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Molecular Structure and Melting: Implications for Phase Change Materials

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2 **Molecular Structure and Melting: Implications for Phase**

3 **Change Materials**

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Abstract

Phase change materials (PCM) offer a promising technology for thermal energy storage, load leveling, and peak shifting applications. A desirable PCM has a melting temperature within the temperature boundaries of its application, and a high change in enthalpy on melting. Knowledge of the relationships between these thermodynamic properties and molecular structure would advance informed selection of PCM candidates for a given application. In the present investigation, the relationship between structure (length of alkyl chains) and properties has been investigated for isomeric esters, showing that esters containing longer individual alkyl chains have higher melting temperatures, and higher enthalpy changes on melting. The melting entropy changes, however, are relatively independent of the alkyl chain distribution.

Keywords:

Thermodynamics

Energy storage

Phase change materials

1. Introduction

One of the barriers to a large-scale shift to renewable energy is the inherent intermittency of renewable energy sources, especially wind and solar, leading to an imbalance between the supply of renewable energy and the demand from the grid. As such, storage technologies are required to make renewable energy available at times when its source is not. Furthermore, energy demand needs to be reduced through energy conservation and increased energy efficiency. While considerable focus is placed on electrical energy, there are gains to be made in terms of thermal energy too, especially when the end use is heat. Solar thermal energy can be used to heat homes and water, but requires energy storage for use when solar flux is low. Approximately 50 % of domestic energy use goes toward heating and cooling of buildings.¹ As such, reduction of heating and cooling requirements, and increase in insulation efficiency, are attractive targets.

Sensible heat storage materials, using the heat capacity of the material, have been used for millennia.² These are materials with high heat capacity and, once heated, they radiate heat for an extended period. Examples include rocks heated in the sun or with fire, and water. Sensible materials also can be used for cooling, as they absorb relatively large inputs of energy for a given increase in temperature. For example, this is the premise of cold cellars constructed of rock or concrete.

More recently, phase change materials (PCM) have been used for thermal energy storage.^{2,3,4} PCMs store energy via the enthalpy change of a phase transition, typically melting, although solid-solid transitions are also possible.⁵ Over moderate temperature ranges, PCMs can store much more energy per unit mass or volume than a sensible heat storage material. PCMs are used in heat storage applications such as solar thermal hot water⁶ and peak shifting. In the latter case, the PCM is heated/charged using off-peak power, and the heat is recovered later. Similarly,

ice-based PCMs can be solidified using off-peak power and then used later for cooling, in place of conventional air conditioning, throughout the day.² Another important application of PCMs is in moderating temperature swings in a building,⁷ thereby reducing heating and air conditioning requirements. PCMs can be placed within walls, floors, or ceilings⁸ to absorb energy during the warmest parts of the day, before releasing it at night when the temperature has dropped. By doing so, extreme temperature swings can be vastly reduced.⁹

Many materials have been studied for use as PCMs, including salt hydrates, paraffins, fatty acids, and esters.^{10,11,12} A number of materials properties are of concern in the selection of an appropriate PCM for a given application. These requirements include appropriate melting temperature, high enthalpy change of fusion, high heat capacity, high thermal conductivity, controllable hysteresis, low cost, high stability, and low toxicity.² Of these, melting temperature and enthalpy change of fusion are most important. The melting temperature of the PCM must fall within the temperature range of the application: if it does not, the PCM will not change phase, and will act solely as a sensible heat storage material. The enthalpy change of fusion (latent heat) of the material should be as high as possible in order to maximize the energy storage density.

