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Microencapsulated Alkane Wax Melting: Measured by ^1H NMR Relaxometry and Diffusometry

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ABSTRACT

Phase change materials (PCMs) are useful for energy storage. Large latent heats make *n*-alkane waxes effective PCMs. Octadecane and eicosane were studied as both unencapsulated and microencapsulated with NMR relaxometry and diffusometry throughout melting. Each wax was stepped degree-wise through its melting point. At each temperature point, NMR T_2 relaxation, $T_1 - T_2$ correlated relaxation, and PGStE measurements as a function of molecular migration time Δ were acquired. These measurements detected molecular-level disordering due to microencapsulation. NMR relaxometry measurements on the solid waxes measured a major intermediate mobility domain in the microencapsulated waxes. This pseudo interface domain in the solid microencapsulated waxes is consistent with the disruption of long-range order, increasing heterogeneity and extending the melting point range. NMR diffusometry measured diffusion coefficients D in the unencapsulated wax melts, matching values established in the literature. D as a function of $1/T$ was fit for Arrhenius activation energies E_a as a function of Δ for each stage of melting. D values are reported for each solid wax sample, which are not measurements of only molecular diffusion but are consistent with magnetization transport via spin diffusion.

1 | Introduction and Background

Phase change materials (PCMs) are useful for thermal energy storage [1–3]. With large latent heats, *n*-alkane waxes are effective PCMs [2]. Below the melting point, these waxes are solid. At temperatures above the melting point, these waxes melt, absorbing surrounding thermal energy [2]. When melted waxes freeze, they release energy to their surroundings [2]. These waxes are often encased in micron-scale acrylic shells [1, 2]. The shell seals in liquid wax for reusability and can protect the wax from environmental contamination [2]. Some specific applications include heat regulation in automotive engines [2], and batteries [3], capturing solar energy for cooking [4], and improving thermal efficiency of buildings [2, 5].

The thermal properties of *n*-alkane waxes are well studied [6–8], and NMR relaxometry has long been used to measure molecular dynamics in alkane phase transitions [9, 10]. The impact of microencapsulation has been studied with differential scanning calorimetry (DSC) [1, 11], but further understanding of the impact of microencapsulation on melting can improve design as PCMs. Changes in phase transition properties with molecular restriction due to the curvature in pores, the Gibbs–Thomson effect, are well-established for liquid–solid phase transitions [12]. Nuclear magnetic resonance (NMR) techniques based on cryoporometry have been developed using the unfrozen liquid signal to characterize pore size [13–15]. Recently, microencapsulated alkanes have been used as sensors to observe heat transfer in a PCM packed bed [16], T_2 relaxation has been correlated to

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temperature in melting microencapsulated eicosane PCMs [17], and liquid alkane mixtures have been observed to exhibit different diffusion behaviors based on confinement [18]. These works demonstrate the utility in studying PCMs noninvasively using NMR as a complement to DSC studies.

To measure the impact of microencapsulation induced restriction on molecular motion in melting, temperature-controlled NMR relaxometry and diffusometry are used to quantify rotational and translational dynamics of unencapsulated and microencapsulated *n*-alkanes, *n* = 18 octadecane and *n* = 20 eicosane. The impact of microencapsulation on structural rearrangements, such as solid–solid (pre-melt) rotator phase transitions during melting, is elucidated. The data contribute unique molecular-scale insight into DSC observations of the melting behavior of unencapsulated and microencapsulated alkane wax PCMs.

2 | Theory

2.1 | NMR Relaxometry

T_1 and T_2 relaxation processes induce NMR signal attenuation. In NMR, the magnetic moments of ^1H atoms within a sample align with an applied magnetic field B_0 . The net macroscopic magnetization $\mathbf{M}$ of an ensemble of atoms aligns with and precesses around B_0 at the Larmor frequency $\omega_0 = \gamma B_0$, where γ is the ^1H gyromagnetic ratio. Radio frequency (RF) pulses at ω_0 excite spin energy level transitions that rotate $\mathbf{M}$ out of alignment with B_0 . The spin system dissipates this excess energy to its surroundings, returning $\mathbf{M}$ to thermal equilibrium, in a process termed T_1 relaxation. The RF pulse synchronizes the precession frequency of ^1H atoms in a coherence induced detectable transverse magnetization, which decays by dipole-induced local magnetic field fluctuations dephasing the spin precession by T_2 relaxation.

T_1 and T_2 relaxation reflect molecular dynamics of a system. Their rates depend on molecular rotational correlation times τ_c , which mediate dipolar interactions, and ω_0 [19, 20]. The Bloembergen–Purcell–Pound theory of relaxation [21, 22], provides a relation between T_1 and T_2 with atomic properties making up the second moment or variance of the frequency distribution M_2 [23, 24], ω_0 , and τ_c [19, 20, 25].

$$\frac{1}{T_1} = M_2 \left[\frac{4\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{16\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right], \quad (1)$$

$$\frac{1}{T_2} = M_2 \left[6\tau_c + \frac{10\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]. \quad (2)$$

Field cycling NMR applications probe changes to T_1 as a function of ω_0 to measure alkane molecular dynamics [10, 26–29]. Alkanes have evolving τ_c during phase transitions, impacting T_1 and T_2 [9, 10]. A solid alkane wax is a rotationally restricted semicrystalline lattice with long τ_c , the motionally broadened NMR relaxation regime [10], in which T_1 is the order of 1 s and T_2 is of order 10^{-4} s. Alkanes undergo solid–solid rotator transitions in the intermediate NMR relaxation regime near the onset of

melting, with enhanced rotational mobility shortening τ_c . Here T_1 minimizes and T_2 slows as the ordered crystal lattice becomes more disordered [6, 7]. While the models of Equations (1) and (2) are too simple to capture the complex molecular dynamics in alkanes, which include collective translational and uncorrelated rotational motions oriented along various axes of the crystal domain and crystal interfacial structure near the melting point, it provides connection to the average molecular motion correlation time [30]. Liquid state melted alkanes are most mobile with short τ_c causing T_1 and T_2 convergence at the order of seconds, the motionally narrowed NMR relaxation regime [19, 20].

