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Table of Contents

Abstract

**Chemistry and Thermochemistry of Selected Fatty Acids
Using Correlation Gas Chromatography**

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Correlation gas chromatography (c-GC) is a special application of the gas chromatography technique that is used for the measurement of vaporization enthalpies and the evaluation of vapor pressures of organic compounds. Its use in measuring vaporization enthalpies has been extensively documented. This method is also useful for the measurement of vapor pressures of liquids. For substances that are solids, since each analyte is dilutely adsorbed on the condensed phase of the gas chromatographic column and is not crystalline, the vapor pressure that it exhibits behaves as an excellent model for the sub-cooled liquid phase vapor pressure.

Thermochemical measurements are important to several industrial fields such as chemical and pharmaceutical manufacturing as well as to the fields of environmental and petrochemical sciences. Chemical engineers rely on valid thermochemical data for the scale-up of bench-level reactions to reactor-level production. Environmental scientists use thermochemical data to measure and estimate the effect of various chemicals as pollutants. Petrochemical scientists use thermochemical data to design methods for extracting, purifying, and analyzing oil-related products.

This work focuses on the measurement of the vaporization enthalpy of valproic acid and on a series of both liquid and solid fatty acids and evaluation of their corresponding vapor pressures. The evaluation of the vapor pressure of both the liquid and solid phase is possible using this technique as is the vapor pressure of those compounds that are liquids at room temperature.

Fatty acids belong to a class of compounds comprising mainly straight chain carboxylic acids. These acids may be either saturated or unsaturated. The naturally-occurring fatty acids have a chain length between 4 and 28 carbons. The larger acids are crystalline solids at room temperature. Interest in the vapor pressures of the sub-cooled liquid form of these acids arises from the fact that the larger fatty acids are one of many components present in aerosols and are not necessarily present in crystalline form. This work focused on linear saturated, monounsaturated, and polyunsaturated acids with chain lengths between 14 and 26 carbons.

A particular fatty acid, valproic acid or 2-propylpentanoic acid, has been an important pharmaceutical product for many years. Its uses include the treatment of epilepsy, bipolar and other affective disorders, as well as neuropathic pain and neuralgia. There is also the possibility of its use in the treatment of various cancers. Very few thermodynamic properties of this material are available in the literature. This work measured the vaporization enthalpy and evaluated the vapor pressure for this very important compound.

3-Hydroxydodecanedioic acid is another specific fatty acid of interest, although for a reason different than thermochemical. The presence of this acid in the urine of children can be used in the diagnosis of long-chain hydroxyacetyl-CoA-dehydrogenase (LCHAD)

deficiency disorder. This work reports the details of the synthesis of this particular metabolite.

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This dissertation is dedicated to the memory of Barry L. Peuterbaugh – the very definition of a true friend. May he rest in peace.

Chapter I: Methodology

1.1 Introduction

Thermochemistry is the branch of chemistry concerned with making measurements of the energy involved in such things as chemical reactions and phase transitions. Phase transition energies include those associated with solid to liquid (enthalpy of fusion), liquid to gas (enthalpy of vaporization), and solid directly to gas (enthalpy of sublimation). Another thermochemical property of interest is the measurement of the vapor pressure exerted by various compounds. The study of thermochemistry is important to many fields.

The need to understand thermochemical properties is important in industrial applications as well as in experimental and theoretical scenarios. Chemical engineers need this data to be able to design proper equipment and reaction conditions to make chemical reactions efficient and safe when converted from bench-sized scale to industrial reactor-sized scale. Environmental engineers need this data to be able to remediate chemical spills in a safe and ecologically sound manner. Experimentalists and theoreticians alike are interested in this data so that they may design or model reactions more accurately. Knowing the magnitude and nature of intra- and inter-molecular interactions gives a greater insight into understanding the various interactions responsible for behavior such as molecular self-assembly that occurs in both liquid crystals and biological systems.[1]

There has been interest in making precise and accurate thermochemical measurements such as enthalpy changes and vapor pressure for well over one-hundred years. Many methods have been used with varying degrees of certainty in the results. Some of the methods are tedious and require complicated conditions and equipment while others are relatively simple and straightforward. An overview of the methods used to measure both vapor pressure and vaporization enthalpy is provided below.[2]

1. **Static Measurements**: With this method of measuring vapor pressure, a sample is degassed and placed into a closed vessel and then the vessel is evacuated of all gas. The sample is then allowed to equilibrate over a period of time. Various kinds of pressure gauges (mercury manometers, dead-weight piston gauges, capacitance pressure transducers, etc.) can be used to make the measurements. Advantages of this method include precise calibrations and temperature determinations and the ability to measure pressures in the range of dPa to kPa.[3] Disadvantages of this method include considerable time requirements (up to several weeks to make the measurement and the error that would be generated due to any volatile impurities in the original sample, including entrapped gases.

