

On the Relation of Entropy and Enthalpy of Fusion in Triglycerides

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This contribution presents an extensive literature survey of the calorimetric properties, namely enthalpy and entropy of fusion, of alkyl-based molecules. Building on the well-known linear correlation of the named properties to the carbon number in *n*-alkanes, saturated fatty acids (FA), and saturated monoacid triglycerides (TAGs), the calorimetric properties of TAGs are reviewed. No straightforward correlation using a single ordering parameter, i.e., carbon number, can be derived for TAGs. This is not surprising due to the complexity of this particular class of molecules differing in alkyl-chain distribution over the glycerol backbone and chain saturation. A linear correlation of enthalpy and entropy of fusion is evident for molecule classes for which both properties correlate linearly with the carbon number, e.g., *n*-alkanes. Despite the complexity of TAGs, it is possible to establish a linear correlation between enthalpy and entropy of fusion even though no underlying single ordering parameter can be identified. A linear fit reveals discrepancies between saturated and unsaturated molecules but independence of polymorphic forms and chain length differences in mixed-acid TAGs. Moreover, the slopes of the linear fits for data on *n*-alkanes, saturated FA, and saturated mono-acid TAGs are found to be in the vicinity of the melting temperature of polyethylene.

by basic thermodynamic solid–liquid equilibrium calculations. To successfully model the behavior of the multicomponent TAG mixtures, the availability of enthalpy change upon melting and melting temperature data of constituting pure components is a necessary prerequisite. For this ambitious task, not only a large quantity of data is mandatory but also data of high quality.

The calorimetric properties of TAGs, namely enthalpy of fusion and melting temperature, can be experimentally determined, e.g., using differential scanning calorimetry (DSC). Since TAGs reveal monotropic polymorphism, these data are the result of equilibrium and quasiequilibrium determinations. The data quality depends on the sample purity and the experimental conditions, e.g., stabilization method and scan rate. To determine the crystallization behavior of complex systems is especially error-prone. This is also due to the fact that TAGs are not limited to occur in the three polymorphic forms (α , β' , β) most commonly

used for structure classification.^[2] So, assigning one specific polymorph in complex systems is more complicated if no additional crystal analysis is performed, e.g., via X-ray diffraction (XRD) measurements. Coupled DSC-XRD analysis and time-resolved XRD studies have proven to be helpful techniques in this field.^[3–7]


Contrary to the enthalpy of fusion and the melting temperature, the entropy of fusion can exclusively be determined indirectly by the ratio of the former. Consequently, its determination depends on the availability of high-quality enthalpy of fusion and melting temperature data. This study uses literature data from various sources. Besides the fact that data quantity is naturally limited, data quality is rather difficult to assess. This includes judgment on the reliability and consistency within a dataset of a class of molecules. In this context, a concise consistency test could substantially benefit the evaluation of different experimental datasets.

Mathematical modeling offers a valuable extension to reduce the number of experimental studies. Models predicting the thermodynamic properties of pure TAGs often approximate these properties by using the (total) carbon number as a significant attribute.^[8,9] This is based on well-known correlations for *n*-alkanes and related alkyl-series.^[10–12] However, the extension of this approach to TAGs is limited to the properties of saturated

1. Introduction

Reliable data are essential to understand how materials and compositions behave. Since practically all materials in food are mixtures, the characterization and the behavior of raw materials form the basis of product development. In fat-based products, understanding the solid–liquid phase behavior of triglycerides (triacylglycerols, short: TAGs) as major components of fats is of interest.^[1] The phase behavior is described and can be predicted

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mono-acid TAGs—TAGs which only consist of fatty acid (FA) moieties with identical carbon numbers—within one polymorphic form.

The approximation of the thermodynamic properties of TAGs, in general, is not as straightforward as suggested in the references mentioned above but instead complicated since the structural attributes of TAGs are more diverse. They differ in their FA composition, FA chain lengths, degree of saturation, the FA positions on the glycerol backbone, and the glycerol backbone configuration. To overcome the deficiency to cover the relevant composition space, Wesdorp^[9] introduced correction terms to the chain length-based models to account for mixed-acid TAGs and TAGs containing unsaturated FA. A different approach solely estimating the properties based on the chain-chain interactions was proposed by Zéberg-Mikkelsen et al.^[13] However, this model only describes the properties of mono-acid and mixed-acid saturated TAGs. Recently, a large number of experimental enthalpy of fusion and melting temperature data along with crystal structure data was utilized to generate a model predicting the properties of saturated and unsaturated TAG.^[14] This new model gives reliable estimates of the physical properties of TAGs based on three main contributions to the overall crystal energy, i.e., the lateral interaction between alkyl-chains, contributions from glycerol moieties, and the methyl end planes.