2.2 | NMR Diffusometry

Pulsed gradient spin echo (PGSE) NMR measures molecular self-diffusion in homogeneous liquids [20, 31]. The pulse sequence RF and magnetic gradient field pulses encode displacement of molecules containing ^1H species, with a gradient pair separated by a displacement time Δ [31]. PGSE measures an effective diffusion coefficient D in saturated porous media [20, 32]. Repeated measurements over a range of Δ times reveal the system's diffusive behavior $D(\Delta)$ [20, 32–34]. Comparison with bulk fluid diffusion dynamics measures pore size and tortuosity α in two time-limiting regimes [33]. In the limit $t \rightarrow \infty$, $D(t) = \langle z^2(t) \rangle / 2t$ approaches 0 for isolated pores and D_0/α for interconnected pores [34], where D_0 is the coefficient of free molecular self-diffusion of the liquid. A functional form for fitting is

$$D(t) = \frac{D_0}{\alpha} + \frac{\beta}{t} + \frac{\gamma}{(D_0 t)^{1/2}} + \dots, \quad (3)$$

where β and γ are geometric factors [34]. In the short-time limit, $t \rightarrow 0$ and $D(t)$ approaches D_0 . $D(t)$ near this limit deviates from D_0 due to molecules interacting with pore walls [34].

$$D(t) = D_0 \left(1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V} (D_0 t)^{1/2} \right), \quad (4)$$

where S/V is the surface to volume ratio, the reciprocal of the effective pore size, of the encapsulating pore.

Pulsed gradient stimulated echo (PGStE) can be advantageous over PGSE when T_2 is short and T_1 is long [20, 35]. PGSE stores magnetization in the transverse plane during Δ , resulting in T_2 relaxation limits on displacement time Δ . PGStE NMR stores magnetization longitudinally during Δ , where T_1 controls signal relaxation, a useful capability for solid-like materials, large molecule liquids or viscous fluids [20, 35], where $T_1 \gg T_2$. PGStE NMR measures total molecular motion within liquid systems including coherent displacements over Δ due to velocity, while double PGStE (DPGStE) refocuses phase shifts due to coherent displacements to measure pure molecular self-diffusion [36, 37]. The echo attenuation from a PGStE experiment is due to total motion in the system [20]. $E(g) = \exp(i\gamma\delta g \cdot v\Delta - \gamma^2 g^2 \delta^2 D(\Delta - \delta/3))$, where $E(g) = S(g, t)/S(0, t)$ is echo amplitude, δ is gradient pulse length and g is gradient amplitude. The $i\gamma\delta g \cdot v\Delta$ term is the mean phase shift due to velocity induced coherent motion. The $\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)$ term represents the variance or second cumulant magnetization phase fluctuations caused by stochastic

motion during time Δ [20]. DPGStE NMR combines back-to-back PGStE sequences, which refocuses constant bulk motion, producing an echo signal dependent only on random diffusive motions in the echo attenuation $E(g) = \exp(-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3))$. The use of a stimulated echo in solid-like systems, such as soft waxes and polymer melts, introduces signal attenuation due to longitudinal magnetization spin diffusion during storage period which is proportional to Δ [38]. This signal attenuation due to exchange of ^1H magnetization between domains of differing dipolar coupling, for example, strong dipolar coupled short T_2 crystalline and weaker dipolar coupled longer T_2 amorphous domains, results in a larger measured $D(\Delta)$ than in the absence of spin diffusion.

3 | Materials

Microencapsulated octadecane and eicosane from Microtek (Westminster, CO, USA) were studied. These are ~ 3 mm beads filled with 10- to 20- μm diameter particles containing octadecane $\text{C}_{18}\text{H}_{36}$ or eicosane $\text{C}_{20}\text{H}_{42}$. Reference 99% pure octadecane wax (Lot MKCM5285), with melting point range 299.15–302.15 K, and eicosane wax (Lot MKBJ7060V), with melting point range 308.15–310.15 K, were acquired from Sigma Aldrich (St. Louis, MO, USA).

4 | Methods

4.1 | Experimental Setup

Each sample was loaded into a 5-mm NMR tube and inserted into a 250-MHz Bruker (Billerica, MA, USA) superconducting magnet paired to a Bruker Avance III spectrometer and custom 5-mm high-power RF probe with diff30 gradient coil. Each sample was temperature-controlled using the Bruker VTU to step through a temperature range in increments of 1 K. At each fixed temperature step, the sample equilibrated for 30 min, a protocol established by observing FIDs over time at a range of temperatures, before relaxometry and diffusometry scans were run. Unencapsulated octadecane was measured each degree from 293 to 308 K and microencapsulated octadecane from 288 to 308 K. Unencapsulated and microencapsulated eicosane were measured each degree from 293 to 313 K.

4.2 | Relaxation Data Acquisition and Analysis

T_2 relaxation measurements were made with a Carr–Purcell Meiboom–Gill (CPMG) pulse sequence [39, 40], with 60,000 echoes spaced 24 μs apart ($\tau = 12 \mu\text{s}$), 1- μs dwell time for a 0.5-MHz sweep width, 30-s interexperiment delay, and 32 averages. RF pulses were 100 W and applied for 3.24–3.41 μs for 90° pulses and 6.48–6.82 μs for 180° pulses, dependent on the sample.

$T_1 - T_2$ correlation measurements were made on all samples with a combined inversion recovery and CPMG pulse sequence [20, 27, 41]. The inversion recovery component was acquired over 32 pseudo log spaced steps between 0.001 and 50 s. The CPMG component was set up identically to the 1D T_2 measurements.

NMR T_2 and $T_1 - T_2$ voltage signals were processed by a MATLAB (Natick, MA, USA) based Tikhonov-regularized non-negative least squares fit to a Fredholm integral of the first kind [41–43], often referred to in NMR literature as an inverse Laplace transform or ILT [44]. The ILT fits a probability distribution of relaxation rates with the integral of total probability normalized to unity. A regularization smoothing parameter was selected to minimize the residual without overfitting and generating pearling artifacts. Each signal decay was analyzed with this value to reduce smoothing bias. $P(T_2)$ distributions (Figure 2) and a subset of $T_1 - T_2$ correlation distributions (Figure 3) are shown.

To further analyze $T_1 - T_2$ correlation distributions, T_1/T_2 ratios were calculated and plotted for all populations at each temperature (Figure 4). Prior to integration, $T_1 - T_2$ populations were identified by cluster analysis using a MATLAB-based Gaussian mixture model fit, fitgmdist, [45, 46] with full unshared covariance matrices, a regularization value of 1×10^{-10} and 5×10^4 maximum iterations. For reproducibility, model initial conditions were provided by assigning each point to its nearest maximum. The total number of local maxima provided the number of clusters k . Probability weighted average T_1 and T_2 was calculated for each cluster with $T_x = \sum_{i=1}^N P^i T_x^i$, where T_x is averaged T_1 or T_2 , N is the size of each cluster, P^i is the probability for each point, and T_x^i is T_1 or T_2 for each point. Averaged T_1/T_2 were used to categorize populations based on mobility with outliers ($T_1/T_2 < 1 \times 10^{-1}$ and $1 \times 10^7 < T_1/T_2$), restricted ($5 \times 10^2 \leq T_1/T_2 \leq 1 \times 10^7$), intermediate ($1 \times 10^1 < T_1/T_2 < 5 \times 10^2$), and mobile ($1 \times 10^{-1} \leq T_1/T_2 \leq 1 \times 10^1$). Figure 4 tracks populations of restricted mobility in blue, intermediate mobility in red and high mobility in yellow during melting of each material.

