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Molecular dynamics of palmitic acid and lead palmitate in cross-linked linseed oil films: Implications from deuterium magnetic resonance for lead soap formation in traditional oil paintings☆

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A B S T R A C T

Many oil paintings, dating from the 15th century to the present, are affected by the formation of heavy-metal carboxylates (soaps) that alter the structural integrity and appearance of the works. Through transport phenomena not yet understood, free fatty acids formed from oils used as binders migrate through the paint film and react with heavy-metal ions that are constituents of pigments and/or driers, forming metal carboxylates. The local molecular dynamics of fatty acids and metal carboxylates are factors influencing material transport in these systems. We report temperature-dependent ^{2}H NMR spectra of palmitic acid and lead palmitate as pure materials, in cross-linked linseed oil films, and in a lead white linseed oil paint film as part of our broader research into metal soap formation. Local dynamics at the α carbon, at the terminal methyl group, and at the middle of the fatty acid chain were observed in specifically deuterated materials. Changes in the dynamic behavior with temperature were observed by the appearance of two species, a solid-like material and a liquid-like material. The relative amounts of the two phases and their deuterium NMR parameters indicate that the amount of liquid-like material and the local dynamics at that site increase with temperature. At the three locations along the chain and at all temperatures, there is a larger percentage of acyl chains of both palmitic acid and lead palmitate that are "mobile" or liquid-like in linseed oil films than there are in the pure materials. However, the percentage of liquid-like species is decreased in a lead white paint film, as compared to a linseed oil matrix. In addition, these experiments indicate that there is a larger percentage of liquid-like acyl chains of palmitic acid than of lead palmitate under identical conditions in these model paint systems.

1. Introduction

Paintings are heterogeneous multilayer systems composed of organic and inorganic molecules. As a painting is exposed to varying and adverse environmental conditions such as changes in temperature, relative humidity, and light intensity, or exposure to aqueous or organic cleaning agents, it is subjected to deterioration processes. The formation of heavy-metal soaps, i.e. carboxylates of metals such as lead, zinc, and copper, has been reported to be a widespread cause of visible deterioration of hundreds of oil paintings dating from the fifteenth century to the present [1–10]. The molecular structure and dynamics of the carboxylic acid/carboxylate phases involved and the migration mechanisms remain unclear. The current hypothesis for the formation of metal soap aggregates assumes that free monoacids, primarily palmitic and stearic, formed during the curing process of the oil matrix by hydrolysis of the glyceryl esters, migrate to particles of heavy-metal pigments such as basic lead white (lead hydroxycarbonate) and lead tin yellow (lead stannate), where they can react to form metal carboxylates [9]. Further migration of the metal soaps leads to aggregation and the appearance of soap protrusions on the surface of the painting or to an increased transparency of the paint film, causing the preparatory drawing, the wood or canvas support, and/or the artist's alterations to become visible to the naked eye

☆ Lex Vega, one of the great polymaths in our scientific community, has treated many theoretical and practical issues in NMR spectroscopy. Importantly, he has been involved in analysis of complex materials, particularly during his tenure at E. I. du Pont de Nemours. Early in his career, he realized the inherent usefulness of deuterium NMR spectroscopy to analyze materials. For example, in early work he and Dick Eckman studied deuterated molecules sorbed in zeolites, to discern dynamics and structure. He also applied the technique of deuterium NMR spectroscopy to study the dynamics of polymers such as bulk poly(methyl methacrylate). The work on paint samples in this article follows the line of study of materials with deuterium NMR spectroscopy he and several others started. So, it is with great pleasure that we acknowledge how Lex's work has pointed the way to use deuterium spectroscopy to understand structure and dynamics in materials.

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The deuterium NMR line shape is sensitive to the local configurational dynamics of a molecule. In a polycrystalline or amorphous solid, the random distribution of C-D bond orientations leads to an inhomogeneously broadened line shape, the so-called Pake-like powder pattern [14]. Configurational changes affect the line shape in specific ways that depend on the rate and geometry of motion. For example, for a C-D bond in a methyl group, rapid rotation of the methyl group about its three-fold axis gives a similar Pake-like pattern, but with a time-averaged quadrupolar splitting that is one-third of the static value [14–16]. The effects of other anisotropic motions, such as a two-site hop or a 180° phenyl-ring flip, on deuterium line shapes were observed and reported in work by the Jelinski group [17]. As a result, deuterium NMR spectroscopy has been used to study local dynamics in a wide variety of systems including macromolecules [18], small molecular complexes [19], and small molecules in association with substrates such as zeolites [20,21], silica [22], or intercalants in clays [23–25], and in biological systems [26]. The development of more advanced computational methods for modelling these motions has permitted line-shape analysis of deuterium spectra in terms of the effects of multiple simultaneous motions [27].

The local dynamics of fatty acids and metal carboxylates are important in any consideration of transport phenomena in paint films [28]. Such films are analogous to polymers [29] and liquid crystals [30], which have been successfully studied with deuterium NMR spectroscopy. Little is known of the dynamic state of molecules in the binder matrix of paint films and how that state changes when conditions are changed. The temperature dependence of the magnetic resonance parameters of deuterons in the chains of a fatty acid can provide insight into local dynamics [30,31].