An understanding of the connection between chemical structure and thermodynamic properties would allow for informed selection of potential PCMs. By determining which structural features contribute to high enthalpy change on melting, it would be possible to define which classes of materials hold the most promise for latent heat storage applications. Furthermore, knowledge of the link between molecular features and melting temperatures would allow PCMs within a class of materials to be tailored for specific applications at a variety of temperatures. The main question addressed here is: how does molecular structure influence thermodynamic properties associated with melting? Although the overarching question is

general, in this work we examine a specific example: the impact of carbon atom distribution in linear, saturated esters. For a linear, saturated ester containing 12 carbon atoms, it is possible to form 11 different esters, depending on how the carbon atoms are distributed between the alkyl chains on either side of the bridging oxygen atom. All have the same molecular mass, but their thermodynamic properties differ. Here, the influence of structure on melting temperature, enthalpy change, and entropy change are determined by examining three such esters: ethyl decanoate, butyl octanoate, and hexyl hexanoate. The 12-carbon fatty acid, dodecanoic acid, can be considered as a related case, in which all 12 carbon atoms are part of a single alkyl chain. It is a structural isomer of these esters, and is also included in this analysis.

2. The Thermodynamics of Melting

The melting temperature (T_{fus}) and the enthalpy change on fusion ($\Delta_{fus}H$) are intimately linked to the entropy change on fusion ($\Delta_{fus}S$) by the equality of the Gibbs energy of the solid and liquid phases, whereby at the melting point equilibrium,

$$T_{fus} = \frac{\Delta_{fus}H}{\Delta_{fus}S} \quad (1)$$

Immediately it can be seen that when two materials with equal entropy changes on melting are compared, the more stable solid, *i.e.* the one with the higher $\Delta_{fus}H$, will have a higher melting point.¹³ Conversely, for two materials of equal $\Delta_{fus}H$ and the same absolute entropy of the melt, the lower entropy solid, *i.e.* the material with higher $\Delta_{fus}S$, would melt at a lower temperature. Furthermore, for a given melting point, the enthalpy and entropy changes will be directly proportional, and so high $\Delta_{fus}S$ leads to high $\Delta_{fus}H$. Therefore, by understanding how structure relates to the thermodynamic properties of a material as it melts, it could be possible to predict

which materials are the best candidates for use as PCMs. Note that the focus here is on molecular materials, as they are one of the common families of PCMs.

The investigation of the relationship between molecular structure and melting has a long history. In 1882, after reviewing information for 15000 compounds, Carnelley,^{14,15} showed that symmetrical molecules with compact and efficient crystal packing tend to have higher melting points. A similar conclusion was reached more recently by Boese *et al.*¹⁶ who showed that the melting point of the symmetrical 1,4-dichlorobenzene (326 K) is significantly higher than the asymmetrical 1,2- and 1,3-isomers (256 K and 246 K, respectively). It is the efficient packing of symmetrical molecules that leads to a more stable solid, and therefore a high melting point.

Another general finding is that melting temperature increases with molar mass so long as the increase in mass does not significantly change the symmetry or packing. This trend can be observed in the even-numbered alkanes. The melting points of the alkanes increase with the addition of methylene units to the chain, forming two nearly linear trends, one for even number of carbons in the chains and one for odd, reflecting the two types of packing.^{17,18} However, branched alkanes have significantly lower melting points than their corresponding structurally isomeric linear alkanes.

Gilson¹⁹ compiled entropy changes of fusion for the 358 compounds with listed enthalpy changes of fusion available at that time in the *CRC Handbook of Chemistry and Physics*,²⁰ and found three groupings of materials. The recent compilation by Acree and Chickos^{21,22} of thermodynamic properties for over 7000 organic and organometallic compounds allowed us the opportunity to extend Gilson's study to include >5000 organic compounds, and again we distinguished three groupings (Figure 1).

The small grouping at the low end, $\Delta_{fus}S \sim 5$ to $25 \text{ J mol}^{-1} \text{ K}^{-1}$, typically includes compounds that are disordered crystals of rigid molecules. The disorder already present in the crystalline phase makes the additional entropy gain upon melting relatively small. An example in this category is cubane (C_8H_8) for which $\Delta_{fus}S$ is $22 \text{ J mol}^{-1} \text{ K}^{-1}$.²³ In the crystalline phase of cubane, just below the melting point, the cubane molecules rotate rapidly on their lattice sites, and the entropy of fusion is low because the rotational degrees of freedom are already active in the solid.

