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Short communication

Identification of mixed-valence metal clusters in drier solutions for alkyd-based paints by electrospray ionization mass spectrometry (ESI-MS)

Fabrizio Miccichè [a,b], Marion A. van Straten [a], Weihua Ming [a,*], Eef Oostveen [b], Jacco van Haveren [b,*], Rob van der Linde [a], Jan Reedijk [c]

[a] *Eindhoven University of Technology, Laboratory of Coatings Technology, Materials and Interface Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Agrotechnology & Food Innovations B.V., Department of Sustainable Chemistry & Technology, P.O. Box 17, 6700 AA Wageningen, The Netherlands*
[c] *Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

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Abstract

The oxidative drying of alkyd paints has many similarities with the way lipids are oxidized in biological systems. Metal salts based on Co, Fe and Mn are added to accelerate the oxidative drying of conventional alkyd paints. Although the mechanism by which alkyd paints dry has been the subject of numerous investigations, little information is available on the structure and the actual mechanism by which driers catalyze the oxidation process. In this communication we describe the identification of metal clusters in drier solutions by electrospray ionization mass spectrometry (ESI-MS). Evidence is provided for the presence of several metal clusters ranging from M_3 up to M_6 as well as the coexistence of mixtures of (mixed-valence) clusters in the same solution.

Keywords: ESI-MS; Driers; Metal clusters; Iron

1. Introduction

The oxidative drying of alkyd-based paints can be regarded as a lipid oxidation process taking place at the fatty acid chains attached to the backbone of so-called binders (polyesters modified with polyunsaturated fatty acids, such as linoleic and linolenic acid). The oxidation process consists mainly of three different steps: initiation, propagation and termination [1]. In the absence of proper catalysts (or driers) the drying process would be far too slow for practical applications. Cobalt-based catalysts, such as cobalt-2-ethylhexanoate (Co-eh), are currently used as primary driers for alkyd systems. However, recent studies have shown that Co-based catalysts are suspected of carcinogenicity in aerosol [2], which may force the paint industry to search for suitable environmentally friendlier alternatives.

Although efforts have been made to develop alternative driers based on manganese [1], iron has not been considered suitable for two generally assumed reasons: (1) iron is not effective in the oxidative drying of alkyd coatings at room temperature, and (2) the dark color of paint films due to the presence of iron salts. Contrary to this general idea, a new and very effective drier system based on the combination of iron-2-ethylhexanoate (Fe-eh)/ascorbic acid derivatives has been developed in our laboratories [3].

In the past two decades numerous investigations have been carried out to clarify the chemistry involved in the drying of alkyd-based paints [4]. To the best of our knowledge, apart from a few studies on the structure and mechanism of cobalt salts in the decomposition of hydroperoxides [5], limited information is available on the actual species involved in the oxidative drying of alkyd paints. The purpose of this communication is to iden-

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Abbreviations: Heh, 2-ethylhexanoic acid (eh is the monoanion); Co-eh, cobalt 2-ethylhexanoate; Fe-eh, iron 2-ethylhexanoate; Mn-eh, manganese 2-ethylhexanoate; ESI-MS, electrospray ionization mass spectrometry

[*] Corresponding authors. Tel.: +31 40 2473066; fax: +31 40 2445619.
E-mail addresses: w.ming@tue.nl (W. Ming), jacco.vanhaveren@wur.nl (J. van Haveren).

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tify species present in solutions of three catalysts, Fe-eh, Co-eh, and manganese-2-ethylhexanoate (Mn-eh) by electrospray ionization mass spectrometry (ESI-MS).

2. Experimental section

2.1. Materials

Iron(II) perchlorate hydrate (∼95%) and sodium 2-ethylhexanoate were obtained from Aldrich. Iron (Nuodex Fe 10), cobalt (Nuodex Co 6) and manganese (Nuodex Mn 578) driers were supplied by Sasol Servo B.V., The Netherlands. All other chemicals were used as obtained from the supplier.

Caution! Inorganic perchlorate salts are potentially explosive and should be handled with care and in small amounts.

