A molecular perspective on the cleaning of oil paintings

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THE STRUCTURE OF ZINC CARBOXYLATES IN OIL PAINT IONOMERS

Parts of this chapter are published in:
5.1 Introduction

Zinc oxide (ZnO) was the white pigment of choice for painters and paint manufacturers from the late 19th century to the middle of the 20th century. ZnO is associated with various types oil paint degradation, sometimes with severe consequences for visual appearance or structural integrity of the paintings. As the triglyceride oil binder polymerises during paint drying, ZnO tends to release zinc ions, which subsequently bind to pendant carboxylate groups in the heavily cross-linked polymer network. This transition of the oil paint binding medium into an ionomer state is usually identified by infrared (IR) spectroscopy; the observation of a broad band centered around 1590 cm\(^{-1}\) assigned to the asymmetric stretch vibration of the carboxylate groups marks the formation of a zinc ionomer. This spectral feature has been observed in numerous artworks, for instance in paintings by Jackson Pollock\(^{102}\), Vincent van Gogh\(^{42}\) and Salvador Dalí.\(^{135}\) Thus, the phenomenon of ionomer formation is of great importance for paintings conservation. It was shown previously that ionomeric zinc carboxylate complexes can represent an intermediate stage in zinc white paint ageing that ultimately leads to the appearance of crystalline zinc soaps.\(^{29}\) These complexes of zinc ions and long-chain fatty acids have been linked to cases of brittleness, loss of opacity, the formation of protrusions and delamination of paint layers.\(^{3}\) Moreover, it was found that the exchange reaction between ionomeric zinc carboxylates (COOZn) and fatty acids that yields zinc soaps is strongly influenced by the amount of water present in the system.\(^{29}\) This result gave rise to the speculation that water may change the coordination environment around zinc ions in the polymerised oil network to make these ions more reactive towards fatty acids. Despite being directly related to the rate of oil paint degradation, the structure of ionomeric zinc carboxylates in oil paint and its sensitivity to water has so far remained elusive.

There are interesting parallels between these questions regarding molecular structure in aged oil paint and research into other metal-containing polymers. Traditionally, the local structure in ionomers has often been described simply in terms of ‘cluster’ and ‘multiplet’ regions with high ion concentration.\(^{76,136}\) Interestingly, it has been noted that variations in water content give rise to significant changes in the carboxylate region of IR spectra recorded on various ionomers.\(^{110}\) Some researchers have used X-ray absorption spectroscopy (EXAFS) in an attempt to resolve this water-dependent metal ion coordination environment in commercial zinc-neutralized poly(ethylene-co-methacrylic acid) ionomers (also known as Surlyn®, manufactured by DuPont\(^{TM}\))\(^{137–139}\) and in isoprene rubber blended with ZnO and stearic acid.\(^{140}\) However, these efforts did not yield a clear assignment of molecular structures, because the Zn-O bond lengths and the zinc coordination numbers did not change in tandem with the observed vibrational features of the carboxylate group. As such, the structure of ionomeric zinc carboxylates is still a highly relevant question for a broad range of polymer systems.

In this chapter, we use a combination of attenuated total reflection Fourier transform
IR (ATR-FTIR) spectroscopy and two-dimensional IR spectroscopy (2D-IR) spectroscopy, which enabled resolving the zinc carboxylate structures found in zinc white oil paint and commercial ionomer systems. For these studies, we employ a model system that is a co-polymer of linseed oil and zinc sorbate (the zinc salt of 2,4-hexadienoic acid). This model system is known to be representative of the binding medium in a typical zinc white oil paint used in many 19th- and 20th-century paintings. Knowing the chemical structure of zinc carboxylate structures in zinc white oil paint, we proceed to study the ‘cluster’ regions containing high ion concentrations with small angle X-ray scattering (SAXS). SAXS enables studying the ordering on length-scales of 1–100 nm, which allows to investigate the effect of water on ion-cluster formation. Using SAXS, we thus investigate if the sensitivity to water on a molecular scale translates to larger scale ion-cluster transformation. Our results give crucial insight into the mechanisms behind the effect of water on oil paint degradation, and provide a foundation for fundamental research on potential strategies to tailor environmental conditions and restoration practice to optimise the conservation of paintings.

5.2 Results and Discussion

5.2.1 The effect of water on ATR-FTIR spectra of paint binding media

IR spectra collected on a small sample from a white area of the painting De houthakkers (‘The woodcutters’) by Bart van der Leck (Figure 5.1a) show a broad asymmetric carboxylate stretch vibration band typical for a zinc white paint (Figure 5.1b). It was shown previously that this broad band is caused by Zn$^{2+}$-coordinated carboxylate groups of the oil polymer network, and that, like ionomers, these zinc carboxylates tend to form ionic clusters in the polymer. While the asymmetry in the broad carboxylate band clearly indicates that it is composed of several overlapping bands (Figure 5.1b), it is not straightforward to isolate its components using conventional IR spectroscopy. The carboxylate band has a maximum around 1560 cm$^{-1}$ in this paint sample. However, maxima at frequencies closer to 1600 cm$^{-1}$ are also commonly reported, for instance in samples from commercial zinc white paints and a painting by Salvador Dalí. These different carboxylate band positions and shapes suggest that there is significant variation in zinc carboxylate coordination in zinc white paint binding media.