In the models of Wesdorp^[9] and Seilert and Floeter,^[14] the enthalpy of fusion was approximated as a function of different contributions from the geometric description of the TAG molecule and the resulting interactions. In both cases, the phase equilibrium condition

$$\Delta G = 0 = \Delta H_f - T_m \Delta S_f \quad (1)$$

is employed, where the Gibbs free energy (ΔG) becomes zero. The melting temperature (T_m) is derived by simple rearrangement to

$$T_m = \frac{\Delta H_f}{\Delta S_f} \quad (2)$$

This, however, necessitates formulating a model for the entropy of fusion, which conceptionally is already more difficult to design than the one for the enthalpy of fusion. For this purpose, Wesdorp^[9] used the same model structure for the entropy of fusion as for enthalpy of fusion. Alternatively, Wesdorp^[9] omitted Equation (2) and used a quadratic function for the computation of melting temperatures without any physical reference, derived solely by parameter optimization.

Besides the correlation between the calorimetric properties and the carbon number, a direct correlation between concurrent enthalpy and entropy changes was discussed in the literature. It is referred to as enthalpy-entropy compensation (EEC). According to the EEC, in case the change of the Gibbs free energy remains practically constant within a limited parameter space variation of a specific process, the change of enthalpy can be expressed as a linear function of the change of entropy and vice versa

$$\Delta H = x \Delta S + y \quad (3)$$

The slope x is of the same order of magnitude as the temperature, while the intercept y is of the same order of magni-

Table 1. Number of available enthalpy of fusion (ΔH_f) and melting temperature (T_m) data on TAGs; Number of entropy of fusion (ΔS_f) data determined by the ratio of ΔH_f and T_m .

Subset	ΔH_f			T_m			ΔS_f		
	α	β'	β	α	β'	β	α	β'	β
Saturated	59	36	56	109	108	115	48	30	52
mono-acid	8	4	8	15	14	13	8	3	8
mixed-acid	51	32	48	94	94	102	40	27	44
Unsaturated	21	18	28	73	44	68	19	9	24
Total	80	54	84	182	152	183	67	39	73

tude as the change of Gibbs free energy.^[15] Equation (3) is very similar to the state function for a thermodynamic process, Equation (1). However, Equation (1) applies to a specific equilibrium, whereas Equation (3) also applies for nonequilibrium states for which $d(\Delta G)/dP \rightarrow 0$ is valid. Here, P denotes the parameter of variation.

The relation is widely discussed in protein-related research addressing unfolding and ligand-binding in enzyme-driven processes and chemical reaction processes.^[15–18] In the area of phase equilibria, the literature on this subject is scarce. For example, in studies on the melting behavior of *n*-alkanol mixtures, a linear relation of the excess enthalpies and entropies was found and discussed in the context of EEC.^[19–21] A rather phenomenological interpretation for the EEC observed for *n*-alkane melting behavior is given in another study.^[22] So far, for TAGs, no relation of the enthalpy and entropy of fusion has been reported.

In this contribution, the systematics behind the calorimetric properties, enthalpy and entropy of fusion, of pure TAGs are investigated. Therefore, data of related homologous series of alkyl-based molecules are evaluated. The carbon number-based approximation of the enthalpy and entropy of fusion of *n*-alkanes is reviewed prior to considering more complex lipid systems, such as FA and TAGs. The relation of experimental calorimetric data with carbon number of the molecules within a homologues series are discussed next to a possible direct correlation of enthalpy and entropy of fusion within a class of molecules.

2. Data Analysis

2.1. Dataset

Experimental data on the enthalpy of fusion and the melting temperatures of several TAGs were gathered from a public-domain literature review.^[7,13,23–44] The review revealed a large number of melting temperatures and enthalpies of fusion of saturated TAGs. However, fewer data of unsaturated TAGs were available. Here, the term “unsaturated TAGs” indicates TAGs containing at least one FA moiety with a double bond. In total, experimental data for 282 TAGs were available. Data on TAGs containing odd chain lengths and single chain lengths greater than 20 were excluded. The resulting dataset comprised 262 TAGs. **Table 1** summarizes the number of available data points. Detailed data can be found in^[14] and.^[45] In any case, the entropy of fusion was calculated by dividing the enthalpy of fusion and the melting temperature.

Table 2. Experimental enthalpy of fusion (ΔH_f) and computed entropy of fusion (ΔS_f) data of selected fatty acids, retrieved from;^[47] notation: carbon number: number of double bonds, double bond in *trans*-configuration (t) or *cis*-configuration (c).

Fatty acids	Notation	ΔH_f [kJ mol ⁻¹]	ΔS_f [kJ mol K ⁻¹]
Myristic acid	14:0	45.29	0.14
Palmitic acid	16:0	54.56	0.16
Stearic acid	18:0	64.38	0.19
Arachidic acid	20:0	74.04	0.21
Palmitoleic acid	16:1t	32.00	0.12
Oleic acid	18:1c	42.99	0.15
Linoleic acid	18:2c	33.40	0.12
Linolenic acid	18:3c	32.02	0.12
<i>cis</i> -11,14-eicosadienoic acid	20:2c	31.81	0.12
<i>cis</i> -4,7,10,13,16,19-docosahexaenoic acid	22:6c	26.97	0.12

Experimental enthalpy of fusion and melting temperature data on 16 *n*-alkanes with even carbon numbers ranging from 6 to 36 were retrieved.^[46] Experimental data on said properties for FA were taken from^[47]—including four saturated FA and six unsaturated FA, from which four are polyunsaturated. **Table 2** summarizes the enthalpy and entropy of fusion data of FA. Data on *n*-alkanes are summarized in **Table 3**.