Figure 1 also shows a second, and large, grouping of compounds with $\Delta_{fus}S$ centered at about $58 \text{ J mol}^{-1} \text{ K}^{-1}$. These compounds form ordered crystals of rigid molecules. Regardless of composition, materials in ordered crystals all tend to have the same entropy change on transforming from solid to liquid. This generalization was noted more than a century ago, and is known as Walden's rule.²⁴ (It is analogous to Trouton's rule,²⁵ in which the entropy change on evaporation is almost the same for most materials, due to the very similar increase in disorder on going from the liquid to the vapour.)

Finally, 1780 of these 7038 compounds were identified with high entropy changes of fusion ($\Delta_{fus}S > 85 \text{ J mol}^{-1} \text{ K}^{-1}$). These are typically non-rigid molecules, including those with long alkyl chains. Upon melting, these materials gain considerable entropy as their non-rigid structures allow them to sample many configurations. From equation 1, it can be seen that these materials with high $\Delta_{fus}S$ could also have high $\Delta_{fus}H$, which would make them attractive candidates for PCMs. Many of these compounds, including alkanes and fatty acids, are already being used in heat storage applications.

Special mention should be made of the values of $\Delta_{fus}H$ and $\Delta_{fus}S$ for solids in which hydrogen-bonding plays an important role. In this case, typically the melting point is higher than

usual due to the stabilizing influence of the hydrogen-bonding on the crystalline structure, so even if $\Delta_{fus}S$ falls in the “normal” range, then $\Delta_{fus}H$ can be exceptionally high (see equation 1). Sugar alcohols are one such example, with exceptional promise as phase change materials, if their inherent hysteresis is not an impediment.²⁶

Saturated fatty acids are a promising family of PCMs.^{11,12,27} They have high melting enthalpy changes, which increase nearly linearly (with a significant odd/even effect¹⁸) with the length of the carbon chain.^{21,22} Their melting temperatures also increase with increasing chain length, although they plateau above a chain of about 20 methylene units.^{21,22} Fatty acids can be used in energy storage applications at a variety of temperatures by selecting a molecule of the appropriate length. Saturated fatty acids also cycle well^{11,12} and can be produced sustainably²⁸. They can be extracted from a variety of renewable sources including plants, such as oil palm, algae, and animal fats. Saturated fatty acids typically have very low embodied energy, and that, coupled with their high energy storage density, means that their energy payback time can be very short when used in devices to store renewable energy.²⁸

While pure materials often have excellent thermodynamic properties for use in heat storage applications, mixtures also can be extremely useful, especially to allow applications in temperature ranges where there is no suitable pure material. In a simple ideal eutectic system, addition of one material to another leads to depression of the melting point. The minimum melting temperature is found at the eutectic composition. In thermal storage applications, eutectics can be used to access melting temperatures lower than for pure materials. Using saturated fatty acids as an example, if one wished to store energy at 22 °C for a temperature moderating application say in residential buildings, the closest melting temperatures one could achieve using pure materials are 16.5 °C with octanoic acid, or 28.4 °C with undecanoic acid,

neither very useful. However, the eutectic mixture of undecanoic acid (~ 81.5 mol%) and tetradecanoic acid has a very useful melting temperature of $21.7\text{ }^{\circ}\text{C}$.²⁹ Without the use of eutectics, compromises such as more expensive materials, or materials with lower energy storage density might be required. Furthermore, some fatty acid eutectic mixtures are found in nature.³⁰ Such a mixture can be directly extracted and used in its natural proportions, avoiding energy-intensive separation processes which would then be followed by re-mixing.