4.3 | Diffusometry Data Acquisition and Analysis

PGStE measurements were made with a spoiler recovery delay of 5 s, 64 linearly ramped g steps to a maximum of 5–10 T/m, 2 ms δ , and 16 averages. Echoes were acquired with dwell times of 1 or 2 μs over 4096 or 8192 points, producing sweep widths between 0.25–0.5 MHz. Measurements were repeated at displacement observation times $\Delta = 10, 50, 75, 100, 400$, and 1000 ms. RF pulses were 100 W for between 3.24 and 3.41 μs for 90° and 6.48–6.82 μs for 180°, depending on the sample.

The unencapsulated waxes were measured with DPGStE NMR because they exhibited convective PGStE behavior, while the microencapsulated waxes did not indicate convection over the measured temperature range. The extra pulses used in the DPGStE sequence lengthened the minimum Δ time to ~ 12.5 ms. Therefore, these scans were set up with identical parameters to PGStE experiments except the shortest Δ time measured was 13 ms rather than 10 ms.

Monoexponential fits to NMR diffusometry echo decays estimate diffusion coefficients D [20, 31]. D values from PGStE and DPGStE experiments on unencapsulated waxes and PGStE on microencapsulated waxes provide comparisons between samples across melting (Figure 5). Each temperature set of D values was fit with Equation (4) to estimate S/V . Fits of D versus $1/T$ also provide an estimate of the activation energy barrier for diffusion E_a , following [7, 47].

$$D_{app} = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

5 | Results and Discussion

5.1 | NMR Relaxometry

It is well-established by XRD data that *n*-alkanes form lamellar structures of triclinic crystal domains which undergo rotator and defect transitions with changes in temperature near the melting point [48, 49]. In Figure 1 a cartoon of typical structures is shown, including regions of interfacial methylene $-\text{CH}_2-$ groups which have greater mobility than central $-\text{CH}_2-$ groups as demonstrated in molecular dynamics simulations where this interface extends two $-\text{CH}_2-$ groups from the highly mobile methyl $-\text{CH}_3$ end groups [30]. Thus, in the discussion below, the

T_2 populations do not directly correlate to the number of $-\text{CH}_2-$ and $-\text{CH}_3$ groups on a molecule.

NMR T_2 relaxation distributions in Figure 2 compare unencapsulated octadecane (a) and eicosane (c) with microencapsulated octadecane (b) and eicosane (d), across the solid to liquid melting transition. At 293 K, unencapsulated octadecane (Figures 2a and S1a and Table S1) has a low mobility and high mobility ^1H spin population at 0.309 and 432 ms, accounting for 49.6% and 46.4% of the signal. These populations correspond roughly to methylene ($-\text{CH}_2-$) and methyl ($-\text{CH}_3$) ^1H spins, respectively, with the rotational mobility of CH_3 chain end groups having greater averaging out of dipolar coupling. Two small populations at 7.68 and 51.0 ms, accounting for 1.0% and 3.0% of the signal indicate restricted mobility relative to the most mobile CH_3 groups at 432 ms. At 298 K, just below the melting point range of 301 to 303 K, the least mobile

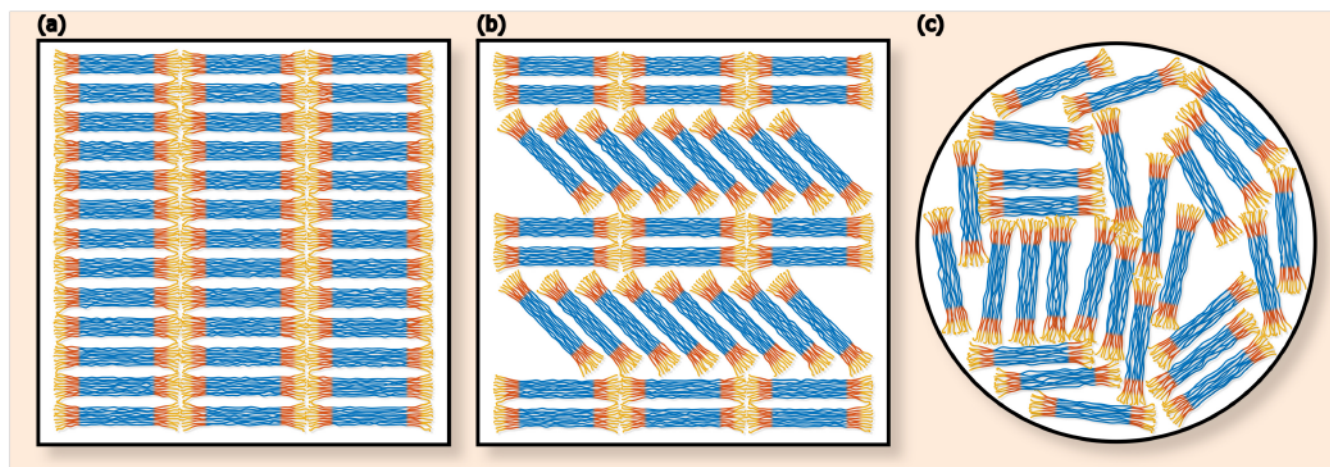


FIGURE 1 | Cartoon depicting the different ^1H populations in (a) unencapsulated bulk in a crystalline phase, (b) unencapsulated bulk in a rotator phase, and (c) microencapsulated *n*-alkane waxes. The highly rotationally mobile $-\text{CH}_3$ end groups are yellow, the pseudo interfaces of $-\text{CH}_2-$ are red, and the restricted crystalline ordered lattice atoms are blue. Domains of oriented crystals exhibit greater long-range order when unencapsulated. The steric hindrance of the microencapsulated wax prevents it from forming solid lattice crystalline domains, leading to larger yellow and red populations.