We observed a significant change in the carboxylate region upon reducing the water content in the polymer binding medium. When a linseed oil/zinc sorbate polymer sample (Znpol) was heated above 110 °C, the components of the broad band envelope changed in relative intensity, revealing at least three separate maxima at 1555, 1595 and 1625 cm$^{-1}$ (labelled A, B, and C). To confirm that this entirely reversible change was caused by evaporation of water rather than a transition in polymer structure induced by temperature, we measured IR spectra on a Znpol sample that was cycled through a heating and
Figure 5.1 ATR-FTIR spectra of linseed oil ionomer and liquid zinc palmitate. a: De houthakkers (‘The Woodcutters’) by Bart van der Leck, (1928, oil paint on canvas, Gemeentemuseum Den Haag (Wibbina-Stichting)). b: The carboxylate and carbonyl regions of an IR spectrum collected on a cross-section sample from the painting. c: The carboxylate region in IR spectra of a zinc white binding medium model ionomer. The broad band at ambient conditions shows three maxima upon drying at 130 °C in a dry N₂ atmosphere, which persisted as the polymer was cooled back down to room temperature. Only when moisture was reintroduced, the broad band returned to its original band shape. The sample was equilibrated at each environmental condition for 30 minutes, after which no spectral changes were observed. d: Asymmetric carboxylate stretch vibration bands of liquid zinc palmitate. Pure dry zinc palmitate forms a chain complex upon melting, while an oxo complex is formed in the presence of water or oxygen-containing impurities (see text).

humidity program. Figure 5.1c shows sequential spectra recorded after equilibration at ambient conditions, followed by 130 °C under a flow of dry N₂, 25 °C in dry N₂ and finally 25 °C under a flow of N₂ saturated with water. As long as the atmosphere above the polymer remains dry, the carboxylate band envelope maintains its shape with three distinct maxima. These ‘dry’ spectra could also be reproduced by conditioning Znpol in vacuum (10⁻² mbar) for three weeks at room temperature. Interestingly, for paint films composed of ZnO and linseed oil, the IR spectrum showed only minor differences upon drying (Figure A.1).

Similar changes in the carboxylate region of IR spectra upon water absorption were observed in zinc-neutralised poly(ethylene-co-methacrylic acid) ionomers (pEMAA-Zn). In these reports, the spectra showed only band B at ambient humidity, and a combination of band A and C under completely dry conditions, suggesting that two types of zinc carboxylate structure exist in ionomers. With this hypothesis in mind, we fitted a combination of three Gaussian band shapes to the carboxylate band envelope of dry Znpol, and investigated whether a simple change in relative concentration of species could explain
5.2. RESULTS AND DISCUSSION

Figure 5.2 Quantification of the change in the carboxylate band envelope upon drying. Three Gaussian band shapes (labeled A, B and C) were fitted to the carboxylate band envelope in spectrum of a dried Znpol, after linear baseline subtraction. To investigate the differences between the ‘wet’ and ‘dry’ polymer, the center position of each Gaussian band was fixed and the band intensities were coupled so any increase in the height of band B causes a reduction of bands A and C while maintaining the intensity ratio of A and C. This procedure with only a conversion factor and band width multiplication factor as adjustable parameters allowed the reproduction of the ‘wet’ spectrum, with a conversion of species of approximately 50% and an increase in band width of 30%.

Figure 5.3 a: Schematic molecular structure of zinc carboxylates of the oxo type (central $O^{2-}$ ion is indicated with an arrow) and b the linear coordination chain type. Side-chains behind the carboxylate group have been omitted for clarity.