The entropy change for melting eutectic mixtures is greater than for a mixture of the pure compounds, raised by the mixing entropy. For the eutectic mixture of decanoic acid (82 mol%) and tetradecanoic acid, the measured $\Delta_{fus}S$ is $96\text{ J mol}^{-1}\text{ K}^{-1}$,³¹ *i.e.*, at the high end in Figure 1. However, if $\Delta_{fus}S$ were to be calculated based on the linear proportionality of the amounts of the pure components and their entropy changes on fusion,³¹ excluding mixing, the expected entropy change would be only $87\text{ J mol}^{-1}\text{ K}^{-1}$. The $\Delta_{fus}H$ of the same eutectic, however, is 28.2 kJ mol^{-1} ,³¹ which is very close to the value (28.4 kJ mol^{-1}) calculated from the molar percentages of each compound (*i.e.*, rule of mixtures). In this case, $\Delta_{fus}S$ is higher for the mixture but $\Delta_{fus}H$ is in proportion to the composition, and therefore (Equation 1), T_{fus} is depressed, as observed. The rule of mixtures does not always predict $\Delta_{fus}H$ accurately for eutectics, especially if there are strong interactions between the components of the eutectic in the liquid phase. For example, the succinonitrile-phenanthrene eutectic system shows³² $\Delta_{fus}H$ much larger than would be expected based on the rule of mixtures, likely due to non-ideal behaviour as exemplified by liquid-liquid phase separation.

Inagaki and Ishida³³ have examined the four six-carbon sugar alcohols: galactitol, mannitol, sorbitol and iditol, both computationally and experimentally, for potential use as PCMs. All four alcohols have the same chemical formulae, and identical, linear carbon

backbones. They differ only in stereochemistry, with the hydroxyl groups on the four chiral centers arranged differently. Galactitol and mannitol were found to have high values of $\Delta_{fus}H$ (60 kJ mol⁻¹, 52 kJ mol⁻¹) and T_{fus} (460 K, 439 K), while sorbitol and iditol were found to have lower values (34 kJ mol⁻¹, 372 K, 31 kJ mol⁻¹, 353 K).³³ The authors ascribe the differences to the distribution of the hydroxyl groups. Sorbitol and iditol have adjacent hydroxyl groups which have large electrostatic repulsions that destabilize the crystalline phase. The decreased stability (increase in enthalpy) of the solid phase produces a smaller change in enthalpy upon melting. Based on additional data for sugar alcohols with carbon backbones of 4 to 8 carbons, three suggestions have been made for selection of sugar alcohols for thermal energy storage applications:³³ longer backbones provide higher $\Delta_{fus}H$; the hydroxyl groups should be well separated in their distribution; and backbones with even numbers of carbons provide higher values of T_{fus} and thereby higher $\Delta_{fus}H$.

Stamatiou *et al.*³⁴ examined linear fatty esters for use as PCMs. They showed that both T_{fus} and $\Delta_{fus}H$ had strong positive correlations with the molar mass of the ester. In the present work, three linear, 12-carbon esters, and also dodecanoic acid have been examined. These compounds are isomers with linear alkyl chains totalling 12 carbons, differing in their distribution of their 12 carbon atoms between the alkyl chains. The influence of this distribution on T_{fus} , $\Delta_{fus}H$, and $\Delta_{fus}S$ was determined, and provides deeper insight concerning how molecular structure can be used to predict PCM properties, and aid in PCM selection.

3. Materials and Methods

Experimental values of T_{fus} and $\Delta_{fus}H$ were determined using a TA Instruments Q200 differential scanning calorimeter (DSC). The DSC was calibrated for T_{fus} and $\Delta_{fus}H$ at 2 and 10 K min⁻¹ scan rates with both mercury and indium standards³⁵ before the measurements were taken.

Samples of dodecanoic acid (Aldrich, 98%), ethyl decanoate (Sigma-Aldrich, > 98%), butyl octanoate (Aldrich), and hexyl hexanoate (Sigma-Aldrich, >97%) were each analysed three times successively with 2 and then 10 K min⁻¹ scan rates. Measurements were made in crimped aluminum pans, under a flow of helium at a rate of 25 mL min⁻¹. The sample masses were between 8.5 and 10 mg. The values of T_{fus} were determined from onset temperatures from the 2 K min⁻¹ scans. A slow heating rate was used for melting point determination to minimize ‘thermal lag’ in the sample.³⁶ Melting temperatures determined by this method typically have uncertainties within 1 K. The values of $\Delta_{fus}H$ were determined from the 10 K min⁻¹ scans. A faster heating rate was used for $\Delta_{fus}H$ measurement because it results in sharper peaks, reducing the contribution of $\Delta_{fus}H$ swept into the baseline. A well-calibrated DSC with excellent thermal contact between the sample and pan (as is the case for samples melted into the pan) can give transition enthalpy change values with as little as ~5 % uncertainty.