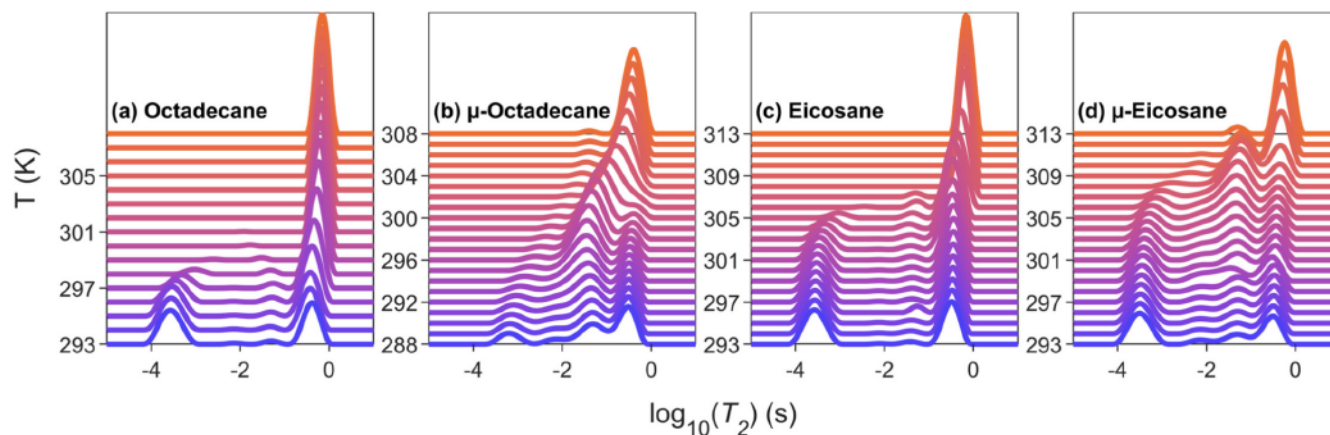


FIGURE 2 | NMR T_2 distributions of unencapsulated and microencapsulated waxes across the measured temperature ranges. Panels show change in T_2 relaxation with melting for (a) unencapsulated octadecane, (b) microencapsulated octadecane, (c) unencapsulated eicosane, and (d) microencapsulated eicosane. The colors guide the eye through relative temperatures. The solid unencapsulated waxes (a) and (c) have one restricted and one mobile population. The melted unencapsulated waxes have a single mobile population. Microencapsulated waxes replicate this behavior with an intermediate population that has a T_2 that varies strongly with temperature in (b) but not in (d).

population T_2 increases to 1.02 ms but decreases to 5.3 % of the total signal, while the most mobile increases to 91.5 % of the signal with a T_2 increase to 555 ms. The small intermediate populations merge at 48.8 ms, accounting for 3.2 % of the signal. At 300 K, the low mobility population has disappeared, and the high mobility population continues increasing to 633 ms and accounts for 99.2 % of the signal. The intermediate mobility population at 17.0 ms accounts for 0.8 % of the signal at 300 K. In the full liquid phase at 308 K only the most mobile population remains at $T_2 = 734$ ms.

At 288 K, below the melting point range in the solid, microencapsulated octadecane (Figures 2b and S1b and Table S1) also has a low mobility and high mobility population at 0.736 and 297 ms, accounting for 14.8 % and 47.5 % of the signal, and two intermediate mobility populations at 6.71 and 48.8 ms accounting for 5.8 % and 33.2 % of the signal. The shortest relaxation time at 0.736 ms is over twice the unencapsulated system's, indicating a decrease in CH_2 group ordering due to encapsulation, while the longest time decreases from unencapsulated to microencapsulated due to more restricted mobility. The presence of intermediate relaxation times reflects more interfaces between the less ordered crystalline domains. By 290 K, the intermediate mobility populations have merged giving a sole peak at 42.1 ms, making up 45.3 % of the signal. Here the low mobility population at 0.884 ms makes up 12.2 % of the signal, while the high mobility population at 306 ms has decreased to account for 43.4 % of the signal. At 293 K, the least mobile population T_2 increases to 1.40 ms and makes up 7.9 % of the signal, while the most mobile population decreases to 34.5 % of the signal with a T_2 increase to 315 ms. The intermediate population continues to grow making up 58.4 % of the signal at 38.9 ms. At 298 K, the least mobile population T_2 increases to 4.53 ms and makes up only 2.5 % of the signal. The most mobile population decreases further to 18.1 % of the signal with continued T_2 increase to 387 ms. The intermediate population now makes up 79.9 % of the signal and has increased in T_2 to 53.0 ms. This response demonstrates the increased complexity of the molecular rotational dynamics in the encapsulated alkane. At 300 K, the low mobility population at 7.79 ms accounts for 1.8 % of the signal and the high mobility population has merged with the intermediate mobility population at 140. ms which accounts for 98.2 % of the signal. At 308 K, both of these populations persist at 41.6 and 424 ms, accounting for 2.2 % and 97.8 % of the signal originating from wall restricted mobility and bulk liquid restricted mobility populations.

Unencapsulated eicosane at 293 K (Figures 2 and S1c and Table S1) has a low mobility and high mobility population at 0.307 and 338 ms, accounting for 49.0 % and 47.7 % of the signal and two small populations at 8.23 and 38.3 ms accounting for 0.6 and 2.6 % of the signal. The primary peaks in the solid phase again reflect the $-\text{CH}_2-$ protons in the ordered crystalline domains and the most mobile $-\text{CH}_3$ protons, with the $-\text{CH}_2-$ relaxation time nearly identical to the solid unencapsulated octadecane and the most mobile relaxation time reduced significantly from the smaller chain alkane. At 300 K, the low and high mobility populations are at 0.368 and 376 ms and account for 34.7 % and 61.7 % of the signal. The intermediate mobility populations at 7.67 and 42.6 ms make up 0.4 % and 3.3 % of the signal. At 304 K, the low and high mobility populations at 0.634 and 369 ms and make up 12.7 % and 93.1 % of the signal. The

intermediate populations have merged by 304 K at 36.4 ms and account for 4.2 % of the signal. At 307 K, the low mobility population disappears and the remaining intermediate and high mobility populations at 51.4 and 551 ms make up 3.2 % and 96.8 % of the signal. In the initial liquefaction at 308 K, the beginning of the melting range, the intermediate mobility population also disappears, leaving a sole highly mobile population of a pore liquid at 655 ms which continues to increase in T_2 to 720. ms by 313 K due to the increase in rotational diffusion with T .

