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Jaclyn Catalano

Montclair State University, catalanoja@mail.montclair.edu

Anna Murphy

University of Delaware

Yao Yao

University of Delaware

Nicholas Zumbulyadis

Independent Researcher

Silvia A. Centeno

Metropolitan Museum of Art

See next page for additional authors

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Authors

Jaclyn Catalano, Anna Murphy, Yao Yao, Nicholas Zumbulyadis, Silvia A. Centeno, and Cecil Dybowski



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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[☆]



Jaclyn Catalano^a, Anna Murphy^b, Yao Yao^b, Nicholas Zumbulyadis^c, Silvia A. Centeno^d, Cecil Dybowski^{b,*}

^a Department of Chemistry and Biochemistry, Montclair State University, Montclair, NJ, USA

^b Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, 19716, USA

^c Independent Researcher, Rochester, NY, USA

^d Department of Scientific Research, The Metropolitan Museum of Art, New York, NY, USA

ABSTRACT

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 ²H 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.

* Corresponding author.

E-mail address: dybowski@udel.edu (C. Dybowski).

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[5,11–13].

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 ¹³C CPMAS and ²⁰⁷Pb 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 (CD₂), at the terminal methyl group (CD₃), and at carbons 7 and 8 at the middle of the chain (C₂D₄), 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-D₃ (PA-CD₃), palmitic acid-7,7,8,8-D₄ (PA-C₂D₄), and palmitic acid-2,2-D₂ (PA-CD₂) 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 cm² 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-CD₃ was prepared by physically mixing 22 mg of PA-CD₃ 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-CD₃. The disappearance of palmitic acid and formation of lead palmitate was monitored by ¹³C 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-CD₃ and LP-CD₃ labeled samples, with a $\pi/2$ pulse width of 7 μ s and a delay between pulses of 40 μ s. 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-CD₂ and LP-CD₂) and the mid-chain methylenes (PA-C₂D₄ and LP-C₂D₄), 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 μ s 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-CD₂ and LP-CD₃ 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 μ s, 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

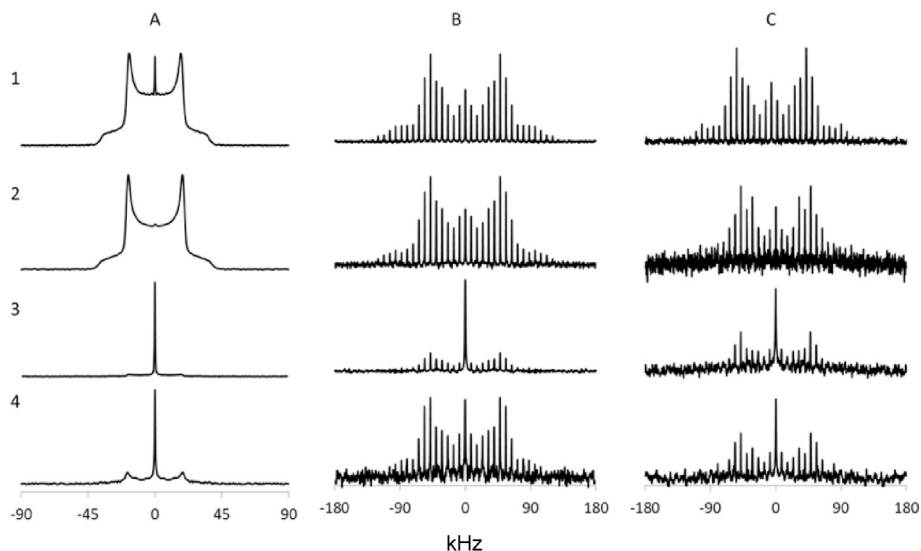


Fig. 1. Deuterium line shapes determined around 297 K. (A) palmitic acid and lead palmitate labeled with deuterium at the methyl group (CD_3); (B) labeled at the mid-chain (C_2D_4); and (C) labeled at the alpha-carbon (CD_2). (1) pure palmitic acid, (2) pure lead palmitate, (3) palmitic acid in a cross-linked linseed oil film, and (4) lead palmitate in a cross-linked linseed oil film. The spectra of the CD_3 -containing samples were determined with a quadrupole-echo sequence under static conditions, whereas the spectra of the much-broader CD_2 - and C_2D_4 -containing materials were determined under conditions of magic-angle spinning.

of pure PA at 297 K also show it to be a relatively solid-like material at 297 K, although spectra of the methyl group indicate a tiny amount of isotropically mobile material. By contrast, spectra of PA and LP in linseed-oil-based films indicate the presence of both liquid-like and solid-like phases in these materials at 297 K, no matter where deuterium is incorporated on the fatty acid chain.