4. Results and Discussion

The four compounds analysed all have the molecular formula C₁₂H₂₄O₂, and the chemical structure R₁-O-C(O)-R₂. They differ only in their distribution of methylene units between R₁ and R₂. At one extreme is dodecanoic acid, in which R₁ is a proton and all carbon atoms belong to R₂. The other extreme is hexyl hexadecanoate, in which the carbon backbones are distributed evenly on either side of the bridging oxygen.

4.1 Melting Temperature

DSC was used to determine T_{fus} , using a 2 K min⁻¹ scan rate (Figure 2). The results are summarized in Table 1. (No solid-solid phase transitions were found in the temperature ranges examined.) Over three melting cycles, there was no observable change in the melting

temperature. In all cases the standard deviation in T_{fus} was less than 0.1 K. The melting points of these compounds increased with increasing length of R_2 , from 217 K (hexyl hexanoate) to 316 K (dodecanoic acid). Despite the fact that these molecules are isomers and that all their alkyl chains are linear, it is the longest uninterrupted alkyl chains that produced the highest melting points, likely due to their stability due to maximized van der Waals interactions between the chains. Stamatiou and coworkers³⁴ examined the melting points of eight linear fatty ester PCMs, including two structural isomers: ethyl tetradecanoate and butyl dodecanoate. Again, in this case, the ester with the longer uninterrupted alkyl chain, ethyl tetradecanoate, was found to have the highest melting temperature.³⁴ From the melting points for 53 linear, saturated esters as compiled by Acree and Chickos,^{21,22} it can be seen that this is, in fact, a general phenomenon. As shown in Figure 3, the plot of T_{fus} vs. number of carbons has a trend of increasing melting temperature with increasing number of carbons. This is expected given that the molar masses of the esters increase with increasing carbon number, and the number of favourable chain-chain interactions in the solid phase increases as well, thereby increasing the stability of the solid phase and increasing the melting point. At each number of carbon atoms (x-axis in Figure 3), however, there is a spread of values for T_{fus} . These different values correspond to different structural isomers of linear esters. As also found here, the highest melting temperatures correspond to the esters with the longest uninterrupted alkyl chains. For example, among the esters for which data are available for 32 carbons, ethyl triacontanoate (341.5 K) has a significantly higher T_{fus} than either of tetradecyl octadecanoate (322.8 K) or octadecyl tetradecanoate (324.4 K). Similarly, at 26 carbons, methyl pentacosanoate (332.2 K) has a higher T_{fus} than hexadecyl decanoate (302.6 K).²²

From the present results, while the melting points of hexyl hexanoate and butyl octanoate are separated by only 13 K, and those of butyl octanoate and ethyl decanoate by 22 K, there is a much larger jump of 64 K between ethyl decanoate and dodecanoic acid. This difference could be due, in part, to the fact that dodecanoic acid forms dimers, hydrogen-bonded through the carboxyl head groups of the molecules.³⁷ The dimers are found in the crystalline phase, and persist into the liquid phase.³⁷ As such, when dodecanoic acid melts, the dimer is similar to a 24-carbon molecule (*i.e.*, to tetracosanoic acid), rather than a single 12-carbon molecule, and therefore melts at a rather high temperature. However, the 24 carbon atoms of the dodecanoic acid dimer are distributed between two alkyl chains, and thus dodecanoic acid still has a lower melting point and enthalpy of fusion (Table 1) than tetracosanoic acid (356.5 K, 229.22 J g⁻¹).²²

On crystallization, all the three esters investigated here exhibited moderate supercooling. The amount of supercooling ranged from 9 to 10 K, 12 to 13 K, and 8 to 10 K for ethyl decanoate, butyl octanoate, and hexyl hexanoate, respectively. This, in itself, is an important consideration if fatty esters are to be used as PCMs, as the application must have a minimum temperature sufficiently low to nucleate the crystalline phase. Without crystallization, the latent heat which was input in melting cannot be recovered. However, to their benefit, crystallization in these esters occurs at relatively consistent temperatures over several cycles (standard deviation ~ 1 K). This predictable behaviour would be beneficial should they be employed in a PCM capacity.