Microencapsulated eicosane at 293 K (Figures 2d and S1d and Table S1) has a low mobility and high mobility population at 0.362 and 304 ms, accounting for 44.9 % and 36.1 % of the signal, and two smaller populations at 7.74 and 47.7 ms accounting for 5.2 % and 14.5 % of the signal. As in octadecane, eicosane microencapsulation does not impact the mobility of the most ordered crystalline region spins but does generate stronger dipolar coupling due to lower rotational mobility of the most mobile spins; with negligible change of the smallest T_2 and significant decrease of the longest T_2 . At 300 K, the low and high mobility populations increase in T_2 to 0.438 and 351 ms and account for 32.9 % and 31.4 % of the signal. The intermediate mobility populations merged by 299 K and here at 300 K make up 36.2 % of the signal at 44.2 ms. At 304 K the low, intermediate, and high mobility populations at 0.584, 45.2, and 383 ms make up 20.7 %, 52.8 %, and 27.0 % of the signal. Just below the melting point range (308–310 K) of eicosane, at 307 K, the low, intermediate, and high mobility peaks at 1.18, 53.7, and 431 ms make up 8.84 %, 67.6 %, and 24.1 % of the signal suggestive of a rotator-like phase. At 312 K, the low mobility population disappears, leaving the intermediate and high mobility populations at 64.0 and 576 ms, which make up 11.4 % and 88.6 % of the signal, representing the breakdown in molecular ordering of noncrystalline domains. The intermediate mobility population shrinks and shifts to shorter T_2 of 51.1 ms at 313 K and makes up 5.62 % of the signal, while the highly mobile population at 313 K increases to 603 ms T_2 and makes up 94.4 % of the signal. This behavior again reflects particle surface interactions between the alkane-core and the shell and demonstrates general restriction relative to the unencapsulated wax.

To summarize, NMR T_2 relaxation distributions in Figure 2 compare unencapsulated (a) octadecane and (c) eicosane with microencapsulated (b) octadecane and (d) eicosane across melting. Prior to melting, the unencapsulated waxes have one population below 1 ms T_2 and another above 100 ms. The short T_2 peak represents ^1H along the alkane backbone in crystalline ordered domains, the intermediate peaks the more mobile protons in the interfacial domain $-\text{CH}_2-$ groups and the long T_2 peak corresponds to the rotationally mobile $-\text{CH}_3$ end groups (Figure 1). The magnetization in these distinct dipolar coupled domains undergoes exchange resulting in complex multiexponential signal decay [50]. Heating to the melting point breaks down the crystalline structure, seen through the restricted motion population shifting to longer T_2 . To this point, the mobile population remains steady. Above the melting point, the restricted peak decays away. As alkane chains are liberated from the lattice, the restricted peak shrinks while the mobile peak grows proportionally. Increasing disorder of the alkane chains allows interior and terminal ^1H atoms to rotate more rapidly, shortening τ_c and increasing T_2 (Equation (2)). Further heating beyond melting

causes the mobile peak to display liquid-like mobility, as T_2 approaches 1 s. This single population also narrows as τ_c decreases across the system, characteristic of liquids and low molecular weight polymer melts.

The melting encapsulated wax trends parallel the unencapsulated waxes with an additional peak between 10 and 100 ms, representing a pseudo interface of ^1H atoms on $-\text{CH}_2-$ groups near the rotationally mobile $-\text{CH}_3$ end groups, with intermediate mobility. This is due to more disorder in microdomains. Microencapsulation sterically hinders the formation of large continuous crystalline domains, resulting in a substantial population of more mobile $-\text{CH}_2-$ spins and diminished restricted lattice peak. Unlike the unencapsulated waxes, the lattice population does not decay away during melting. As the lattice weakens, mobility of this population increases to that of the pseudo interfaces. For microencapsulated octadecane, the $-\text{CH}_2-$ pseudo interface peak grows and merges with the $-\text{CH}_3$ end group peak. The pseudo interface for microencapsulated eicosane never reaches the mobility of the free ends, as these populations remain separate. Microencapsulation limits the liquid like mobility of the melted waxes, with an enhanced effect on longer chains [18]. Overall, the microencapsulated waxes melt over a broader range than when unencapsulated. Microencapsulation favors intermediate mobilities expanding the melting point range.

$T_1 - T_2$ distributions (Figure 3) reflect the favorability of intermediate mobilities by microencapsulation. The $-\text{CH}_2-$ alkane backbone in the ordered crystal lattice is at $T_2 < 1$ ms and $T_1 > 1$ s and the rotationally mobile $-\text{CH}_3$ end groups are at $T_2 > 100$ ms and $T_1 < 1$ s for the unencapsulated waxes. Even in the solid phase, the $-\text{CH}_3$ end groups are liquid-like with similar T_1 and T_2 . Only the highly mobile population exists in the unencapsulated wax melt. The solid microencapsulated waxes have the same pseudo interface population as in the T_2 distributions. The alkane backbone disappears in the microencapsulated wax melts, while the pseudo interface peak grows indicating the breakdown of the crystalline domains faster than when unencapsulated, due to less long-range multidomain ordering. Above the melting point, the pseudo interface peak disappears, leaving a lone mobile peak at $T_2 = 480$ ms and $T_1 = 800$ ms, which is shorter T_2 than the 800 ms for the unencapsulated waxes. This result again demonstrates the propensity for more complex intermediate molecular mobilities throughout melting in microencapsulated alkanes.

Averaged T_1/T_2 provides another analysis of how microencapsulation limits high and low mobility populations (Figure 4). In the solid unencapsulated waxes, T_1/T_2 of the highly restricted $-\text{CH}_2-$ lattice population (blue) is about 10^5 , while the high mobility $-\text{CH}_3$ end groups (yellow) have a liquid-like T_1/T_2 of ~ 1 . Eicosane shows the emergence of a highly mobile pseudo interface prior to melting. In the liquid state wax melts, all ^1H spins exhibit liquid-like $T_1/T_2 \sim 1$ behavior. The red pseudo interface in the microencapsulated waxes has T_1/T_2 of ~ 10 still indicating more amorphous, less ordered, solid-like behavior. Prior to the melting point, the crystal lattice domain population increases mobility with decreasing molecular order increasing the proportion of amorphous $-\text{CH}_2-$ pseudo interfaces, which remain until above the melting point range. Emergence and persistence

of a region of $-\text{CH}_2-$ spins in a less ordered pseudo interface indicates that microencapsulation decreases long-range crystalline microdomain ordering in solid and melted alkanes, broadening the melting point range.