Indeed, we found that an approximately 50% conversion of band A+C to band B in combination with a 30% increase in band width could explain the observed spectra. The positions of the components of the carboxylate band envelope of Znpol are strikingly similar to the band positions of two types of zinc carboxylate coordination structure (Figure 5.1d). In a series of insightful studies by Berkesi, Dreveni and Andor, it was demonstrated that a tetranuclear zinc complex with a central $O_2^{-}$ ion (hereafter referred to as ‘oxo complex’, shown schematically in Figure 5.3a) can form in the presence of water when the side-chains of the carboxylate ligands are either bulky or disordered. Examples include the crystal structure of zinc 2,2-dimethylpropanoate or the structure of zinc butanoate dissolved in water-containing CCl$_4$. However, under water-free conditions, these zinc salts exist in a linear coordination polymer structure (referred to as ‘chain
complex’, shown in Figure 5.3b). We were able to reproduce the spectral features of the chain and oxo complex in liquid zinc palmitate (zinc hexadecanoate, ZnPa). Figure 5.1d shows the carboxylate region of the IR spectra of pure liquid ZnPa (chain complex) and of ZnPa that contained Zn$_5$(OH)$_8$(Pa)$_2$ as an impurity (oxo complex). The oxo complex features could also be obtained by adding other oxygen-containing impurities like ZnO or H$_2$O to liquid ZnPa. Since the carboxylate groups in pEMAA-Zn and Znpol ionomers are attached to the polymer chains/network, the polymer backbone to which the carboxylate group is attached will be in a disordered state. Therefore, the conclusions of Andor and colleagues strongly suggest that zinc carboxylates adopt an oxo or chain structure in ageing ZnO oil paint ionomers. Using 2D-IR spectroscopy to obtain a ‘fingerprint’ of zinc carboxylates in the chain structure of liquid ZnPa, we confirmed this hypothesis and were able to assign zinc carboxylates bands A+C (Figure 5.1c) in Znpol to the chain complex. For more detail on the 2D-IR spectroscopy experiments, the reader is referred to the original publication.

5.2.2 The identification of the oxo complex in linseed oil ionomers

To study the nature of band B in IR spectra of Znpol, we consider first the central oxygen ion in the oxo complex. Isotope studies have shown that the O$_2^-$ ion can be easily derived from water molecules, making it plausible that water exposure can induce a (partial) structural transition from chain to oxo complex in ionomers. The tetrahedrally coordinated oxygen has a specific asymmetric Zn$_4$O vibration at 530 cm$^{-1}$. The IR spectra of pEMAA-Zn under wet conditions reported by Ishioka et al. also contain this Zn$_4$O band, although a band assignment was not made. In fact, a linear correlation was found between the intensities of the band at 530 cm$^{-1}$ and the carboxylate vibration at 1585 cm$^{-1}$. Additionally, the conversion from carboxylate band B to A+C was only observed in partially neutralised ionomers, i.e. ionomers that still contained protonated COOH groups. This important observation is in complete agreement with a decrease of the Zn/COO ratio (from 2:3 to 1:2) during the reversible transition from an oxo to a chain complex, according to the following reaction:

$$\text{Zn}_4\text{O}$(RCOO)$_6$(oxo) $+ 2$ RCOOH $\xrightleftharpoons[\text{H}_2\text{O}]^{\text{H}_2\text{O}}$ $2$Zn$_2$(RCOO)$_3$(RCOO(chain)) $+ \text{H}_2\text{O}$

Therefore, it can be concluded that ionomeric zinc carboxylates have an oxo structure in pEMAA-Zn in the presence of water. We found that liquid ZnPa exists in the oxo form when an oxygen source was present in the liquid (e.g. water or ZnO impurities) (Figure 5.1d). The IR spectrum of ZnPa under these conditions also showed the Zn$_4$O band at 530 cm$^{-1}$, though it was significantly broader and weaker than reported for oxo complexes of short-chain zinc carboxylates, both pure and in solution. Surprisingly, in polymerised Znpol films in either wet or dry conditions, the Zn$_4$O band could not be
5.2. Results and Discussion

Figure 5.4 ATR-FTIR spectra supporting the assignment of band B to an oxo structure. a: Time profiles of integrated IR bands during curing of LO-Zn at 190 °C on the ATR crystal. The disappearance of the C=CH stretch vibration band at 3009 cm⁻¹ is a measure for the extent of polymerisation, while the reduction of the band at 530 cm⁻¹ is attributed to a loss of symmetry in the central Zn₄O unit. b: Time profiles of absorbance at the frequencies corresponding to the components A, B and C of the broad carboxylate band envelope during curing. c: The evolution of the Zn₄O band at 530 cm⁻¹ during curing of Znpol. Time series of ATR-FTIR spectra recorded during heating of a <5 µm thick layer of Znpol at 190 °C in air on top of the ATR crystal, showing gradual weakening of the band at 530 cm⁻¹.

detected, despite the presence of a strong carboxylate band B. However, when we followed the entire curing process of Znpol with ATR-FTIR spectroscopy by heating a <5 µm thick layer on the ATR crystal, it was found that a weak band at 530 cm⁻¹ does exist in the early stages of curing (Figure 5.4c).