4.2. Melting Enthalpy Change

Using a 10 K min⁻¹ scan rate, the enthalpies of fusion also were determined using DSC, with high reproducibility (standard deviation <1 J g⁻¹). The $\Delta_{fus}H$ values for the three esters and the fatty acid follow the same trend as T_{fus} , decreasing with decreasing maximum individual

alkyl chain length. This finding would seem to indicate that more energy is required to separate single long chains than to separate multiple shorter chains with the same additive length, and that the rankings of $\Delta_{fus}H$ and T_{fus} among linear isomers of esters are the same.

The picture becomes slightly less clear when considering the data compiled by Acree and Chickos^{21,22} for 53 linear esters, as presented in Figure 4. The molar melting enthalpy change increases more or less linearly with the overall number of carbon atoms in the ester. This is logical given that each addition of a methylene unit increases the number of chain-to-chain intermolecular interactions which must be separated on melting, each requiring an input of energy. Again, the spread in values at a given number of carbon atoms is due to the different enthalpy changes on fusion for the different isomers. While in many cases the highest enthalpy change on fusion for esters of a given length belongs to the ester with the longest uninterrupted alkyl chain (methyl pentacosanoate, methyl heneicosanoate, methyl tetradecanoate, *etc.*), this is not always the case. And, in several cases, within esters of a given length, the ordering of the enthalpy values does not match the ordering of the longest individual alkyl chains or melting temperature. Ethyl triacontanoate is the 32-carbon ester with the longest individual alkyl chain for which data are available. It had the highest melting temperature of the 32-carbon esters, but the lowest $\Delta_{fus}H$ value. Instead, for 32 carbons, it is the ester with the shortest maximum individual alkyl chain and the lowest melting point – tetradecyl octadecanoate – that has the highest $\Delta_{fus}H$. Among the 26-carbon esters, the highest melting isomer and isomer with the longest single alkyl chain, methyl pentacosanoate, also has the highest $\Delta_{fus}H$. However, hexadecyl decanoate, the lowest melting isomer, does not have the lowest $\Delta_{fus}H$. Instead, the lowest $\Delta_{fus}H$ belongs to ethyl tetracosanoate. Ethyl tetracosanoate had the second highest melting

point, and the second longest individual alkyl chain, and so would have been expected to have had the second highest $\Delta_{fus}H$.

Note that the data from Acree and Chickos^{21,22} are thoroughly tabulated but not assessed for accuracy. As we have indicated elsewhere,² for some PCMs, widely varying values of physical properties have been reported, and some of the reports are not accurate. For example, Acree and Chickos²² present 16 values of $\Delta_{fus}H$ for dodecanoic acid, ranging from 25.4 kJ mol⁻¹ to 44.9 kJ mol⁻¹. (We take some comfort that the present value, 36 ± 1 kJ mol⁻¹, agrees well with our own previously published values of 37 ± 2 kJ mol⁻¹ and 35 ± 3 kJ mol⁻¹.^{11,12}) In principle, different polymorphs can have different melting properties so that could account for some of the spread of reported properties, but for dodecanoic acid, which has three polymorphs, the other two, A and B, convert to the C-form and only the C-form melts.³⁸ Especially when only a single data source is given, only general trends should be concluded from the Acree and Chickos^{21,22} data, and specific details would require further experimental investigation.