2.2. Synthesis of Fe-eh

Fe-eh was synthesized with the purpose of making the iron salt soluble in ethyl linoleate (EL, a model compound for alkyd resins) and resembling a commercially available iron-based drier (Nuodex Fe 10).

Fe-eh was synthesized as follows: 15.2 g (0.042 mol) of iron(II) perchlorate hexahydrate was dissolved in 50 mL of CH_3CN. 19.9 g (0.12 mol) of sodium 2-ethylhexanoate was added in small amounts to the iron solution, resulting in a color change of the solution from light green to dark brown. The reaction was allowed to proceed for 1.5 h at 40 °C, under magnetic stirring and a nitrogen atmosphere. The reaction mixture was transferred into a round-bottom flask, a few milliliters of acetone added and the solvents evaporated in vacuum. The residue was dissolved in diethyl ether and filtered. A white precipitate of $NaClO_4$ was removed. This procedure was repeated three times till complete removal of the $NaClO_4$ salt. The final product appeared as a dark brown tacky solid. The iron content in the complex was found to be 12.3%, and typical IR absorptions appeared at (cm^{-1}): 2960 (m), 2958 (m), 2875 (m), 2877 (m), 1529 (s), 1419 (s), 1325 (m), and 1028 (w).

2.3. ESI-MS

Electrospray ionization mass spectrometry (ESI-MS) measurements were performed on an Agilent MSD type SL (G1946D). Spectra were obtained by direct injection of the sample (previously dissolved in the appropriate solvent at concentration of approximately 10 mg/mL) to the MS unit using 100% methanol (HPLC-grade, Biosolve) containing 0.1% acetic acid (p.a. Merck) as eluent at a flow rate of 0.3 mL/min. Typical injection volumes were 2 μL. Spectra were obtained in positive and negative mode in the mass range 50–1500 Da.

3. Results and discussions

The ESI mass spectrum of Fe-eh prepared in our laboratories in 1-propanol is shown in Fig. 1 (a solution of commercial Fe-eh, Nuodex Fe 10, showed the same results).

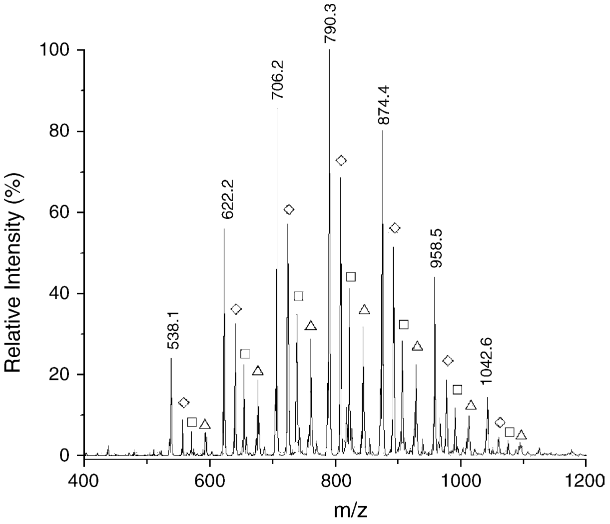

Fig. 1. ESI mass spectrum (positive mode) of Fe-eh in 1-propanol; the main series of peaks corresponds to $[Fe_3^{III}(\mu_3\text{-O})(eh)_{6-x}(1\text{-propoxo})_x]^+$ (**1**, $x = 0$–6, from high to low *m/z*).