While the band increased in parallel with band B at 1590 cm⁻¹ on short timescales (Figure 5.4a,b), after approximately 150–200 minutes, the Zn₄O band became obscured by background noise. This reduction in band intensity correlated with the disappearance of the C=CH stretch vibration at 3009 cm⁻¹, which is a measure for the degree of oxidation and polymerisation in the system (Figure 5.4a). In contrast, band B at 1590 cm⁻¹ remained approximately constant after 200 min. A similar broadening and weakening of the Zn₄O band in cast films of oxo complexes observed by Berkesi et al. was attributed to a gradual lowering of the symmetry of the tetrahedral Zn₄O core of the oxo complex. We also used X-ray absorption near-edge structure (XANES) spectroscopy in an attempt to characterise the coordination environment around Zn²⁺ in Znpol films equilibrated in liquid water or under vacuum (Figure 5.5). While the differences between the wet and dry XANES spectra were minor, comparison with calculated spectra showed that the changes were consistent with a partial transition from an oxo complex to a chain structure upon drying.

Finally, we observed a significant stoichiometric effect of the COOH concentration on the degree of conversion between the two zinc carboxylate species in zinc ionomers. A series of samples with decreasing COOH neutralisation (Znpol-So, prepared by partially replacing zinc sorbate by sorbic acid before polymerisation) showed an increasing conversion of band B to A+C upon drying (heating to 150 °C, see Figure 5.6c and d). This
Figure 5.5 Calculated and experimental XANES spectra of Znpol. a: Calculated XANES spectra of pure oxo and chain complexes. b: Experimental XANES spectra showing the difference between water-saturated LO-Zn and dried LO-Zn. Though the differences are small, the observed reduction in edge peak intensity, increase in post-edge peak intensity and the shift in the third peak upon drying are all consistent with an increased relative concentration of chain complex in the polymer sample.

Effect demonstrates that the zinc carboxylate species corresponding to band B must have a higher Zn/COO ratio than the chain complex that is responsible for band A+C. It is important to note that even Znpol with no added sorbic acid contains a significant concentration of non-neutralised COOH groups, because carboxylic acid groups are formed during the antioxidative curing of linseed oil. However, because of the high degree of crosslinking in linseed oil polymer networks, it is likely that not all COOH groups are available for reaction during changes in water concentration in the polymer, causing an incomplete conversion between species. This incomplete conversion is more pronounced at 100% neutralisation (Figure 5.6a and b). Based on this variety of spectroscopic evidence, we conclude that linseed oil-based ionomers such as Znpol contain a significant fraction of zinc carboxylates with the structure of an oxo complex. The rigid polymer network backbone is prone to induce some disorder, which causes the characteristic Zn₄O band to be either weak or absent in fully cured samples.

In summary, the great similarities in material composition and IR spectral features between our Znpol model system and ZnO-containing paint support the conclusion that the polymerised binding medium in historical zinc white oil paint also contains both chain and oxo type ionomeric zinc carboxylates. Our investigations should have important implications for the conservation of oil paintings. We now know the exact coordination environment around zinc ions in oil paint binding media. The relative concentration of chain and oxo structures will depend on the local concentration of carboxylic acid groups, as well as the humidity in the environment of a painting. The differences in the shape of the broad zinc carboxylate band envelope in IR spectra of samples from
paintings directly reflect the differences in the relative concentrations of the oxo and chain structures. With the newly acquired structural knowledge and the capability to prepare both the chain and oxo complexes in isolation, it has become possible to investigate the differences in reactivity of the two zinc carboxylate complexes towards the formation of zinc soaps. Additionally, ionomers are known to be electrically conductive through an ion hopping mechanism, a process which is probably responsible for the migration of metal ions from pigment particles into the polymerised oil network. To forecast changes in the mechanical properties of oil paint films or the rate of zinc soap formation, it will be interesting to link the structure of ionomeric zinc carboxylates to metal ion diffusion. Lastly, because tetranuclear zinc acetate oxo complexes have been reported to catalyse transesterification reactions, it should be investigated whether the zinc carboxylate complexes in ionomers play a catalytic role in the degradation of the polymerised binding medium itself.
5.2.3 Ion cluster morphology in linseed oil ionomers

Taking into account the evident effect of water on the coordination environment of zinc carboxylates in oil paint described above, we investigated if the coordination changes detected with IR affect the size and concentration of ionic aggregates (clusters with high ion-content). The ionic aggregates are investigated with Small Angle X-ray Scattering (SAXS). Although it has been shown that these clusters can exist in our model systems, the newly found oxo or chain coordination geometries around zinc ions give rise to the question if, and to what extent, these complexes are involved in clustering. We also consider the option that part of the zinc complexes in the tested polymers do not participate in cluster formation and are homogeneously distributed in the polymer matrix. This form is referred to as ‘background zinc’ and can not be observed with SAXS. Both oxo and chain complexes may be present in ion clusters and as background zinc.