4.3. Melting Entropy Change

The entropies of fusion of the examined isomers (Table 1) are all high in the context of values presented in Figure 1. Hexyl hexanoate has the lowest value of $\Delta_{fus}S$ (and T_{fus} and $\Delta_{fus}H$). The entropy changes for the other three compounds show a slightly different order from the T_{fus} and $\Delta_{fus}H$ order, with the highest $\Delta_{fus}S$ belonging to butyl octanoate, and dodecanoic acid and ethyl decanoate having equal values of $\Delta_{fus}S$. When also considering the 53 esters from Acree and Chickos (Figure 5),^{21,22} the general trends in $\Delta_{fus}S$ mirror that of $\Delta_{fus}H$: there is a strong linear correlation between $\Delta_{fus}S$ and the number of carbons, and in most cases, among esters of equal carbon number, the one with the longest unbroken alkyl chain has the highest $\Delta_{fus}S$. The

exceptions to this rule are largely the same compounds which deviated from the general trend for $\Delta_{fus}H$.

Considering equation 1, for a constant T_{fus} , a high value of $\Delta_{fus}S$ should give a high $\Delta_{fus}H$, and so it is logical for $\Delta_{fus}S$ and $\Delta_{fus}H$ to correlate well. A plot of $\Delta_{fus}S$ as a function of $\Delta_{fus}H$ for the esters studied here, and the 53 esters from Acree and Chickos,^{21,22} results in a linear relationship with $R^2=0.991$ (Figure 6). Long alkyl chains provide the opportunity for many chain-chain interactions, stabilizing the solid phase (high $\Delta_{fus}H$), but also increase the entropy gain upon melting as they gain many degrees of freedom in the liquid phase.

4.4. PCM Selection

As described earlier, if T_{fus} is unchanged, high $\Delta_{fus}S$ leads to high $\Delta_{fus}H$. Therefore, when selecting a material for use as a PCM for thermal energy storage, increasing the linear alkyl chain length of the material can lead to higher energy storage density. (Although the theoretically more meaningful quantities are the molar enthalpy or entropy changes, in practical terms the gravimetric enthalpy change is more meaningful. This is why comparisons of isomers is particularly instructive.) While molar mass generally has a direct correlation with melting temperature, the distribution of the atoms is important. Within a series of materials with equal total linear alkyl chain length, materials with longer uninterrupted alkyl chains have higher T_{fus} , which means that if $\Delta_{fus}S$ is unchanged, then $\Delta_{fus}H$ will be higher, and the material will have a higher thermal energy storage density. From Figure 3, the 26-carbon hexadecyl decanoate melts at a ~20 K lower temperature, and has lower $\Delta_{fus}H$, than the shorter and lighter 24-carbon ethyl docosanoate. The presence of the 22-carbon chain in the lighter compound results in the high melting point relative to the heavier compound containing only 10 and 16 carbon alkyl chains, despite having nearly equal $\Delta_{fus}S$ (242 vs. 244 J mol⁻¹ K⁻¹).^{21,22}

5. Conclusions

The interplay between molecular structure and thermodynamic properties is a valuable tool for PCM selection, and prediction of PCM properties. Increased molar mass leads to higher melting temperature, which in turn give rise to higher enthalpy change on fusion. Compact, symmetrical structures stabilize the solid phase and also give higher enthalpy changes. Materials with long alkyl chains have a high entropy change upon melting, and thereby also have high enthalpies of fusion.

In this study, the effect of carbon atom distribution in linear molecules of formula $C_{12}H_{24}O_2$ on T_{fus} , $\Delta_{fus}H$, and $\Delta_{fus}S$ was determined. Dodecanoic acid and three esters (hexyl hexanoate, butyl octanoate, and ethyl decanoate) were analyzed by DSC. It was determined that the highest melting temperatures and enthalpies of fusion could be achieved in the molecules with the longest individual alkyl chains. As such, hexyl hexanoate had the lowest melting temperature and enthalpy change, followed by butyl octanoate, ethyl decanoate, and finally dodecanoic acid had the highest. Comparing with data compiled by Acree and Chickos^{21,22}, this seems to be a general trend amongst the unbranched, saturated fatty esters.

The compounds analyzed in this study follow many general trends for $\Delta_{fus}S$ exhibited by the ester data compiled from Acree and Chickos,^{21,22} with the highest values for $\Delta_{fus}S$ typically found for the isomers with the longest alkyl chains. The high entropy change gives rise to a high enthalpy change on melting.