2. **Ebulliometry**: This is the most frequently employed dynamic method of measurement for measuring vapor pressure. In this method, a liquid is brought to a gentle, even boiling under reflux conditions that also allow for variable pressure adjustments above the boiling liquid. Several incarnations of ebulliometers have been used over the years, with advancements allowing smaller and smaller sample sizes and correction for "bumping" of the boiling liquid in addition to allowing the ability to boil a liquid at very high temperatures. The main advantages of this method over the static method are the ability to determine sample purity and the need for much less time to make the measurements compared with the static method. The main disadvantage of this method is the need for relatively large samples of the substances to be tested (four or more milliliters), which limits its value for complex substances that are in short supply.[4]

3. **Knudsen Effusion Methods for Vapor Pressure Measurement**: Effusion is a technique for measuring vapor pressure by measuring the mass loss of a carefully weighed sample of a substance through an orifice into a vacuum. There are many variations of the Knudsen Effusion method (conventional mass loss technique, torsion-effusion method, isothermal effusion method in thermogravimetric-type apparatus, Knudsen cell with differential scanning calorimetry, etc.) that are in use. Some of these methods require complex apparatus and all of these methods require very low pressures.[5]

4. **Langmuir Effusion Methods for Vapor Pressure Measurement**: This method utilizes free evaporation of a substance from an open surface. Vapor pressure of the substance is determined by the rate of the vaporization of the substance from an open crucible into a vacuum or into an inert gas purge. This method can also be used to measure the sublimation rate of a solid substance if an inert gas purge is used at ambient pressure. The advantages of this method include the need for relatively small sample sizes, relatively easy apparatus set up, and relatively short experiment durations.[6]

5. **Transpiration Method**: This method is also called the transportation or gas saturation method. In this method for measuring vapor pressure, an inert gas is passed over a thermostatically controlled saturator packed with the substance being investigated at a slow rate such that equilibrium conditions are achieved. The substance being studied is then captured using impingers, sorbents, or traps and weighed. Dalton's Law of Partial Pressures is then used to calculate the pressure of the substance of interest in the inert gas / analyte mixture. The advantages of

this method are that it is not affected by small amounts of impurity in the substance being investigated, the time to conduct the experiment is relatively short, and that vapor pressures can be measured close to ambient temperature. This method also gives results that are in good agreement with other established techniques.[7]

6. **Chromatographic Methods**: The transpiration method described above set the stage for modern gas chromatographic techniques. In the gas chromatographic method, the substance to be investigated is volatilized in a heated chamber where it mixes with an inert carrier gas. This mixture is then passed through a stationary phase to separate multiple components, if present, and then passed through a detector. The retention time, the time the substance of interest takes to pass from the injector to the detector, is related to the vapor pressure of the substance. This method is also used to measure the vaporization enthalpy of the substance of interest. The particular application of this method that is of interest here is the correlation gas chromatographic method (c-GC). This method is described in detail in the next section of this chapter.

7. **Calorimetric Methods**: These methods are used for measuring the vaporization enthalpies of substances. Calorimetric vaporization experiments are based on the measurement of the amount of heat energy needed to vaporize a known amount of the substance of interest. Calorimetric methods include adiabatic calorimetry, drop calorimetry method, and differential calorimetry. The accuracy of the results of calorimetric methods depends upon the complexity of the apparatus used and the precision of the equipment making the measurements.[8]

1.2   The Correlation Gas Chromatography (c-GC) Method

For nearly twenty years, the technique of correlation gas chromatography has been demonstrated to be a relatively fast and very reliable method for measuring vaporization enthalpies and evaluating vapor pressures.[9,10] This method requires the use of compounds whose vaporization enthalpies and vapor pressures are already reliably known in the literature.   These compounds serve as standards for each experiment.   One or more compounds, called targets, are then investigated in each experiment.   This method has been shown to work equally well with both liquid and solid compounds.[11]

Though not necessary, this method works best for homologous series of compounds. Otherwise, standards included in the mixture must contain the same functionality as the compounds under investigation. A series of standards is usually chosen such that at least one standard has a known vaporization enthalpy less than the expected vaporization enthalpy of the smallest target compound and at least one standard has a known vaporization enthalpy greater than the expected vaporization enthalpy of the largest target compound. In situations where this is not feasible, extrapolation from the correlation of the standards is used to make the measurement for targets outside the boundaries of the standards.   There is no real limit on how many target compounds can be analyzed simultaneously so long as all of the substances used elute separately from each other.

