superficial layer of a metal soap covering an internal layer of hydroxide. Consequently, a structural study has been undertaken on carboxylates synthesised from aqueous solutions and mainly devoted to the Zn, Mg, Pb and Gd carboxylates. Seven structures has been solved. All these salts have a two-dimensional character, also mentioned in close compounds<sup>2,3</sup>, with sheets built from one or two plans of metal cations ( $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Gd}^{3+}$ ) and carboxylates chains growing on both sides of the plan(s). The four coordination polyhedra are different : tetrahedral for Zn(II), very distorted for Pb(II) with a coordination number of six, octahedral for Mg(II). Finally, the coordination of Gd(III) can be described by a distorted three-vertex trigonal prism with a coordination number of nine. In the case of zinc carboxylates, the melting points decrease with the n increase. Also, several crystallographic structures can be observed for the same anion  $\text{C}_n^-$ , proving weak difference between the thermodynamical properties, as for the lead heptanoate, it presents two liquid crystal phases. For a given cation, a mixture of chains with different lengths leads to new and original structures, next for a given  $\text{C}_n^-$ , a divalent cation can be partially substituted by a trivalent one (Zn/Gd) which contributes to decrease the solubility of the soap. These last results suggest the possibility to build "à la carte" protective coatings, in order to optimise the coherence between the film and the substrate<sup>4</sup>.

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