5.2 | NMR Diffusometry

Diffusion coefficients $D(\Delta)/D_0$ plotted in Figure 5a show that unencapsulated wax in the liquid phase, at 2 K above the unencapsulated wax melting point, have a slight Δ displacement time dependence with $D \sim 2 \times 10^{-10} \text{ m}^2/\text{s}$, consistent with values reported in Von Meerwall et al. [47]. In contrast, the microencapsulated liquid wax shows a classic decrease in $D(\Delta)/D_0$ with increasing Δ due to the restricted diffusion in the core shell particle [33, 34, 51]. Fits using Equation (4) give a particle size $V/S \sim 3.4 \text{ }\mu\text{m}$ for microencapsulated eicosane and $3.1 \text{ }\mu\text{m}$ for microencapsulated octadecane, which for spherical pores scales as $r = 3V/S$ resulting in $10.1 \text{ }\mu\text{m}$ for the eicosane and $9.4 \text{ }\mu\text{m}$ for the octadecane. These values are in good agreement with the high end of the 5- to $10\text{-}\mu\text{m}$ manufacturer specified particle radius. At 3 K below each respective unencapsulated wax's melting point (Figure 5b), the microencapsulated waxes again show the classical $D(\Delta)/D_0$ decrease of a liquid with a transition from the short displacement time, with $\Delta^{1/2}$ scaling behavior, to a constant value at large Δ [33, 34]. The unencapsulated wax diffusivity $D(\Delta)/D_0$, in the solid phase, decreases nearly linearly with increasing diffusion time $\Delta^{1/2}$. This observed behavior is consistent with diffusion of longitudinal magnetization during the magnetization storage time of the stimulated echo sequence, that is, spin diffusion [10, 50, 52].

An Arrhenius type plot of D for $\Delta = 400$ ms is shown in Figure 5c (see Figure S2 for data from all Δ times). In the unencapsulated wax, the larger molecular weight eicosane has a broader $1/T$ (K^{-1}) transition region from solid to liquid than octadecane, indicative of the difference in activation energy (Figure 6) and temperature during melting from a more crystalline state (Figures 5c and S2). In the microencapsulated waxes, the liquid to solid transition is broader in $1/T$ than in bulk, consistent with increased melting ranges observed in DSC measurements of microencapsulated wax relative to bulk [53]. The smaller D of the encapsulated waxes in the liquid phase is due to the restriction of the core shell as indicated above. The lower diffusivity in the melting and solid regimes indicates the intermediate T_2 relaxation time spin populations substantially impact the diffusion. Near the melting point, molecular mobility of the interfacial $-\text{CH}_2-$ groups is enhanced and extends further into the molecule, increasing the intermediate T_2 component. This increases longitudinal magnetization transport between the crystalline and less ordered dipolar coupled domains during the PGStE magnetization storage time [30, 38, 50]. This is consistent with the solid phase spin diffusion measured scaling as $D \sim 1/T_2$, with the intermediate larger T_2 dominating the spin diffusion [54].

A novel aspect of the diffusion time dependent NMR data is exemplified in the activation energy calculated for the liquid, transition, and solid regimes (Figure 6) from linear fits on the Arrhenius plots (Figure S2). To our knowledge, no such data have previously been generated. Increasing Δ generates a longer diffusion length scale $l_d \sim (D\Delta)^{1/2}$. In the liquid state (Figure 6a),

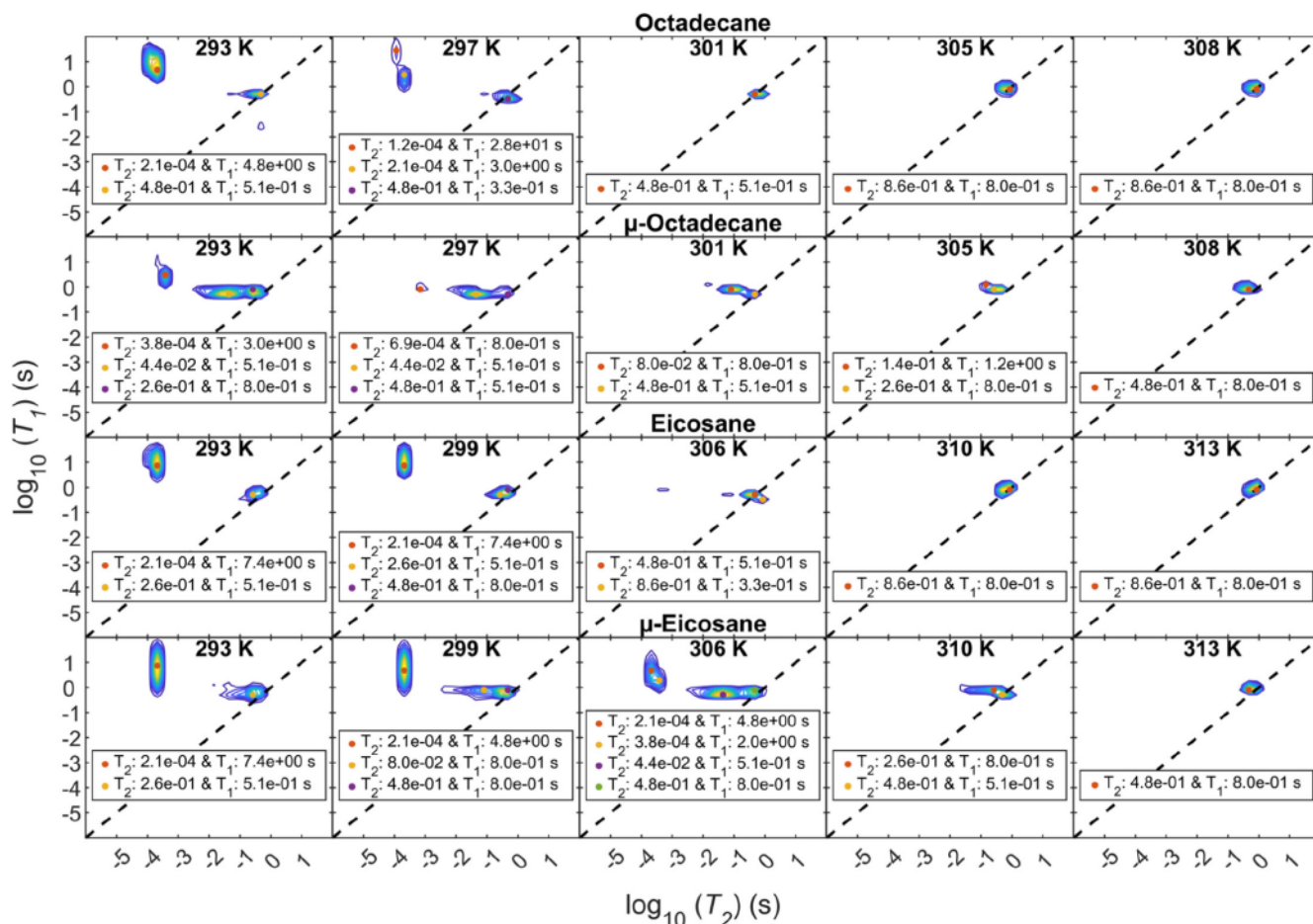


FIGURE 3 | subset of NMR $T_1 - T_2$ correlations from unencapsulated and microencapsulated waxes across the measured temperature range. From top to bottom, the rows are unencapsulated octadecane wax, microencapsulated octadecane wax, unencapsulated eicosane wax, and microencapsulated eicosane wax. For each panel, major peaks are labeled with a colored dot and their respective T_2 and T_1 times are displayed in the legend. The dashed line is the $T_1 = T_2$ parity line.