A suitable low molar mass solvent (e.g., pentane, acetone, methylene chloride) is chosen to dissolve the compounds used in an experiment. The function of the solvent serves two purposes – to dilute the amount of the compounds injected onto the column and to serve as the non-retained standard for the experiment.   The temperature range used for the experiments usually is sufficiently high such that the volatile solvent does not appreciably

interact with the stationary phase and is simply transported through the column by the carrier gas. In those situations where the temperature range is too low and the solvent is retained, a gas such as methane or butane bubbled into the mixture can serve as the non-retained standard. Since this solvent or gas standard has no interaction with the stationary phase of the column, it is useful in measuring dwell time on the column. Unlike the other analytes whose retention time decreases with increasing temperature, non-retained substances experience a slight increase in retention time with increasing temperature due to the increase in gas viscosity of the carrier. This is the criterion used to determine whether a substance is being retained. This amount of time, t_{nr}, must be subtracted from the retention time for each of the other compounds, t, in the mixture to give an adjusted retention time, t_a, which is the proper measure of each substance's interaction with the stationary phase.

$$t_a = t - t_{nr} \qquad\qquad (1\text{-}1)$$

The mixture created for each experiment is analyzed isothermally across a thirty-degree temperature range, usually in five-degree increments, for a total of seven measurements. The slope of the line created from the linear relationship obtained from a plot of the natural logarithm of t_o/t_a (where $t_o/\text{min} = 1$) as a function of $1/T_m$ (where T_m is the mean temperature at which the measurements were made) of each analyte is then used to calculate the enthalpy of transfer (ΔH_{trns}) from the solution to the vapor phase of each analyte in the mixture. This enthalpy is found to correlate linearly with experimental vaporization enthalpies (ΔH_{vap}). The linear relationship obtained between ΔH_{trns} and ΔH_{vap} of the standards is then used to evaluate ΔH_{vap} for the target compounds.

The experimental procedure is fairly straightforward. A suitable temperature range is chosen where the compounds elute from a properly chosen column separately from each other. A mixture of standards and at least one target compound is dissolved into the non-retained solvent. A small sample of the mixture, usually less than one microliter, is injected onto the column at a constant temperature ($\pm$ 0.1 K usually) and the chromatogram recorded electronically until all compounds in the mixture have eluted. This procedure is repeated at five degree intervals across the contiguous thirty degree temperature range chosen.

The adjusted retention time of each analyte is inversely proportional to its vapor pressure off the column. A plot of $\ln(t_o/t_a)$ versus $1/T_m$ for each analyte results in a linear relationship. The value of the slope of the line generated from the data points in each plot multiplied by the negative of the gas law constant, R, results in the enthalpy of transfer of the analyte from the stationary phase of the column to the gas phase. Since the vapor pressure of each analyte on the column is affected by its interaction with column, the resulting enthalpy of transfer also reflects the enthalpy associated with this interaction. It is thermodynamically related to the sum of the vaporization enthalpy and the enthalpy of interaction of each analyte with the column.

It has been found that when a series of standards is analyzed using these experimental conditions, a linear correlation exists between the enthalpy of transfer ($\Delta_{sln}^{g} H_m (T_m)$) and the enthalpy of vaporization ($\Delta_{l}^{g} H_m (298.15)$).[12] The equation resulting from this linear correlation derived from the known vaporization enthalpies of the standards is then applied to the target substances.[9] This method has been demonstrated to give reliable

results with simple alkanes as well as both mono-substituted and multi-substituted compounds, provided similar reference compounds are used as standards.[13]

For this method to be successful, the vaporization enthalpies of the standards must be available from the literature. The values from the literature typically are often measured at a temperature other than $T = 298.15$ K. The values in the literature can be adjusted to $T = 298.15$ K by applying the following equation:

$$\Delta H_{vap}(298.15 \text{ K}) = \Delta H_{vap}(T_m) + (10.58+0.26*C_p(l))*(T_m - 298.15) \qquad (1\text{-}2)$$

The heat capacity term ($C_p(l)$) is calculated using a group-additivity model.[14] T_m refers to the mean temperature at which the literature vaporization enthalpy was measured.