The effects of increasing metal concentration (Znpol) and neutralisation (Znpol-So, constant sorbic acid concentration and increasing metal concentration) were studied in zinc ionomers. Knowing that Znpol shows oxo–chain conversion by a reversible reaction with one molecule of water, the effects of drying (by heating to 150 °C) were studied. The hard-spheres scattering model developed by Yarusso and Cooper (YC) was used to fit the obtained ionomer peak in the SAXS data. This model assumes that ionic clusters can be approximated as spherical particles containing a high concentration of ionic groups. These spherical particles are assumed to be distributed with liquid-like order and surrounded by a layer of immobile polymer matrix that limits the distance of closest approach between two particles (clusters). The resulting model is formulated as follows:

\[
I(q) = I_e(q) V \frac{V_1^2 \rho_1^2 \{\Phi(qR_1)\}^2}{V_p + 8V_{CA}\epsilon \Phi(2qR_{CA})} 
\]

in which

\[
\Phi(x) = \frac{3(sin x - x cos x)}{x^3} 
\]

\[
V_1 = \frac{4\pi R_1^3}{3} \quad \text{and} \quad V_{CA} = \frac{4\pi R_{CA}^3}{3}. 
\]

Here, \(I(q)\) is the intensity of the signal as function of the scattering vector \(q\), \(R_1\) is the radius of an ionic cluster, \(R_{CA}\) is the radius of an ionic cluster including immobile polymer shell, and \(V_p\) is average sample volume per scattering particle (ionic cluster). \(I_e\) is the intensity scattered by a single electron under the experimental conditions, \(\rho_1\) is the electron density difference between the spheres and the matrix, \(V\) the sample volume illuminated by the X-ray beam and \(\epsilon\) is a constant very close to one. We have estimated the combined contribution of terms \(I_e, \rho_1, V\) and \(\epsilon\) by grouping these terms together under a single parameter \(A\) as in:
Figure 5.7 Scattering profiles of linseed oil ionomers with varying zinc content and neutralisation with fits (thin black lines) of the YC model of Equation 5.1 to the data. Before fitting, the background signal of a film of pure polymerised linseed oil (Znpol-0) was subtracted and the value at highest $q$ was set to zero. 

- **a**: Znpol-2–6 (100% neutralisation, increasing zinc content from Znpol-2–6) at RT,
- **b**: Znpol-2–6 at 150 °C,
- **c**: Znpol-So2–6 (33–100% neutralisation, increasing zinc content from ZnpolSo-2–6) and
- **d**: Znpol-So2–6 at 150 °C. Only the samples which showed a clear ionomer peak in SAXS are shown.

\[
I (q) = A \frac{V_1^2 \{\Phi(qR_1)\}^2}{V_p + 8V_{CA}\Phi(2qR_{CA})} \quad (5.4)
\]

The resulting fitted value for $A$ (i.e. combining $I_e$, $\rho_1$ and $V$) was subsequently assumed to be constant for our samples, which is the generally accepted procedure in the literature. Subsequently, the parameters $R_1$, $R_{CA}$, $V_p$ were obtained from fits of Equation 5.4. It is important to note that it is generally assumed that all metal ions reside in clusters and do not exist as background zinc. However, if not all zinc ions participate in cluster formation, it may be possible that the electron density difference between the spheres and the matrix ($\rho_1$) is not identical for all samples. Such a scenario would especially influence the fitted values of $V_p$ when $\rho_1$ is assumed constant. Because we have no way of estimating $\rho_1$, we investigated the effects of using $\rho_1$ as a fitting parameter but found that this approach did not significantly improve the fits or change the trends in the other parameters. Moreover, it was found that neither $\rho_1$, nor $I_e$, $V$ and $\epsilon$ combined
changed in a physically meaningful way across samples or conditions because these parameters are highly correlated. As a result, we assume $\rho_1$ to be constant across all samples and conditions and explain the implications of this assumptions in the discussion of the results below. In this scenario, the absolute $V_p$ values are no longer meaningful and we only discuss trends in $V_p$. Because $V_p$ values change less than one order of magnitude upon using different $\rho_1$ values, we can still use $V_p$ values to make a rough estimate of how much zinc is incorporated in clusters.

Figure 5.7 shows that in all cases where an ionomer peak was observed (for roughly >150 mM zinc, lower zinc concentrations did not show a clear ionomer peak), the YC model yielded good fits. The parameters $R_1$, $R_{CA}$ and $V_p$ that were extracted by the fitting procedure are displayed in Figure 5.8 for $Zn$pol and $Zn$pol-So at room temperature (RT, 20 °C) and at 150 °C. Because the upturn at small angles is not incorporated in the YC model, a selected region only covering the ionomer peak was chosen for fitting.\(^{151}\)

The origin of the upturn is generally attributed to large-scale density fluctuations of the scatterers.\(^{154}\) At large angles, multiple contributions due to sample polydispersity can hide the possible appearance of a second peak as theoretically predicted by the YC

![Figure 5.8](image_url)

**Figure 5.8** Fitted parameters of the YC model of Equation 5.4 to the scattering profiles of linseed oil ionomers with increasing zinc content and neutralisation. **a:** $Zn$pol at RT, **b** $Zn$pol at 150 °C, **c** $Zn$pol-So and **d** $Zn$pol-So at 150 °C. It was not possible to obtain a good fit of the YC model for $Zn$pol-So at 150 °C.
model. Therefore, the region between $q \approx 0.3$–1.9 nm$^{-1}$ was used for the fitting procedure (Figure 5.7).