Lead palmitate and lead stearate are the two soaps most commonly found in paintings [2,32]. Lead palmitate and lead stearate have similar ^{13}C CPMAS and ^{207}Pb NMR spectra [33,34]. Therefore lead palmitate and palmitic acid will be used as models for lead stearate and stearic acid, respectively. In this study, selectively labeled palmitic acid (PA) and lead palmitate (LP), with deuterons placed at the α carbon (CD_2), at the terminal methyl group (CD_3), and at carbons 7 and 8 at the middle of the chain (C_2D_4), were used to examine the mobility gradient along the fatty-acid chain. Both palmitic acid and lead palmitate were studied in the pure form and as components in a cross-linked linseed oil film, a typical paint binder, and lead palmitate was analyzed in a lead white linseed oil paint film.

2. Materials and methods

2.1. Synthesis of materials

Palmitic acid-16,16,16-D_3 (PA-CD_3), palmitic acid-7,7,8,8-D_4 (PA-C_2D_4), and palmitic acid-2,2-D_2 (PA-CD_2) were purchased from Cambridge Isotope Laboratories and used without further purification. The corresponding lead palmitate soaps were synthesized by methods adapted from previously published protocols [33,35,36]. Specifically, the various lead palmitate isotopomers were synthesized from equimolar amounts (3.25 mmol) of lead nitrate dissolved in 20 ml of water and the appropriate deuterated palmitic acids dissolved in 50 ml of ethanol. The two solutions were mixed with an equimolar amount of potassium hydroxide (5 M solution) and reacted for 20 min at 80 °C. The reaction mixture was cooled to room temperature, filtered, and washed with water, methanol, ethanol, and acetone. The three isotopically enriched materials were dried and their purity was verified by FTIR spectroscopy.

The samples of LP and PA in linseed oil films were prepared by mixing ~50 mg of the appropriate labeled acid or carboxylate with ~450 mg of linseed oil which was heated to 100 °C. Samples contained ~10% saturated free fatty acid, similar to the amount of saturated fatty acid present in linseed oil [37]. The resulting liquid material was coated on a 7.5-by-2.5 cm^2 glass slide. These films were cured at 40°C in an oven until dry to the touch, approximately 5 months.

A paint sample with additional free PA-CD_3 was prepared by physically mixing 22 mg of PA-CD_3 with 130 mg of previously cured basic lead white linseed oil paint (22% oil by weight) at room temperature and humidity. The sample was then warmed to 347.5 K to form LP-CD_3. The disappearance of palmitic acid and formation of lead palmitate was monitored by ^{13}C ssNMR spectroscopy.

2.2. NMR measurements

The deuterium NMR experiments were performed on a Bruker AVIII-500 with a 4 mm MAS probe at 76.77 MHz. The spectra were obtained from approximately 100 mg of sample packed in a 4 mm rotor. The quadrupole-echo pulse sequence [38] was used to acquire static spectra of the PA-CD_3 and LP-CD_3 labeled samples, with a $\pi/2$ pulse width of 7 μs and a delay between pulses of 40 μs The recycle delay was 5 s. In experiments on static samples the spectra are the result of averaging 512 transients. For samples labeled at the α-carbon (PA-CD_2 and LP-CD_2) and the mid-chain methylenes (PA-C_2D_4 and LP-C_2D_4), spectra were determined with a sample spinning of 8 kHz about the axis inclined at the magic angle to the magnetic field. In these experiments, a 1 μs pulse was used to excite the sample, with a 1 s recycle delay. 1024 transients were used to obtain the spectra. Spectra were measured at temperatures between 235 K and 335 K, with the temperature in the probe sample compartment being calibrated with lead nitrate as an external thermal reference. [39,40] No natural abundance deuterium signal was observed for palmitic acid in a linseed oil film, see Fig. S-2. Room-temperature analyses of the LP-CD_2 and LP-CD_3 samples before and after cycling between 335 K and room temperature showed no difference in relative amounts of solid-like and liquid-like phases.

2.3. Fitting methods

The analysis of the deuterium NMR powder patterns was performed by fitting the powder pattern to the sum of a quadrupole-broadened component and a narrow Lorentzian or Gaussian component. Fits were aided by simulation of the patterns with the program WSOLIDS [41]. Sample fits are shown in Figs. S-3–S-5. The solid-like fraction was determined from the relative peak areas of the broad component (the solid-like fraction) and the sharp central peak (the liquid-like fraction) determined from the fitting. The data for the quadrupolar splittings are defined in Fig. S1 and given in Tables S-1–S-3.

3. Results

3.1. Analysis of two phases with deuterium NMR spectroscopy

Pure PA and LP were examined with deuterium NMR spectroscopy, as were partially cured films containing either the acid (PA) or the carboxylate (LP). As shown in Fig. 1, around 297 K, the deuterium NMR spectra of the four materials contain features characteristic of two components, a sharp central feature (liquid-like phase) and a broad Pake-like feature (solid-like phase). The sharp feature arises from molecules moving fast and isotropically or almost so. The broad feature arises from molecules that are static on the NMR timescale of ~10 μs, or that are moving anisotropically (e.g. the methyl groups). From spectra of the solid-like regions taken at the lowest temperatures (223–233 K), one obtains quadrupolar coupling constants that range from 158 kHz to 166 kHz. The rapid motion of the methyl group about its three-fold axis, even in the absence of overall isotropic molecular motion, reduces the apparent quadrupole splitting to ~40 kHz in samples containing deuterated methyl groups (Table S-1) [42].

At room temperature, around 297 K (Fig. 1), spectra of pure LP show no feature indicative of the liquid-like phase. Only at temperatures at or above 330–340 K (Fig. 2) does one detect the appearance of small amounts of liquid-like material in this sample. Its reported melting point is 385.5 K, well above the highest temperature in this study. The spectra