Fig. 2 shows the solid-like fraction as a function of temperature. The pure materials tend to show a smaller percentage of liquid-like material at a given temperature than the samples in linseed oil. The appearance of isotropically mobile regions in the samples containing linseed oil, even at low temperatures, indicates that being mixed with linseed oil facilitates isotropic mobility for at least a portion of PA and LP. For pure PA, consistent with its lower melting point of 336 K, the spectra show the

onset of a liquid-like phase below that temperature.

The low-temperature spectra of PA- CD_3 and LP- CD_3 in the linseed-oil-based films show that even at the lowest temperatures investigated, there is a substantial fraction of the methyl groups that show fast, isotropic motion, typically leveling off at a solid-like fraction of ~ 0.9 for LP- CD_3 and ~ 0.7 for PA- CD_3 at the lowest temperatures. Thus, it appears that a significant amount of the chain ends are free to execute extensive free motion in the presence of the linseed oil, even at low temperatures.

3.2. Quadrupolar coupling in the solid-like regions

The deuterium NMR spectroscopy of the solid-like phases reflects alkyl-chain dynamics in these regions. Tables S-1–S-3 show the

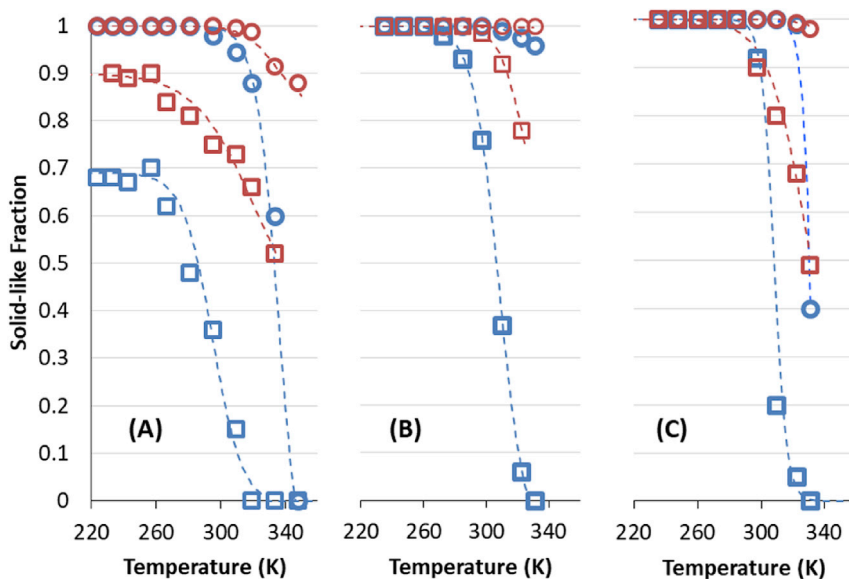


Fig. 2. The solid-like fraction in samples of palmitic acid and lead palmitate as a function of temperature. (A) CD_3 -containing samples; (B) C_2D_4 -containing samples; and (C) CD_2 -containing samples. (●) Pure palmitic acid, (○) pure lead palmitate, (□) palmitic acid in cross-linked linseed oil films, and (◻) lead palmitate in cross-linked linseed oil films. The lines are aids to the eye to indicate general trends. Estimated error for “Solid-like Fraction”: ± 0.02 .

temperature dependence of the major deuterium quadrupole splitting ($\Delta\nu_Q$) for pure PA, pure LP, PA in the linseed oil film, and LP in the linseed oil film. In all four materials, the methyl group (CD_3) at the chain end (Tables S-1) experiences rapid motion around its three-fold axis, which results in a reduced time-averaged quadrupole splitting, even at the lowest temperatures investigated. The effect of free rotation or rapid hopping about the three-fold axis of a methyl group has been seen many times in the deuterium NMR spectra of organic materials containing methyl groups, so the existence of this motion is not unexpected for solid PA and LP [15].

The spectroscopic data at all positions along the chain indicate that the major quadrupole splitting is fairly constant as a function of temperature, although there is a slight systematic decrease as the temperature is increased. Assuming that the major quadrupole splitting is temperature-independent, the average major quadrupolar splitting for deuterons at the α -carbon is 119.9 ± 2.7 kHz. Under the same assumption for deuterons at the midchain, the average major quadrupolar splitting is 119.5 ± 3.1 kHz. The average major quadrupolar splitting for the chain-end methyl group is 39.2 ± 2.0 kHz. These splittings correspond to quadrupole coupling constants of 159.9 ± 3.6 kHz, 159.3 ± 4.1 kHz, and 156.8 ± 8.0 kHz, respectively, essentially the same value for all sites.