2.2. Data Review

In the prevailing approach to approximate the calorimetric properties of homologous series of alkyl-based molecules, the properties are correlated to the carbon number of the alkyl-chain.^[10] Accordingly, the enthalpy of fusion is calculated by a simple linear function of the carbon number, denoted as *C*,

$$\Delta H_f = aC + b \quad (4)$$

The entropy of fusion is described analogously to the enthalpy of fusion. The melting temperature is approximated by the ratio of enthalpy and entropy of fusion and, thus, a nonlinear equation

$$T_m = \frac{\Delta H_f}{\Delta S_f} = \frac{aC + b}{cC + d} \quad (5)$$

Table 3. Experimental enthalpy of fusion (ΔH_f) and computed entropy of fusion (ΔS_f) data of even *n*-alkanes, retrieved from.^[46]

<i>n</i> -alkane	Carbon number	ΔH_f [kJ mol ⁻¹]	ΔS_f [kJ mol K ⁻¹]	<i>n</i> -alkane	Carbon number	ΔH_f [kJ mol ⁻¹]	ΔS_f [kJ mol K ⁻¹]
Ethane	2	2.86	0.03	Octadecane	18	62.10	0.21
Butane	4	6.10	0.05	Eicosane	20	70.07	0.23
Hexane	6	13.10	0.07	Docosane	22	78.12	0.25
Octane	8	20.68	0.10	Tetracosane	24	86.19	0.27
Decane	10	28.74	0.12	Hexacosane	26	91.50	0.28
Dodecane	12	36.79	0.14	Octacosane	28	100.08	0.30
Tetradecane	14	45.03	0.16	Triacosane	30	106.34	0.31
Hexadecane	16	53.43	0.18	Dotriacontane	32	119.70	0.35

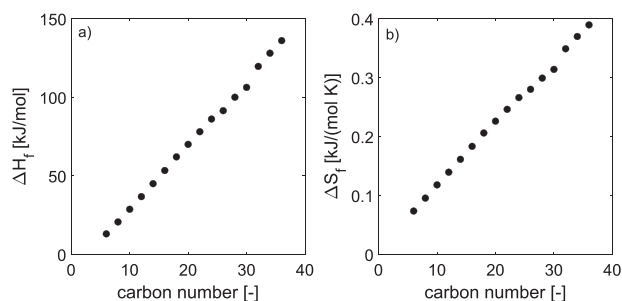


Figure 1. a) ΔH_f versus carbon number and b) ΔS_f versus carbon number for even *n*-alkanes.

In Equations (4) and (5) the parameters *a*, *b*, *c*, and *d* are fit parameters. Equation (5) was successfully employed to correlate the melting temperatures of *n*-alkanes^[48] and selected lipids.^[49] **Figure 1** shows the respective strictly linear relations between enthalpy and entropy of fusion and the carbon number observed for *n*-alkanes. The discontinuities for carbon numbers around 30 are believed to relate to the presence of different polymorphic forms.

In an extensive study by Costa et al.,^[12] several monosubstituted derivatives of *n*-alkanes were examined with respect to the chain length dependence of the thermodynamic properties. A similar trend of increasing calorimetric properties with chain length was reported for *n*-alkenes, *n*-alkyls, *n*-alkanols, among others.

For TAGs, the same approach is used to approximate the calorimetric data in well-known models. In these models, the total carbon number is used as the main attribute to approximate the enthalpy and entropy of fusion of saturated mono-acid TAGs per polymorphic form.^[8,9] The total carbon number describes the sum of the carbon numbers of the three FA esterified to the glycerol backbone. **Figure 2** displays the calorimetric properties as functions of carbon number for saturated FAs and saturated mono-acid TAGs in each of the three main polymorphic forms— α , β' , and β . The homologous series of saturated FA and mono-acid saturated TAGs, essentially being also monosubstituted derivatives of *n*-alkanes, also show a linear dependence of enthalpy and entropy of fusion on carbon number. For mono-acid TAGs, the figure illustrates that this linear dependence is different for each polymorphic form. It is further known that correlations of the melting temperatures over carbon number for *n*-alkanes^[48] and selected lipids^[49] reveal an asymptotic increase of the melting temperature with chain length.

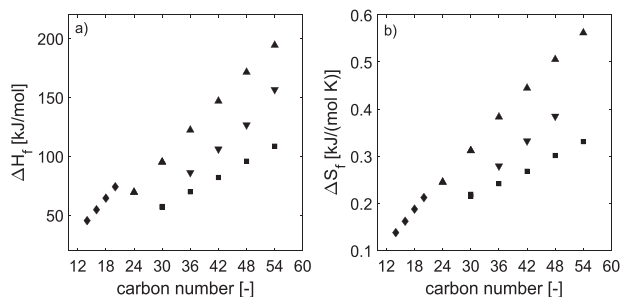


Figure 2. a) ΔH_f versus carbon number and b) ΔS_f versus carbon number for saturated FAs (diamonds). Saturated mono-acid TAGs in α -polymorph (squares), β' -polymorph (downward-pointing triangle), and β -polymorph (upward-pointing triangle).