For Znpol at RT (Figure 5.8a) the scattering volume $V_p$ increases slightly with increasing zinc content at 100% neutralisation from 697 to 755 nm$^3$. The concentration of ion clusters thus decreases with increasing zinc content in absence of (available) free COOH groups. At the same time, $R_1$ increases with increasing zinc concentration from 1.16 to 1.39 nm and $R_{CA}$ is relatively constant (within the 95% confidence interval) with an average of $\approx$2.6 nm. It is quite unexpected that increasing the zinc concentration at 100% neutralisation does not lead to an increase of zinc ions located in clusters (decrease in $V_p$).

Upon heating Znpol to 150 $^\circ$C (Figure 5.8b), a more significant increase in $V_p$ is observed compared to RT, indicating that the cluster concentration decreases rapidly at 150 $^\circ$C and full neutralisation. The signal intensities in the raw data collected at 150 $^\circ$C were also consistently lower compared to RT (Figure 5.7), showing that the scattering was much weaker. Such an effect is also described in the literature on commercial ionomers, where the complete disappearance of the ionic peak at elevated temperatures is observed and is explained by the ionic aggregates dissolving into the matrix. At 150 $^\circ$C, $R_{CA}$ is also consistently larger compared to RT, probably due to expansion of the polymer matrix, while $R_1$ remains similar in size.

For Znpol-So (Figure 5.8c and d), the inverse trend in $V_p$ with increasing zinc content is found: the cluster concentration increases with increasing zinc concentration at both RT and 150 $^\circ$C. Furthermore, the cluster concentration is consistent lower in partly neutralised ionomers (Figure 5.8c and d) than in fully neutralised samples (Figure 5.8a and b). Apparently, zinc ions do not cluster to the same extent when free COOH groups are available, but are spread out more homogeneously in the polymer matrix. When neutralisation is increased within the series (free COOH decreases), the cluster concentration increases. The radius of the clusters is slightly larger (average 1.40 nm$^3$) than for Znpol and does not change significantly with degree of neutralisation.

While it is tempting to explain the differences in cluster concentration between partly and fully neutralised samples in term of a (partial) conversion from oxo to chain complex (Figure 5.6), we currently have no reason to assume this conversion is visible in SAXS. Taking into account that the absolute concentrations (i.e. $V_p$ values) may change if significant amount of zinc do not participate in cluster formation due to changes in $\rho_1$, it is currently not possible to assign these concentrations to the oxo or chain coordination environment inside clusters. However, an attempt was made to estimate how much zinc is ‘lost’ as background zinc using some assumptions. To do that, the volume that one zinc ion would theoretically occupy in the uncured polymer matrix was calculated and compared with the typical volume of a zinc ion inside the clusters according to SAXS. We assumed that clusters occupy a sphere with a radius $R_1$ of 1.0–1.5 nm (see Eqn. 5.1: $V_1 = \frac{4}{3}\pi R_1^3 = 4.2$–14 nm$^3$, $R_1$ obtained from fits of Eqn. 5.4). Subsequently, the typical number of a zinc ions inside such a sphere with volume $V_1$ was calculated assuming either
oxo or chain coordination and the values of $V_p$ were used to calculate the final volume per zinc ion in a cluster (assuming oxo unit cell coordination, roughly 20–30 nm$^3$ at RT and 100–180 nm$^3$ at 150 °C). This analysis showed that roughly 60–85% of zinc ions is not observed with SAXS at RT, whereas >90% does not cluster at 150 °C. These values do not change significantly if either pure oxo or pure chain coordination is assumed in clusters. The fact that such a large part of the zinc ions does not cluster is quite different than is generally assumed for commercial ionomers$^{157}$ and raises the question if SAXS analysis could provide additional insights in future oil paint research. Nevertheless, SAXS analysis showed that ionic clusters with a relatively constant radius exist in linseed oil based zinc ionomers and these clusters decrease in concentration at high temperatures. Although it was not possible to make a direct link between the molecular coordination environment and the SAXS response, we found that the major part of the zinc ions does not cluster.