When selecting a PCM from long-chain organic molecules, longer chains, *i.e.*, higher molar mass, will give higher melting points, and higher enthalpy changes and entropy changes on fusion. With regard to the main question asked here, namely “how does molecular structure influence thermodynamic properties?”, it was found that amongst isomeric ester PCMs, the

highest T_{fus} , $\Delta_{fus}H$, and $\Delta_{fus}S$ will be found for the ester with the longest individual alkyl chain. Furthermore, fatty acids have higher melting temperatures and higher enthalpy changes than a corresponding ester isomer. However, even the low-melting esters with evenly distributed carbon atoms, such as hexyl hexanoate, have appreciable values of $\Delta_{fus}H$ and could find use in refrigeration and cooling applications.

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Draft

Table 1. Thermodynamic properties of three esters and a fatty acid, each with chemical formula

$C_{12}H_{24}O_2$.*

Compound	T_{fus} / K	$\Delta_{fus}H / \text{kJ mol}^{-1}$	$\Delta_{fus}H / \text{J g}^{-1}$	$\Delta_{fus}S / \text{J mol}^{-1} \text{K}^{-1}$	$\Delta_{fus}S / \text{J g}^{-1} \text{K}^{-1}$
Hexyl Hexanoate	217 ± 1	22 ± 1	108 ± 5	100 ± 5	0.50 ± 0.03
Butyl Octanoate	230 ± 1	28 ± 1	140 ± 7	122 ± 6	0.61 ± 0.03
Ethyl Decanoate	252 ± 1	29 ± 1	143 ± 7	114 ± 6	0.57 ± 0.03
Dodecanoic Acid	316 ± 1	36 ± 2	180 ± 9	114 ± 6	0.57 ± 0.03

*Errors represent overall experimental uncertainties.

Figure 1. Entropies of fusion of 7038 organic compounds. Values from the data taken from Acree and Chickos.^{21,22}

Figure 2. DSC traces showing melting for three 12-carbon linear esters and dodecanoic acid, taken at 2 K min^{-1} . Endothermic peaks point down, and curves are displaced vertically for ease of viewing.

Figure 3. Melting temperatures for the linear, saturated esters as compiled by Acree and Chickos^{21,22} and the present data. Among the esters for which data are available, at each carbon number, the ester with the longest individual alkyl chain has the highest T_{fus} .

Figure 4. $\Delta_{fus}H$ for the linear, saturated esters as compiled by Acree and Chickos^{21,22} and present data.

Figure 5. $\Delta_{fus}S$ for the linear, saturated esters as calculated from Acree and Chickos^{21,22} and present data.

Figure 6. Relationship between $\Delta_{fus}S$ and $\Delta_{fus}H$ for the linear, saturated esters as compiled from Acree and Chickos^{21,22} and present data. The line is a linear fit to the data.

Figure 1. Entropies of fusion of 7038 organic compounds. Values from the data taken from Acree and Chickos.^{21,22}

712x593mm (96 x 96 DPI)

Figure 2. DSC traces showing melting for three 12-carbon linear esters and dodecanoic acid, taken at 2 K min⁻¹. Endothermic peaks point down, and curves are displaced vertically for ease of viewing.

177x176mm (300 x 300 DPI)

Figure 3. Melting temperatures for the linear, saturated esters as compiled by Acree and Chickos^{21,22} and the present data. Among the esters for which data are available, at each carbon number, the ester with the longest individual alkyl chain has the highest T_{fus} .

177x172mm (300 x 300 DPI)

Figure 4. $\Delta_{fus}H$ for the linear, saturated esters as compiled by Acree and Chickos^{21,22} and present data.

177x172mm (300 x 300 DPI)

Figure 5. $\Delta_{fus}S$ for the linear, saturated esters as calculated from Acree and Chickos^{21,22} and present data.

177x172mm (300 x 300 DPI)

Figure 6. Relationship between $\Delta_{fus}S$ and $\Delta_{fus}H$ for the linear, saturated esters as compiled from Acree and Chickos^{21,22} and present data. The line is a linear fit to the data.

178x173mm (300 x 300 DPI)