From a mathematical point of view, enthalpy and entropy of fusion can, in line with previous research,^[8,9,48] each be expressed as simple linear functions of the carbon number for these series. Building on this, a linear correlation of these two properties can be derived for the respective simple systems. Therefore, the expression for the entropy of fusion in Equation (5) is rearranged and substituted into Equation (4), yielding

$$\Delta H_f = \frac{a}{c} \Delta S_f + \left(b - \frac{ad}{c} \right) \quad (6)$$

Figure 3 displays enthalpy over entropy of fusion for n -alkanes, saturated FAs, and saturated mono-acid TAGs. A linear correlation between the properties in these homologous series can be observed. Performing a linear fit reveals that the slopes of 392.5, 386, and 390.8 K for n -alkanes, saturated FA, and saturated mono-acid TAGs are very similar. For these systems, the temperature limit is in the range of the melting temperature of polyethylene, i.e., 390–410 K, representing an infinite long alkyl-chain. Surprisingly, the slopes obtained for these homologous series are close to the melting temperature range of polyethylene.

It has to be emphasized here that for the TAGs, the linear fit was performed irrespective of the three different polymorphic forms (α , β' , and β). This implies that even though the param-

eters (a, b, c, d) in Equations (4) and (5) are polymorph-specific, their ratios, e.g., $a(\alpha)/c(\alpha)$ and $a(\beta)/c(\beta)$, appear actually constant. The identification of a single correlation between enthalpy and entropy of fusion for saturated mono-acid TAGs valid for all polymorphic forms is hence unexpected. It must also be mentioned that the data of all three datasets displayed in Figure 3 cover substantial temperature ranges so that the analysis performed here does not fall into the context of the EEC. To illustrate this, the melting temperatures of mono-acid saturated TAGs span from 219.15 to 346.25 K (tricaprylin (8:8:8) in α -polymorph, tristearin (18:18:18) in β -polymorph). Furthermore, it has to be acknowledged that both Equations (3) and (1) are certainly satisfied for the data sets shown here. However, it appears counter-intuitive that the relation of enthalpy and entropy of fusion covers different polymorphs within the homologous series of saturated mono-acid TAGs.

Considering FA and TAGs, the structural and chemical attributes are far more diverse than for the homologous series displayed in Figures 1–3. The FA constituting the TAGs in natural fats and oils differ in chain length and their degree of saturation. Simply combining FA in TAG-triplets leads to a substantial number of different TAGs. This complex dataset can be structured into subcategories of different TAG-“derivates” taking into account the constituting FA, their chain length differences, and their position on the glycerol backbone. Following the findings for n -alkane derivatives,^[12] the calorimetric data on FA are first reviewed. **Figure 4a,b** shows the enthalpy and entropy of fusion as a function of carbon number for the relevant FA listed in Table 2. The calorimetric properties as a function of the carbon number for TAGs are given in Figure 4c,d.

Unlike for the homologous series of n -alkanes, saturated FA, and saturated mono-acid TAGs shown in Figures 1 and 2, no linear dependence of the caloric properties on the carbon number can be derived for unsaturated FA. Even less so do these unsaturated FA data adhere to the correlation found for the saturated FA. Furthermore, for mixed-acid saturated TAGs and unsaturated TAGs, no such straightforward correlation as given in Equation (4) can be derived either. This is expected considering the variability of TAGs with the same carbon number. The saturation of FA-moieties and distribution of the (total) number of carbons over the three FA-moieties of TAGs are known to have a major influence on their properties. These variations

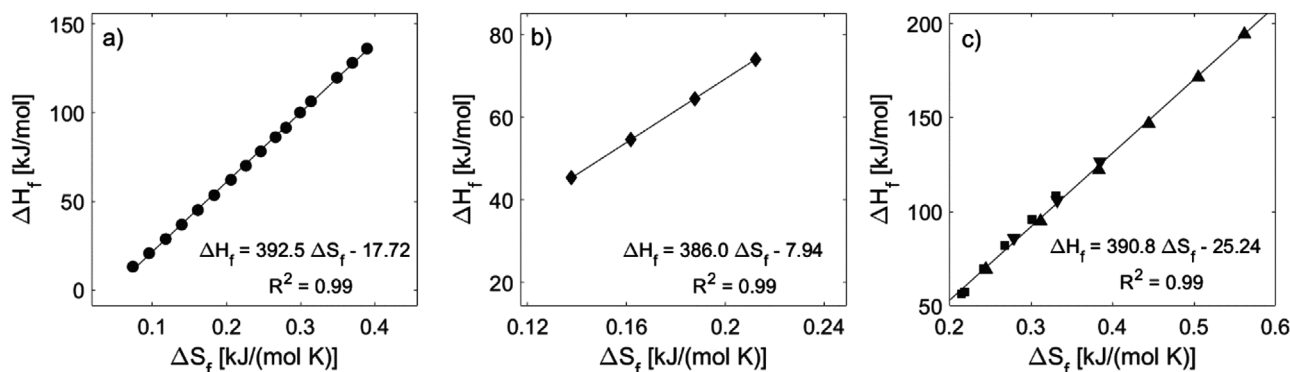


Figure 3. ΔH_f versus ΔS_f for a) n -alkanes, b) saturated FAs, c) saturated mono-acid TAGs in α -polymorph (squares), β' -polymorph (downward-pointing triangle), and β -polymorph (upward-pointing triangle); linear fit parameters and coefficient of determination as indicated.