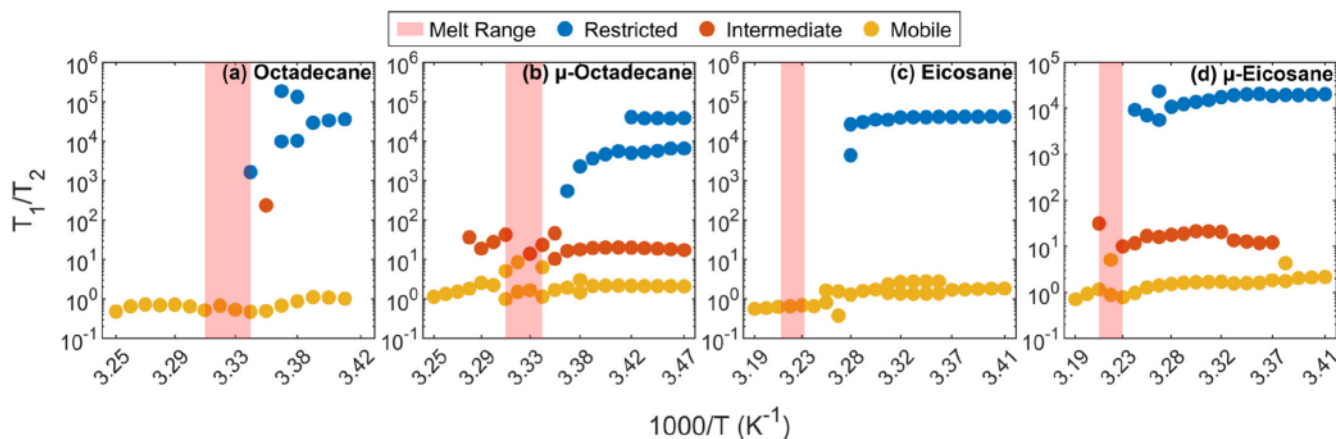


FIGURE 4 | T_1/T_2 for unencapsulated and microencapsulated waxes throughout melting as a function of $1000/T$ (K^{-1}). Panels show change in T_1/T_2 with melting for (a) unencapsulated octadecane, (b) microencapsulated octadecane, (c) unencapsulated eicosane and (d) microencapsulated eicosane. The solid pink rectangle highlights the melting point range of each wax. Blue dots indicate highly rotationally restricted $-\text{CH}_2-$ lattice ^1H , red dots indicate intermediate rotational mobility $-\text{CH}_2-$ pseudo interfaces and yellow dots are high rotational mobility $-\text{CH}_3$ end groups. The solid unencapsulated waxes do not have $-\text{CH}_2-$ pseudo interfaces due to more long-range order at crystalline microdomains and after melting only the high mobility $-\text{CH}_3$ end groups remain. The microencapsulated waxes have $-\text{CH}_2-$ pseudo interfaces throughout melting which only disappear above the melting point.

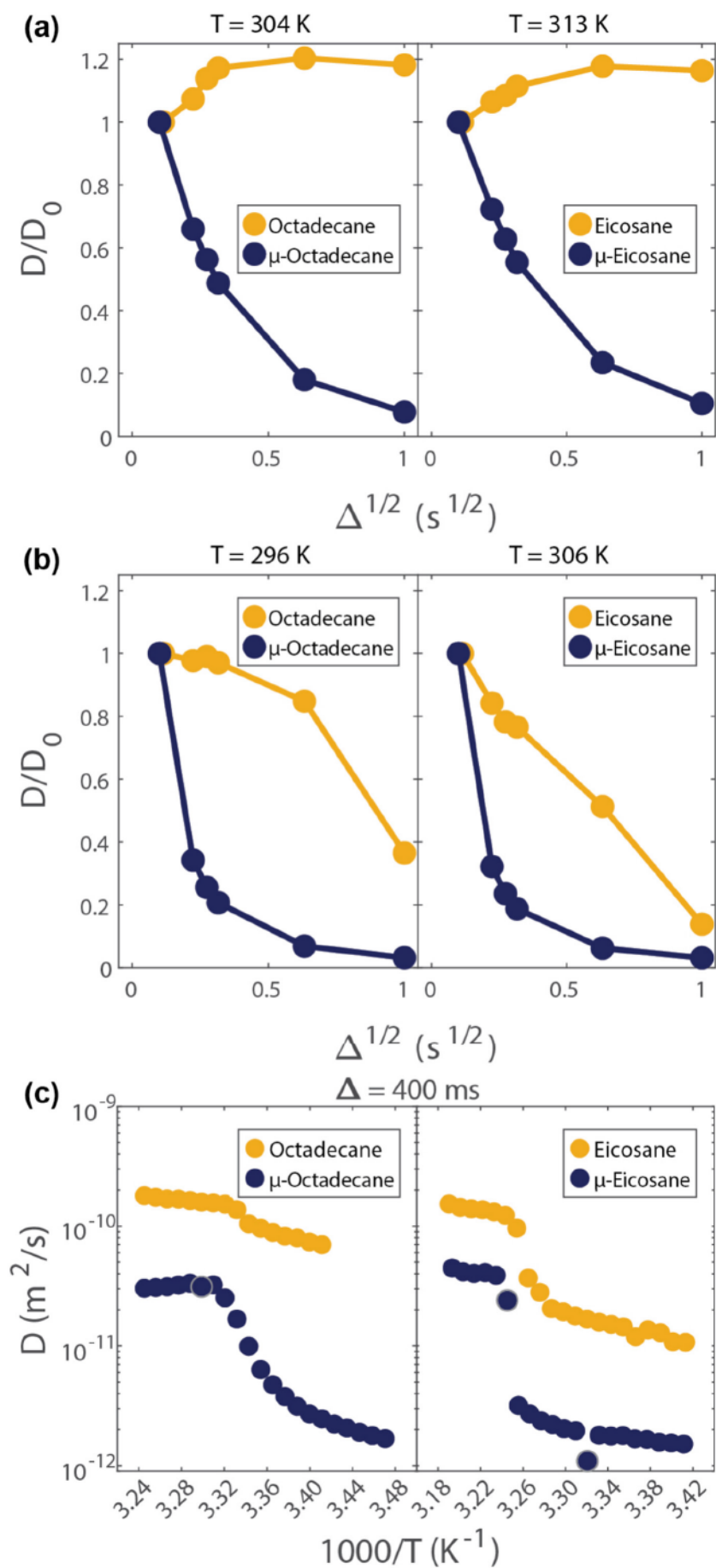


FIGURE 5 | Legend on next page.