The pattern observed clearly indicates the presence of high-molecular-weight species with the difference between the main peaks (Δ) equal to 84. The peak at $m/z = 1042$ was identified as a μ_3-oxo bridged trinuclear iron(III) cluster, $[Fe_3^{III}(\mu_3\text{-O})(eh)_6]^+$; similar oxo-centered, carboxylate-bridged trinuclear complexes of general formula $[M_3O(O_2CR)_6L_3]^{n+}$ are known for some transition metal ions [6]. Complexes of this structure contain a triangular arrangement of the metal ions bridged by a center oxo group and are structurally related to the active site of numerous iron-oxo proteins [6]. The existence of the trinuclear Fe(III) cluster identified in this study was confirmed by IR, UV, and thermogravimetric analysis. The gradual replacement of one negatively charged eh by one solvent molecule, as 1-propoxo (an alkoxide anion), results in the main series of peaks at $m/z = 1042.6$, 958.5, 874.4, 790.3, 706.2, 622.2, and 538.1, corresponding to a general formula $[Fe_3^{III}(\mu_3\text{-O})(eh)_{6-x}(1\text{-propoxo})_x]^+$ (**1**, $x = 0$–6, from high to low *m/z*; the same for below). This replacement was unambiguously confirmed by the perfect agreement between experimental and simulated isotopic distribution of the species at $m/z = 790.3$, $[Fe_3^{III}(\mu_3\text{-O})(eh)_3(1\text{-propoxo})_3]^+$, as shown in Fig. 2a.

The ESI mass spectrum of Fe-eh also reveals the presence of three more series of peaks (Fig. 1), with an increase in *m/z* (compared to the main series) of 18 (◇, with the addition of one solvation water), 32 (□, with the addition of one solvation methanol), and 54 (△, with the addition of three solvation water molecules), respectively. Both water and methanol can be present as solvation molecules, as methanol was used as eluent during ESI-MS experiments.

The ESI mass spectrum (negative mode) of Co-eh in 1-propanol (Fig. 3) turned out to be quite complex but very interesting as three different patterns can be identified. These different series of peaks arise most likely from at least three different species in solution, sharing a difference of $m/z = 84$ (Δ) between neighboring peaks in each series. Similar to the Fe-eh solution, the Δ value is associated with the gradual

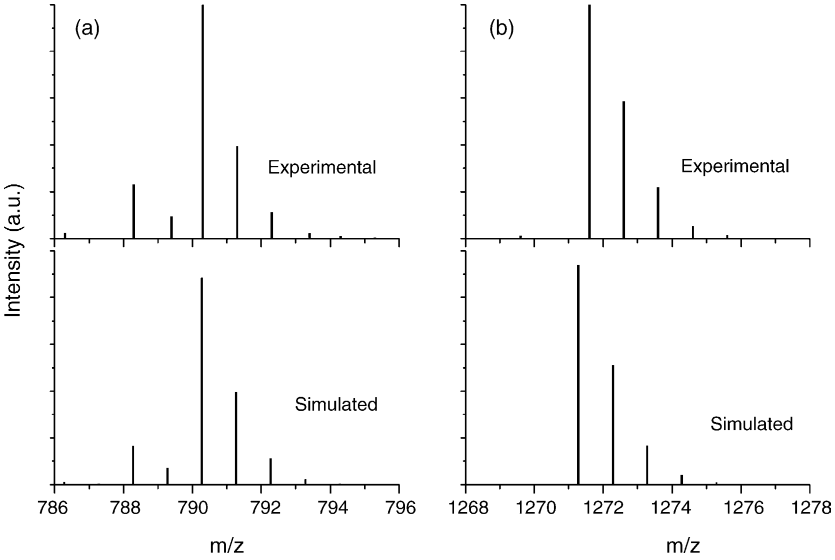

Fig. 2. Comparison between experimental and simulated isotopic distribution: (a) for the peak at *m*/*z* = 790.3 (Fig. 1), $[\mathrm{Fe}^{III}_3(\mu_3\text{-O})(\mathrm{eh})_3(1\text{-propoxo})_3]^+$, and (b) for the peak at *m*/*z* = 1271.6 (Fig. 2), $[\mathrm{Co}^{II}_6(\mathrm{O})_3(\mathrm{H})_2(\mathrm{eh})_4(1\text{-propoxo})_5]^-$.

replacement of one eh by 1-propoxo both bearing a negative charge.