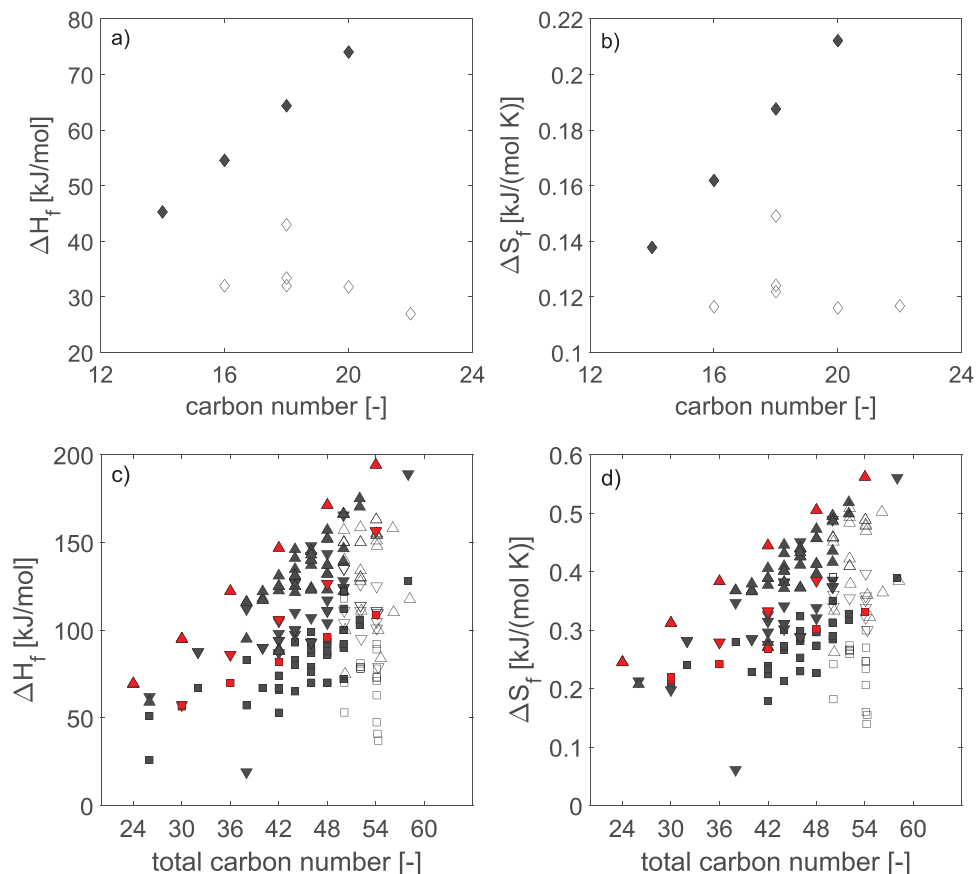


Figure 4. a) ΔH_f versus carbon number and b) ΔS_f versus carbon number of FA; saturated FA (filled diamonds), unsaturated FA (empty diamonds); c) ΔH_f versus carbon number and d) ΔS_f versus carbon number of TAGs in α -polymorph (squares), β' -polymorph (downward-pointing triangle), and β -polymorph (upward-pointing triangle); saturated TAGs (filled markers), unsaturated TAGs (at least one double bond in one FA) (empty markers), saturated mono-acid TAGs (red markers).

Table 4. Selection of enthalpy of fusion (ΔH_f) and melting temperature (T_m) data on pairs of TAGs with the same carbon number.

TAG	Notation	Carbon number	α		β'		β		Ref.
			ΔH_f [kJ mol ⁻¹]	T_m [°C]	ΔH_f [kJ mol ⁻¹]	T_m [°C]	ΔH_f [kJ mol ⁻¹]	T_m [°C]	
PPP	16:0.16:0.16:0	48	95.8	44.7	126.5	55.7	171.3	65.9	[9]
LSS	12:0.18:0.18:0	48	70.0	36.0	104.0	51.4	123.0	—	[9]
SSS	18:0.18:0.18:0	54	108.5	54.7	156.5	—	194.2	72.5	[9]
SOS	18:0.18:1.18:0	54	47.4	23.5	104.8	36.5	151.0	43.0	[31]

are illustrated in **Table 4**, in which the reported enthalpies of fusion and melting temperatures for selected pairs of TAGs are listed.