FIGURE 5 | (a) Normalized NMR derived diffusion coefficients as a function of Δ for (left) unencapsulated and microencapsulated octadecane and (right) unencapsulated and microencapsulated eicosane at 2 K above each wax's unencapsulated melting point range. (b) Normalized NMR derived diffusion coefficients as a function of Δ for (left) unencapsulated and microencapsulated octadecane and (right) unencapsulated and microencapsulated eicosane at 3 K below the start of each wax's unencapsulated melting point range. (c) NMR derived diffusion coefficients at $\Delta = 400$ ms for (left) unencapsulated and microencapsulated octadecane and (right) unencapsulated and microencapsulated eicosane during melting. Scans circled in gray had a low signal voltage and should be interpreted cautiously.

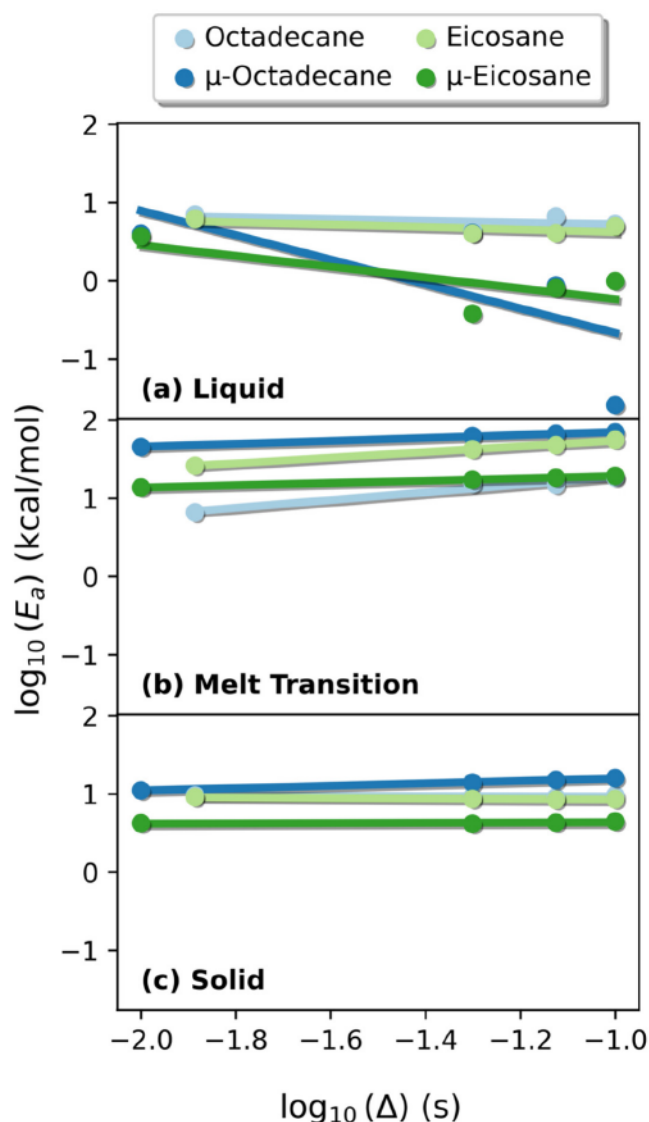


FIGURE 6 | Delta-dependent results of Arrhenius fits to diffusion data for the (a) liquid wax melt, (b) transitionary solid, and (c) solid wax regions of each sample. The slopes of these regions from Figure S2 gave $-E_a/R$.

the unencapsulated waxes show near constant E_a in agreement with other published values [47], while the decrease of E_a in the microencapsulated systems is an artifact of the restricted translational motion when molecules diffuse longer distances. In the melt transition (Figure 6b), E_a increases with spin diffusion over longer distances due to spatial variations in the ordered crystalline and disordered amorphous mesodomains. In the solid phase (Figure 6c), E_a is fairly constant with varying diffusion lengths, indicating fixed crystalline and amorphous domain

length scales. Increases in E_a near the melt transition reflect the complex molecular dynamics present, including collective translational motions which impart a time dependent dynamics [30]. Since E_a in classical theory is the energy barrier for kinetic energy to overcome intermolecular forces, the time dependence measured reflects the increased energy of multiple structural and orientational rearrangements in time Δ .

6 | Conclusion

NMR relaxometry and diffusometry on unencapsulated and microencapsulated C_{18} and C_{20} *n*-alkane waxes provide unique insight into molecular-scale transport processes and structure during melting. NMR T_2 and $T_1 - T_2$ relaxation measurements are sensitive to structural modifications in the solid waxes, revealing a major intermediate relaxation domain exclusive to the microencapsulated waxes. These relaxometry data demonstrate how microencapsulation alters the range of molecular mobilities compared to unencapsulated waxes, favoring intermediate mobilities. These intermediate mobilities are related to more amorphous domains in the microencapsulated wax, relative to the unencapsulated wax. Diffusion data from PGStE on the microencapsulated waxes estimate radius (S/V) in the liquid phase, informing hindered diffusion within particles. The diffusion data provide a new means to calculate activation energies from Arrhenius plots which depend on the diffusion displacement observation length scale. This novel result has potential to further characterize the impact of spatial variations of structural crystalline and amorphous domains on melting processes and latent heat.

Author Contributions

Matthew C. Young: conceptualization, methodology, investigation, writing – original draft and review and editing, visualization. **Madison L. Nelson:** conceptualization, methodology, writing – review and editing. **Matthew E. Skuntz:** conceptualization, methodology, writing – review and editing. **Sarah L. Codd:** conceptualization, resources, writing – review and editing. **Ryan Anderson:** conceptualization, resources, writing – review and editing. **Joseph D. Seymour:** conceptualization, methodology, investigation, resources, writing – original draft and review and editing, visualization, supervision.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data will be made available upon request.

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Supporting Information

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