Despite the apparent complexity, patterns **A**, **B** and **C** (Fig. 3) were successfully identified as follows. The main series **A**, including peaks at *m*/*z* = 1523.9, 1439.8, 1355.7, 1271.6, 1187.5, 1103.5, and 1019.4, corresponds to a hexanuclear Co(II) cluster, $[\mathrm{Co}^{II}_6(\mathrm{O})_3(\mathrm{H})_2(\mathrm{eh})_{9-x}(1\text{-propoxo})_x]^-$ (**2**, $x = 2$–8). The difference of 84 is again the result of the gradual replacement of eh by 1-propoxo. The three oxygen and the two protons in the formula of complex **2** may represent μ-O, μ-OH, and H_2O in various combinations according to the *m*/*z* observed in the spectrum. A definitive assignment of the number of bridges and their coordination mode however cannot be made from this study as an X-ray analysis of the complex may be required to unfold such structural details. A similar, large Co(II) cluster with phenylcinnamic acid as ligand has been recently reported by Kumagai et al. [7]. The isotopic distribution for the species $[\mathrm{Co}^{II}_6(\mathrm{O})_3(\mathrm{H})_2(\mathrm{eh})_4(1\text{-propoxo})_5]^-$ (*m*/*z* = 1271.6) is in good agreement with the simulated one (Fig. 2b).

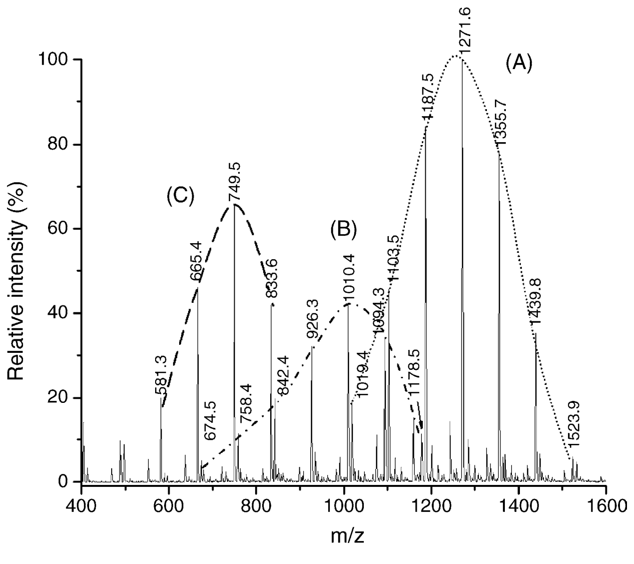

Fig. 3. ESI mass spectrum (negative mode) of Co-eh (purchased from Aldrich Chemicals) in 1-propanol.

The series **B** (Fig. 3) with peaks at *m*/*z* = 1178.5, 1094.3, 1010.4, 926.3, 842.4, 758.4, and 674.5, can be assigned as a mixed-valence tetranuclear Co-cluster of general formula $[\mathrm{Co}^{II}\mathrm{Co}^{III}_3(\mathrm{O})_5(\mathrm{H})_4(\mathrm{eh})_{6-x}(1\text{-propoxo})_x]^-$ (**3**, $x = 0$–6). The series C (peaks at *m*/*z* = 833.6, 749.5, 665.4 and 581.3) is due to a μ-oxo trinuclear Co(III) cluster of formula $[\mathrm{Co}^{III}_3(\mathrm{O})_3(\mathrm{H})_2(\mathrm{eh})_{6-x}(1\text{-propoxo})_x]^-$ (**4**, $x = 3$–6). It is interesting to notice the similarity between the cluster **4** and the trinuclear Fe(III) cluster **1** (Fig. 1) as analogous metal core centers may be involved in both clusters ($[\mathrm{Co}^{III}_3(\mu\text{-O})]^{7+}$ and $[\mathrm{Fe}^{III}_3(\mu_3\text{-O})]^{7+}$).