Comparing two TAGs with the same carbon number of 48, LSS (12:0.18:0.18:0) and PPP (16:0.16:0.16:0), the values for LSS are lower than those for PPP. The same observation is made for SOS (18:0.18:1.18:0) and SSS (18:0.18:0.18:0), both TAGs with carbon number 54. The reduction in enthalpy of fusion and melting temperature, i.e., reduced crystal energy, can be attributed to chain length mismatches in saturated mixed-acid TAGs (LSS of six vs PPP of zero) and double bonds in unsaturated TAGs, among other properties.

In summary, the analysis of the calorimetric data for TAGs reveals that these can certainly not be considered a homologous series. It is not surprising that variation within a group of molecules, such as TAGs, cannot be captured in a single ordering parameter, e.g., (total) carbon number. Instead, any parametrization must account for different cumulative carbon numbers, distribution of the carbon atoms over the FA, degree of saturation, and the distribution of the FA over the glycerol backbone. Additionally, any comprehensive description of the solid-liquid equilibrium of pure TAGs is hampered by the fact that the molecular arrangement in the crystal structure allows for numerous configurations based on variables such as polymor-

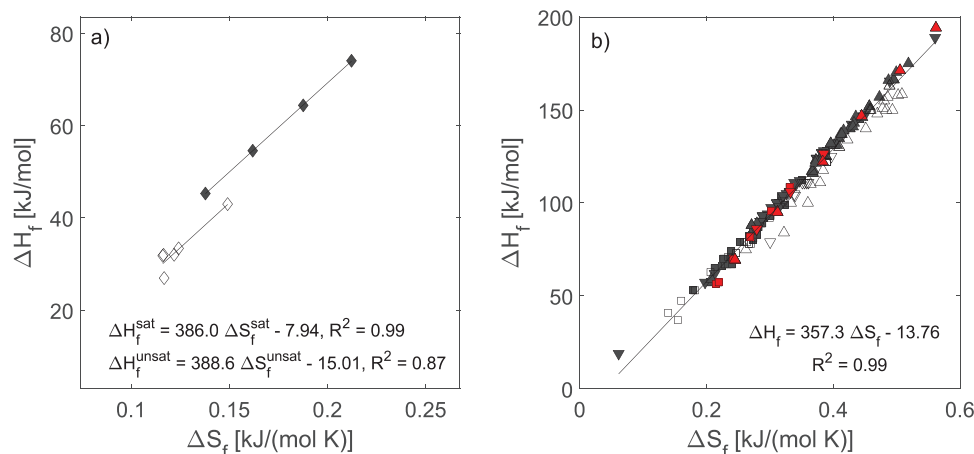


Figure 5. ΔH_f versus ΔS_f for a) FA; saturated FA (filled diamonds), unsaturated FA (empty diamonds) and b) TAGs in α -polymorph (squares), β^2 -polymorph (downward-pointing triangle), and β -polymorph (upward-pointing triangle); saturated TAGs (filled markers), unsaturated TAGs (empty markers), saturated mono-acid TAGs (red markers); linear fit parameters and coefficient of determination as indicated.

phic form, chain length packing, and glycerol conformation, to name a few.

Nonetheless, the calorimetric properties for all FA and TAGs are displayed in Figure 5. In this representation, the data reveal an astonishing systematic.

A similar linear correlation for FA as for *n*-alkanes discussed above can be found, Figure 5a. Fitting data of unsaturated FA separately from saturated FA reveals a slope of 388.6 K. This is close to the slope found for saturated FA of 386 K and similar to that of *n*-alkanes, being 392.5 K. It remains to the judgment of the reader to evaluate the effect of quality of the experimental data displayed—see in particular long-chain poly-unsaturated FA.

The display of the data of TAGs in Figure 5b is most striking. The data can be described very well by one linear fit covering both saturated and unsaturated TAGs. Considering the information displayed in Figure 4c,d and the supporting data in Table 4 illustrating that small changes in the chemical nature of TAGs, e.g., degree of saturation and chain length mismatches, have a profound effect on the physical properties, this finding is far from expected. This linear relation of enthalpy and entropy of fusion appears to be independent of the chemical nature of the TAGs. Considering the subset of saturated TAGs, the data sets for saturated mono-acid TAGs and mixed-acid TAGs with respect to the linear fit are indistinguishable. Even though the data points of unsaturated TAGs are also very well represented by the linear fit for the saturated TAGs, their description can be improved with a separate linear fit analogously to unsaturated FA data. Table 5 summarizes parameters and fit quality of linear fits performed on selected subsets of the TAG data.

Separate linear fits for saturated and unsaturated TAGs yielded a coefficient of determination of 0.9942 and 0.9842, respectively. It is noticeable that the slopes are very similar to each other, being 368.0 and 343.3 K for saturated and unsaturated TAGs, respectively. Considering the linear fit parameters obtained for *n*-alkanes and saturated mono-acid TAGs, it is evident that the slopes are again comparable. Again, for any judgment of the quality of fit, the quality of experimental data displayed cannot be ignored. Any experimental determination of the calorimetric properties is influenced by sample purity and execution of the

Table 5. Summary of linear fits performed on TAG data.