These results for the solid-like regions suggest a model in which the chain is immobile at low temperatures in all four materials, with some slight dynamic effects that become evident as the temperature is increased above about 300 K. Importantly, the quadrupole splittings of PA or LP do not change when either is in a linseed-oil matrix. This fact strongly suggests that the solid-like regions in the linseed-oil-based films are dynamically similar to the pure materials. One model that explains this observation assigns the solid-like regions in the linseed-oil-based films to essentially pure PA or LP that have little or no direct contact on the atomic scale with linseed oil. This model is consistent with the suggestion that cooling, such as done to form these samples, results in nucleation of solids in the oil matrix, rather than forming a molecularly dispersed solution.

3.3. Molecular mobility as seen by deuterium NMR spectroscopy

The deuterium spectra of Fig. 1 and the solid fractions in Fig. 2 indicate the existence of two phases in these samples. For all samples, lowering the temperature at which spectroscopy is done increases the solid-like fraction. At a given temperature, there is a larger amount of liquid-like component for samples containing linseed oil than for the pure material, especially at room temperature (where paintings are commonly displayed) and above. Indeed, for the samples containing linseed oil, the majority of molecules are executing rapid isotropic motion at temperatures just above 300 K, whether with PA or LP.

For the pure samples, at temperatures up to 300 K or slightly above, the spectroscopy indicates that there is only a single, solid-like phase by measurements at all three points on the chain. Only above that temperature does the liquid-like signal appear. The liquid-like phase appears most prominently for pure PA, and the liquid-like phase appears only at higher temperatures for LP, which is consistent with their different melting points.

The appearance of a liquid-like phase in PA seems to be associated with the onset of premelting mobility, particularly for the chain ends. The solid-like fractions for PA observed by spectroscopy of PA-CD_2 and $\text{PA-C}_2\text{D}_4$ decrease markedly within a few degrees of the reported melting point of 336 K, whereas the chain ends show a substantial isotropically mobile component 30–40 K below that temperature. Lead palmitate, on the other hand, is completely solid-like over most of the range, and only shows a slight amount of liquid-like chain-end mobility around 330–340 K, about 30–40 K below its reported melting point. It seems that the appearance of liquid-like regions is related to proximity to the melting point for both materials and starts by fast dynamics at the chain end. In CPMAS ^{13}C spectra of these materials [33], two

carboxylate chain conformations were observed for lead palmitate at 298 K. One cannot distinguish the two conformations from the deuterium spectra.

The dynamic state of the linseed-oil-based films is especially telling. At temperatures as low as 230–235 K, these samples appear to have an appreciable amount of isotropically mobile material at the chain ends. By contrast, at these low temperatures, spectra of the mid-chain and α -carbon sites indicate that there is not significant isotropic mobility in those positions. This provides evidence that, at least in some regions of the sample, the chain ends are fairly free to move isotropically, whereas in other regions the molecules do not exhibit such behavior.

3.4. Liquid-like mobility at low temperatures

Although we name one phase “liquid-like” because at sufficiently high temperature it shows a sharp line shape characteristic of an isotropic liquid, at lower temperatures, the lines corresponding to this liquid-like phase become broad, as seen for palmitic acid in linseed oil (Fig. 3), and to a lesser extent for lead palmitate- CD_3 cured in linseed oil (Fig. S-6). Such line shapes are known to arise from molecules undergoing intermediate exchange between a solid-like regime and a liquid-like regime [16,21]. Thus, at low temperatures, some fraction of the PA molecules in the linseed-oil-based film undergoes an exchange process with a correlation time on the order of 100 ns–700 ns.

3.5. Mobility of lead palmitate in a paint matrix

A sample was prepared by mixing deuterated PA-CD_3 with a cured lead white paint and then heated at 347.5 K, to react all the palmitic acid with the lead white paint. The sample was held at temperature until ^{13}C NMR spectroscopy indicated the total disappearance of PA, producing a sample that had only LP mixed with the lead white paint.

The sample was subsequently cooled and examined with deuterium NMR spectroscopy as a function of increasing temperature. As shown in Fig. 4, at the very lowest temperatures, the LP seems to be almost completely solid-like, with very little liquid-like phase present, unlike the sample of LP mixed with linseed oil only. As it is warmed, a liquid-like material appears, slightly more than was found for the pure LP until ~ 350 K, at which point the spectra of the two samples look quite similar and the amounts of liquid-like material are essentially the same. The same experiment could not be performed for palmitic acid in the paint matrix, since the two species react to form lead palmitate under the experimental conditions.