The ESI-MS spectrum of Co-eh recorded in positive mode turned out to be very complicated (not shown). Despite the busy spectrum, a pattern with peaks at *m*/*z* = 1041.4, 957.3, 873.2, and 789.2 is likely due to a tetranuclear mixed-valence Co cluster $[\mathrm{Co}^{II}\mathrm{Co}^{III}_3(\mathrm{O})_2(\mathrm{eh})_{6-x}(1\text{-propoxo})_x]^+$ (**5**, $x = 1$–4).

In a recent study, Warzeska et al. [8] have isolated and solved the structure of a tetranuclear mixed-valence manganese cluster from a commercial drier solution (Nuodex Mn 578) containing Mn-eh and 2,2′-bipyridine (bpy) of general formula $[\mathrm{Mn}^{II}_2\mathrm{Mn}^{III}_2(\mu_3\text{-O})_2(\mathrm{eh})_6(\mathrm{bpy})_2]$. A similar solution was subject to ESI-MS measurement, and its mass spectrum is shown in Fig. 4. Four sets of peaks can be easily distinguished. The series **D** can be assigned as $[\mathrm{Mn}^{II}_4(\mathrm{O})(\mathrm{OH})(\mathrm{eh})_{6-x}(1\text{-propoxo})_x(\mathrm{bpy})_2]^-$ (**6**, $x = 0$–2, from high to low *m*/*z*). When $x = 0$ (*m*/*z* = 1423.9), the species is indeed similar to that proposed by Warzeska et al. [8].

The other three series, **E**, **F** and **G**, are interpreted as follows: series **E**, $[\mathrm{Mn}^{II}\mathrm{Mn}^{III}(\mathrm{O})(\mathrm{eh})_{4-x}(1\text{-propoxo})_x(\mathrm{bpy})_3]^-$ (**7**, $x = 0$–3); series **F**, $[\mathrm{Mn}^{IV}\mathrm{Mn}^{III}_3(\mathrm{O})_3(\mathrm{eh})_{9-x}(1\text{-$

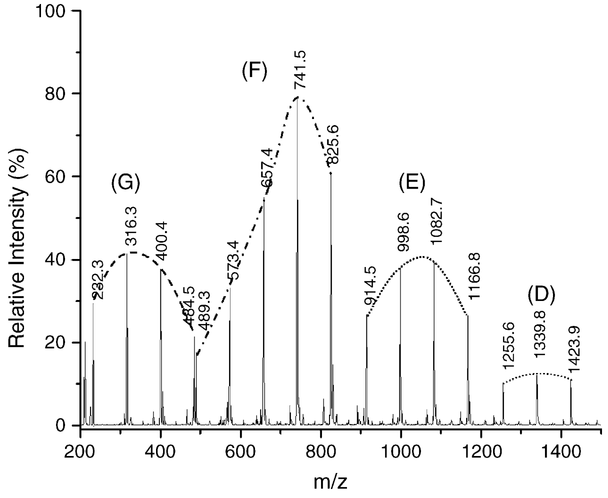

Fig. 4. ESI mass spectrum (negative mode) of Mn-eh and bpy in 1-propanol.

propoxo)$_x$(CH$_3$OH)$_3$]$^{2-}$ (**8**, $x=0$, 2, 4, 6, 8); and series **G**, [Mn$^{\mathrm{II}}$(eh)$_{3-x}$(1-propoxo)$_x$]$^-$ (**9**, $x=0$–3). Recently similar tetranuclear mixed-valence Mn clusters to **8** have been synthesized and isolated [9].

4. Conclusions

In summary, we have demonstrated that ESI-MS, especially in combination with isotopic distribution analysis, is a powerful technique to identify metal complexes in complex solutions. The results presented above show that commercial drier solutions for conventional alkyd paint formulations are complex mixtures of several metal ion clusters of different sizes. The activity of these driers may be related to the presence of mixed-valence clusters. Although this study is not conclusive to define the absolute structure of metal driers active in the oxidative drying of alkyd-based paints, the presence of mixed-valence metal clusters in commercial drier formulations should be taken into account for future research to properly understand the mechanism by which these catalysts oxidize lipids during the oxidative drying of alkyd-based paints.

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