Dataset	Fit parameters		Fit quality	
	Slope	Intercept	R^2	No. of data points
Mono-acid saturated	390.8	-25.24	0.9969	17
All	357.3	-13.76	0.9853	183
Saturated	368.0	-15.92	0.9942	131
Unsaturated	343.3	-12.42	0.9842	52

experiment. It must be noted as well that the dataset retrieved from a literature review contains data spanning three decades.

All slopes, except for the unsaturated TAGs, determined in this work are within the range of approx. 360–390 K. This remains an interesting finding considering that the systems cover a wide temperature and material range, i.e., *n*-alkanes, FA, and TAGs. It is, however, beyond the scope of this manuscript to formulate any underlying hypothesis here.

3. Discussion

3.1. The Relevance of Carbon Number

The linear dependence of the calorimetric data on the carbon number was reviewed for different homologous alkyl-series. For relatively simple series as *n*-alkanes and monosubstituted derivatives, such as saturated FA and, in a wider sense, saturated mono-acid TAGs, a strictly linear relation could be confirmed (see Figure 3). Not surprisingly, the dominant effect of the alkyl-chain on the calorimetric properties is conditioned to a minimum chain length. These straightforward correlations are used in well-known models to describe and predict the thermodynamic properties for said systems.^[8,9] However, reviewing the dependence of the calorimetric data on the carbon number for more diverse molecule series, such as FA naturally occurring in fats and oils and several TAG subsets, revealed that no such simple relation

could be derived (see Figure 4). This is due to the fact that chain length mismatches and double bonds cause a significant perturbation of the crystal structure and, hence, the enthalpy and entropy of fusion decreases. Even though an additive build-up of the enthalpy of fusion from elements of chain molecules is straightforward, the fact that also the entropy of fusion can be easily understood as additive quantity only dependent on the number of elements in a chain seems somewhat elusive.

However, in well-known models predicting the thermodynamic properties of TAGs, the projection of the enthalpy and entropy of fusion onto the carbon number of TAGs was chosen as a simplification. Since several chemical and structural attributes of TAGs determine the overall crystal energy, the simple linear correlation needs to be corrected by accounting for chain length mismatches and their relative contribution (in mixed TAGs) and double bonds (in unsaturated TAGs). One can assume that a projection of the calorimetric properties onto every single attribute, e.g., chain length mismatches and double bonds, reveals a systematic relation taken other variables are kept constant. This way, a fine mesh of structural attributes is generated, allowing reliable predictions to be generated. This approach was successfully implemented in a model predicting the enthalpy of fusion and the melting temperature of TAGs.^[14] In the present contribution, the linear correlation between the enthalpy and entropy of fusion found indicates a systematic but complex correlation of calorimetric properties with TAG attributes certainly beyond carbon number.

3.2. The Relation of Enthalpy-Entropy

A possible linear relation of change of enthalpy and change of entropy, referred to as EEC in literature, was intensely discussed in the last decades. However, researchers neither agreed on a phenomenological explanation nor an adequate statistical explanation.

The change of enthalpy and entropy of fusion of a specific component A ($\Delta H_{f,A}$ and $\Delta S_{f,A}$) on temperature change concerning any reference temperature T_{ref} is given by the integral relations

$$\Delta H_{f,A}(T_{m,A}) = \Delta H_{f,A}(T_{ref}) + \int_{T_{ref}}^{T_{m,A}} \Delta c_{p,A}(T) dT \quad (7)$$

$$\Delta S_{f,A}(T_{m,A}) = \Delta S_{f,A}(T_{ref}) + \int_{T_{ref}}^{T_{m,A}} \frac{\Delta c_{p,A}(T)}{T} dT \quad (8)$$

Ignoring that the change in heat capacity is a function of temperature, which is a commonly made simplification if the temperature interval ($T_{m,A} - T_{ref}$) remains small, Equations (7) and (8) can be rearranged to

$$\Delta H_{f,A}(T_{m,A}) = \Delta H_{f,A}(T_{ref}) + \Delta c_{p,A}(T_{m,A} - T_{ref}) \quad (9)$$

$$\Delta S_{f,A}(T_{m,A}) = \Delta S_{f,A}(T_{ref}) + \Delta c_{p,A} \ln\left(\frac{T_{m,A}}{T_{ref}}\right) \quad (10)$$

To derive a slope according to Equation (3), Equations (9) and (10) are rearranged and combined such that the change of $\Delta H_{f,A}$ with temperature is related to the change of $\Delta S_{f,A}$ with temperature

$$z_A(T_{m,A}) = \frac{\Delta H_{f,A}(T_{m,A}) - \Delta H_{f,A}(T_{ref})}{\Delta S_{f,A}(T_{m,A}) - \Delta S_{f,A}(T_{ref})} = \frac{\Delta c_{p,A}(T_{m,A} - T_{ref})}{\Delta c_{p,A} \ln\left(\frac{T_{m,A}}{T_{ref}}\right)} = \frac{(T_{m,A} - T_{ref})}{\ln\left(\frac{T_{m,A}}{T_{ref}}\right)} \quad (11)$$