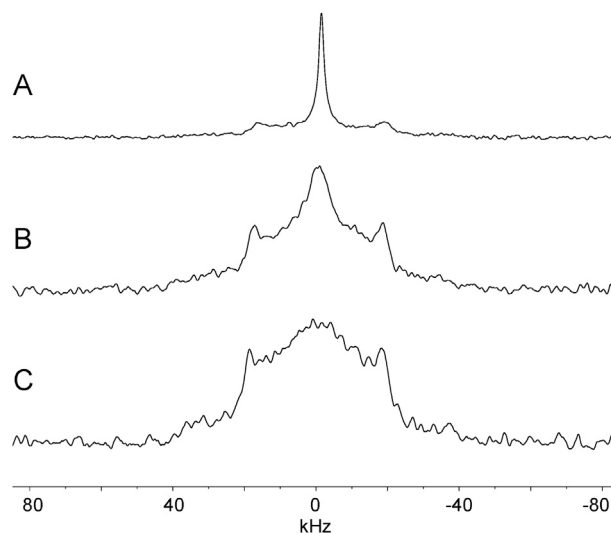


Fig. 3. Deuterium spectra of palmitic acid- CD_3 cured in linseed oil measured at (A) 275 K, (B) 255 K, and (C) 235 K.

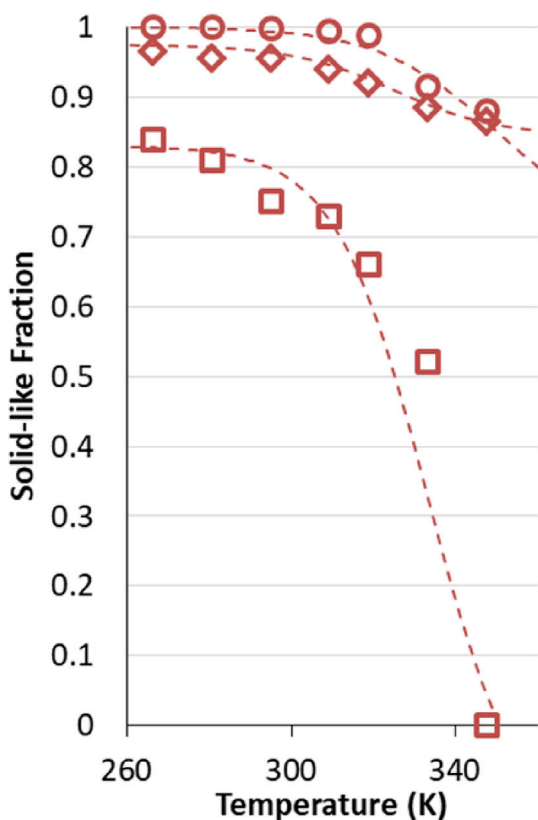


Fig. 4. Methyl-group solid-like fraction for lead palmitate in various environments as a function of temperature. (○) Pure lead palmitate; (◻) lead palmitate in a linseed oil matrix; (◊) lead palmitate in a basic lead white paint matrix. The dotted line indicates a trend, but is not a fit of the data.

4. Conclusions

The local rotational mobility of free palmitic acid and lead palmitate is a significant factor in the formation of soaps in works of art. These deuterium NMR investigations of pure PA and LP, and of models of PA and LP in cross-linked linseed oil films and in mixtures with basic lead white paint show the presence of two phases, the relative amounts of which depend on temperature and the sample matrix. At low temperatures, pure PA and LP are primarily rigid solids that only execute rapid motion about the three-fold axis of the methyl group. At higher temperatures, the appearance of the sharp feature in the deuterium spectrum indicates the existence of a liquid-like phase, which becomes more prominent as the temperature is raised. Only a small fraction of the liquid-like phase is observed for LP at the temperatures at which we could make measurements.

On the molecular level, there appears to be a gradient of mobility along the chain, with the chain ends being most likely to be isotropically mobile at a particular temperature. This is in agreement with a previous study that showed there is a partial melting of the aliphatic chains before the phase change [43,44].

The present results support the current hypothesis on lead soap formation, showing that at room temperature there is a considerable fraction of PA that is mobile in a linseed oil film and can migrate to areas of lead pigments. The spectra of PA and LP in linseed-oil-based films show the effect of linseed oil on the materials. In particular, at a given temperature, PA and LP in linseed-oil-based films have a larger liquid-like fraction at the chain ends than do the pure materials. These results are relevant to understanding soap formation at the beginning of the drying process when the oil paint films contain microfluid domains.

Soaps have been frequently detected in paint layers that are below or

above layers that contain a relatively high proportion of the binding medium. This is typically the case of paints composed of pigments such as carbon-base black and iron earth-base pigments [5,45]. A comparison of the liquid-like fraction of a sample consisting of LP in a physical mixture with cured basic lead white paint to that of LP in a linseed-oil-based film not containing lead white shows that LP has more local mobility in samples that contain a higher percentage of linseed oil. The observation of mobility of LP in a linseed oil matrix suggests that lead soaps can migrate through a matrix to form aggregates. As seen in our results, the mobility of these lead soaps is dependent on the composition of the paint matrix.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.ssnmr.2017.12.003>.

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