Due to the great similarities between the molecular structure of the aged binding medium in pigmented zinc paints and zinc ionomers (see e.g. Figure 5.1, Figure 5.6 and Figure A.1), one would expect that clusters with high ion content also exist in pigmented paint samples. To investigate if the ionomer peak can be observed in the presence of pigments, we recorded SAXS data on pigmented LO-ZnO-TiO$_2$ and LO-ZnO-BaSO$_4$ model systems with increasing ZnO concentrations (2.5–100 wt% ZnO, as described in Chapter 4). However, the intense scattering at low angles in these pigmented samples did not allow for the detection of an ionomer peak (Figure A.2). It remains to be investigated if SAXS analysis of pigmented zinc-containing samples is possible using different experimental procedures.

5.3 Conclusions

We have shown that the polymerised binding medium in historical zinc white oil paint contains both chain and oxo type ionomeric zinc carboxylates. Our investigations have important implications for the conservation of oil paintings. We now know the exact coordination environment around zinc ions in oil paint binding media. The relative concentration of chain and oxo structures will depend on the local concentration of carboxylic acid groups, as well as the humidity in the environment of a painting. The differences in the shape of the broad zinc carboxylate band envelope in IR spectra of samples from paintings directly reflect the differences in the relative concentrations of the oxo and chain structures.

SAXS analysis showed that ionic clusters with a relatively constant radius exist in linseed oil based zinc ionomers and these clusters decrease in concentration at high temperatures. Although it was not possible to make a direct link between the molecular coordination environment and the SAXS response, we found that the major part of the zinc ions does not reside in clusters. In the field of oil paintings conservation, this research brings us to a point where we can start to draw direct molecular links between the chemical
5.4 Experimental

Sample preparation The zinc-containing binding medium model systems Znpol0–6 were prepared by grinding increasing amounts of zinc sorbate (ZnSo) together with cold-pressed untreated linseed oil (LO, Kremer Pigmente) with mortar and pestle. ZnSo was synthesised as described previously. A portion of the resulting paste was spread onto glass slides with a draw-down bar to a wet thickness of 90 µm (or 15 µm for transmission measurements), and cured overnight in an air-circulated oven at 150 °C. A series of zinc ionomers with varying neutralisation (Znpol-So0–6) was prepared in a similar fashion by using mixtures of zinc sorbate and sorbic acid in linseed oil to achieve neutralisation levels of 0-17-33-50-67-83-100% (excluding the COOH groups formed as a result of linseed oil oxidation) while the total sorbate/sorbic acid concentration was kept constant. The sample composition is given in Table 5.1. Zinc palmitate (ZnPa) was synthesised by adding a solution of either 180 mg or 300 mg Zn(NO$_3$)$_2$ · 6 H$_2$O in 2 mL demineralised water to a solution of 300 mg palmitic acid (HPa) and 0.25 mL triethylamine in 10 mL demineralised water at 85 °C, corresponding to a Zn:HPa ratio in the mixture of 1:1.93 and 1:1.16, respectively. After stirring for 10 min, the precipitated white product was washed with a sequence of demineralised water, ethanol and acetone on a Büchner funnel. While no impurities were detected with ATR-FTIR spectroscopy and powder X-ray diffracton in ZnPa prepared with 180 mg zinc nitrate, the excess of Zn$^{2+}$ ions in the alkaline reaction mixture with 300 mg zinc nitrate resulted in the co-precipitation of an additional crystalline phase identified as Zn$_5$(OH)$_8$(Pa)$_2$ with powder X-ray diffraction (diffractogram not shown).

ATR-FTIR spectroscopy ATR-FTIR spectra were measured on a PerkinElmer Frontier FT-IR spectrometer fitted with a Pike diamond GladiATR module equipped with a top-plate heatable to 200 °C. Spectra of polymer samples under different environmental conditions were collected by placing a metal cylinder around the sample between the top-plate and the pressure clamp of the ATR module (this setup is described in more detail in Chapter 2). The resulting compartment could be flushed with either dry N$_2$, or with water-saturated gas by bubbling N$_2$ through a water reservoir. The curing process of Znpol was followed by spreading a very thin layer (<5 µm) of a paste of LO and ZnSo with a draw-down bar on the ATR diamond, and collecting spectra every 1 min while heating at 190 °C in air. These spectra were baseline-corrected and normalised to the CH$_2$ stretching vibration at 2920 cm$^{-1}$. The bands at 530 and 3009 cm$^{-1}$ were sufficiently isolated to be integrated by summation over the width of the bands. Due to extensive band overlap, the time profiles of bands A, B and C contributing to the broad asymmetric
Table 5.1 Overview of the composition of samples for SAXS measurements. LO is linseed oil, So is sorbic acid, MSo is zinc sorbate and COOM/COOH refers to the proportion of total sorbate molecules that is bound to zinc.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LO (mg)</th>
<th>So (mg)</th>
<th>MSo (mg)</th>
<th>COOM/COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Znpol-0</td>
<td>1000</td>
<td>0.0</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>Znpol-1</td>
<td>1002</td>
<td>0.0</td>
<td>26.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Znpol-2</td>
<td>998.8</td>
<td>0.0</td>
<td>51.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Znpol-3</td>
<td>1001</td>
<td>0.0</td>
<td>77.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Znpol-4</td>
<td>1000</td>
<td>0.0</td>
<td>103</td>
<td>1.0</td>
</tr>
<tr>
<td>Znpol-5</td>
<td>999.4</td>
<td>0.0</td>
<td>128</td>
<td>1.0</td>
</tr>
<tr>
<td>Znpol-6</td>
<td>999.5</td>
<td>0.0</td>
<td>154</td>
<td>1.0</td>
</tr>
<tr>
<td>Znpol-So0</td>
<td>998.7</td>
<td>122</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>Znpol-So1</td>
<td>1001</td>
<td>100</td>
<td>26.2</td>
<td>0.17</td>
</tr>
<tr>
<td>Znpol-So2</td>
<td>1002</td>
<td>79.8</td>
<td>52.9</td>
<td>0.33</td>
</tr>
<tr>
<td>Znpol-So3</td>
<td>998.3</td>
<td>60.4</td>
<td>78.0</td>
<td>0.50</td>
</tr>
<tr>
<td>Znpol-So4</td>
<td>998.8</td>
<td>40.5</td>
<td>102</td>
<td>0.67</td>
</tr>
<tr>
<td>Znpol-So5</td>
<td>998.2</td>
<td>20.7</td>
<td>129</td>
<td>0.83</td>
</tr>
<tr>
<td>Znpol-So6</td>
<td>999.8</td>
<td>0.00</td>
<td>154</td>
<td>1.0</td>
</tr>
</tbody>
</table>