The right-hand term in Equation (11) clearly shows that $z_A(T)$ is varying with temperature. However, if T is chosen to be the melting temperature of component A, $z_A(T_{m,A})$ has a defined value. Executing the same exercise for component B yields $z_B(T_{m,B})$. Since $T_{m,B}$ is undoubtedly different from $T_{m,A}$, $z_B(T_{m,B})$ is also different from $z_A(T_{m,A})$ since T_{ref} is component independent and constant. Even though $z(T)$ is by no means identical to the slope of enthalpy over entropy of fusion in a homologous series, this little exercise points out that the correlations of ΔH_f and ΔS_f in a series of alkyl-based molecules described above appear not to be trivial. Considering the discussion on the EEC mentioned, the values of z described above show that the data of the reference material and for components A and B are not on a straight line. This, on the other hand, is considered a necessary condition in the EEC.^[15] Consequently, it is fair to conclude that the finding made here is certainly not captured by the phenomenon of EEC. Yet, the strictly linear relation of enthalpy and entropy of fusion within the homologous series discussed and TAGs suggests an interrelation of the heat capacity and the melting temperature differences of the different species.

Compared to *n*-alkanes, where calorimetric properties correlate with carbon number, it remains stunning that the calorimetric properties of TAGs correlate linearly as well, despite the lack of correlation with carbon number. The linear relation of the enthalpy and the entropy of fusion found for any TAG in three polymorphs (see Figure 5) and, further, for related homologous series of hydrocarbons (see Figure 3) is striking. This linear relation is valid for several different systems that are chemically very similar to another (e.g., *n*-alkanes) and systems that are difficult to characterize regarding their thermodynamic properties by their chemical and structural features (e.g., TAGs).

3.3. Testing Consistency

Although the relation discussed above is not fully understood, its significance in terms of a consistency test for experimental data of TAGs is evident. Hence, it is recommended to verify the consistency of experimental data on enthalpy of fusion and melting temperature pairwise with the correlations formulated. Consistent experimental data within a dataset are supposed to be close to the linear fit. Regarding the enthalpy-entropy plot shown in Figure 5b, the question arises if the deviation from the correlation that specific datasets reveal (Figure 5b) originates from the quality of the correlation formulated or the quality of the data. Beyond consistency evaluation, the relation formulated can be used to generate calorimetric data, either melting temperature from

the enthalpy of fusion data or vice versa, applying Equation (12) with the parameters listed in Table 5

$$\Delta H_f = x\Delta S_f + y = x\frac{\Delta H_f}{T_m} + y \quad (12)$$

It also enables the testing of any predictions of calorimetric data obtained by a suitable model. This challenges a model to generate predictions with small residuals to the respective experimental data without systematic bias and deliver thermodynamically consistent predictions. The relation discussed here was successfully implemented in a model predicting the thermodynamic properties of TAGs.^[14] This resulted in consistent data and allowed to reduce the number of adjustable parameters compared to reference models. It has to be stressed here that satisfying the linear relation between enthalpy and entropy of fusion appears to be a necessary but not a sufficient condition for data consistency and hence quality.

4. Conclusion

This work presented an extended data analysis of the calorimetric properties of phase transition, namely enthalpy and entropy of fusion, for homologous alkyl-series such as *n*-alkanes, FA, and TAGs. The well-known linear correlation of the named properties to the carbon number of *n*-alkanes was reviewed concerning more complex lipid systems. It was shown that no such simple correlation could be derived for chemically and structurally diverse FA and TAGs due to double bonds in unsaturated alkyl-chains and chain length differences within a TAG molecule. For the sets of these species, the term homologous series is actually misplaced. Despite this fact, it was shown that a simple linear relation can still be found when correlating the enthalpy of fusion to the entropy of fusion. However, it was shown that this linear correlation within TAG data is neither an expression of the EEC nor a simple combination of dependencies on total carbon number. It has to be acknowledged that the linear fit parameters of FA and TAGs revealed discrepancies between saturated and unsaturated molecules. However, it was found that the linear correlation is independent of the polymorphic form and chain length differences in mixed-acid molecules for TAGs. Currently, it is recommended to use the parameter set derived for all available TAG data irrespective of the level of saturation. It is foreseen that additional experimental data will increase certainty.

From this, a concise consistency test with three potential applications was derived. First, although being only a necessary condition, it allows the evaluation of the consistency of available experimental sets of enthalpies of fusion and melting temperatures. Second, it is possible to determine unavailable experimental data on either the enthalpy of fusion or melting temperature if at least one of the two is available. Last, predictions obtained from any model can be tested using the consistency criterion and, further, can be forced to fulfill the criterion intrinsically when the model is built accordingly. Since the linear correlation holds for systems spanning a wide temperature range, an extrapolation toward molecules with even longer chains seems justified. In conclusion, the relation found represents an additional tool to safeguard that sound input data are available for any modeling utilizing caloric properties of TAGs.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

Keywords

alkyl-based molecules, carbon number, enthalpy of fusion, entropy of fusion, triglyceride properties

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