COO stretch vibration band envelope were approximated by taking the absorbance values at 1555, 1595 and 1625 cm\(^{-1}\), respectively.

**X-ray absorption near-edge structure (XANES)** XANES spectra were collected at the DiffAbs beamline of synchrotron Soleil (Gif-sur-Yvette, France) using a micro-beam spot size of about 10×10 µm\(^2\). The spectra were collected in transmission mode using an ion chamber detector. Zn foil was used to calibrate the XANES spectra. The spectra were normalised and baseline corrected. Samples were prepared by wrapping a stack of five pieces of thick Znpol film tightly in kapton tape (total thickness \(\approx 0.75\) mm) that were either soaked in water or stored under high vacuum (\(10^{-2}\) mbar) for two weeks prior to the measurement. For XANES calculations, the same optimised structures of the oxo complex and terminated chain complex were used as for the calculation of IR frequencies. The XANES calculations were performed using the FEFF9 code\(^{159}\) on the basis of self-consistent-field (SCF) real-space multiple-scattering (RSMS) theory. For the Zn K-edge calculation, a cluster of radius 5.0 Å around the central Zn atom was used to calculate the SCF muffin-tin atomic potentials within the Hedin-Lundqvist exchange potential, and a radius of 5.1 Å was used for the full multiple scattering (FMS) calculation.

**X-ray diffraction** X-ray diffraction (XRD) measurements on cured films were recorded with a Rigaku MiniFlex II desktop X-ray diffractometer using Cu K\(\alpha\) radiation at 2.5°/min on ca. 10×10 mm squares of paint film taped to a glass sample holder.
5.4. Experimental

Small-angle X-ray scattering  Small-angle X-ray scattering (SAXS) measurements were carried out at the Dutch-Belgian Beamline (DUBBLE) station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The sample-to-detector distance (Dectris Pilatus 1M) of the setup was ca. 2.1 m. The scattering vector $q$ is defined as $q = \frac{4\pi}{\lambda} \sin\theta$ with $2\theta$ being the scattering angle and $\lambda$ the wavelength of the X-rays (1.04 Å). The acquisition time at room temperature was 3 to 5 min per sample.

Acknowledgements

We express gratitude to B. Strudwick for help with the 2D-IR spectroscopy setup, D. Martin for performing XANES calculations, S. Hageraats and S. Reguer for assistance with the XANES measurements, R. Hoppe for making the sample of the painting by Bart van der Leck available to us and Janne-Mieke Meijer for help with the interpretation of SAXS data.
5.A Appendix

Figure A.1 Comparison of the asymmetric carboxylate stretch vibration band envelope under ambient and dry conditions in a pigmented paint film (1:1 w/w ZnO in linseed oil, spread on a glass slide to 40 µm thickness, dried and aged for 16 months at 25 °C and 50% RH). While the difference is notably smaller than in Figure 5.1c, it is clear that, upon drying, the relative intensity of bands A+C increases at the expense of band B, causing the overall band maximum to shift to lower wavenumbers.

Figure A.2 Raw data of scattering profiles obtained using SAXS on pigmented LO-ZnO-TiO₂ model systems with increasing ZnO concentrations (2.5–100 wt% ZnO, as described in Chapter 4). No ionomer peak was detected in these scattering profiles.