1.3 The Vapor Pressure Evaluation Method

It has also been found also that $\ln(t_o/t_a)$ of a series of analytes correlate linearly with the their corresponding $\ln(p/p_o)$ values where p refers to vapor pressure of the pure liquid phase of each analyte at a given temperature and p_o is a reference pressure, in this work 101,325 Pa. Thus, the same series of gas chromatography experiments can be used to evaluate vapor pressures of the target compounds so long as the analyte mixture also contains standards with reliably known vapor pressures.[15] In this work, the following equation by Clarke and Glew[16] has been used to calculate the values of $\ln(p/p_0)$ for the standards from literature values:

$$R \cdot \ln(p/p_o) = -\Delta G°(\theta)/\theta + \Delta H°(\theta)(1/\theta - 1/T) + \Delta C_p(\theta)\{\theta/T - 1 + \ln(T/\theta)\} \qquad (1\text{-}3)$$

The terms $\Delta G°(\theta)$ and $\Delta H°(\theta)$ refer to the Gibbs energy and enthalpy difference, respectively, between the vapor and condensed phase, C_p refers to the constant pressure specific heat capacity, θ refers to a reference temperature and refers to the average temperature of the experimental results while p_o is a reference pressure and R is the universal gas constant. This equation has been shown to extrapolate well with temperature.[17] In the calculations where this equation is used to evaluate experimental data, values for these properties have been taken from the literature.[18]

Calculated values of $\ln(p/p_o)$ for the standards, where $p_o = 101,325$ Pa, are correlated with the $\ln(t_o/t_a)$ values at $T_m/K = 298.15$ from the vaporization enthalpy measurements from the c-GC experiments described in the previous section of this chapter. A plot of $\ln(t_o/t_a)$ (*x*-axis) versus literature $\ln(p/p_o)$ (*y*-axis) at a given temperature results in a linear relationship. The equation of the line produced from this correlation of the standards is then used to obtain the calculated values for $\ln(p/p_o)$ for each of the target compounds. This calculation is repeated over ten to fifteen degree intervals from $T = 298.15$ K to the boiling temperature of the most volatile standard.

Based on the shape of the curves, the vapor pressures for both the standards and the targets as a function of temperature have been fit successfully to a third-order polynomial:

$$\ln(p/p_o)_{calc} = AT^{-3} + BT^{-2} + CT^{-1} + D \qquad (1\text{-}4)$$

This equation is then used to estimate the boiling point of each of the compounds as a means of validating the results. This is accomplished by extrapolation to a temperature where $\ln(p/p_o)_{calc}$ changes sign, the point which coincides with the boiling temperature of the substance being evaluated.

1.4 Summary

Many methods exist for the measurement of thermochemical properties of substances. The thermochemical properties of interest here are vaporization enthalpy and vapor pressure. The method of choice for making these thermochemical measurements is correlation gas chromatography (c-GC).

The c-GC method uses traditional gas chromatography to obtain data about substances of interest, and the substances used as standards, at multiple temperature intervals. Plots are then made of $\ln(t_o/t_a)$ (y-axis) versus $1/T_m$ (x-axis). The slope of the line from each plot is multiplied by the negative value of the gas constant R to obtain the enthalpy of transfer for each substance. When these enthalpies of transfer are correlated with the known vaporization enthalpies of the standards used in an experiment, the vaporization enthalpies of the substances of interest are then determined.

The data from each c-GC experiment is also used to calculate the vapor pressure of each substance of interest. It is imperative that the standards used in each experiment also have well-established vapor pressure data. For vapor pressure determinations, plots of $\ln(t_o/t_a)$ (x-axis) versus literature $\ln(p/p_{atm})$ (y-axis) at a given temperature for the standards are made. The equation of the line produced from this correlation of the standards is then used to obtain the calculated values for $\ln(p/p_{atm})$ for each of the substances of interest. By repeating the correlations for the standards from 298 K to the boiling temperature of the most volatile standard, the vapor pressures of the standards were then able to be fit to a third-order polynomial that was then used to estimate the boiling temperatures of the substances of interest.

Advantages to using c-GC as opposed to the others discussed in this chapter include:

1. *Sample purity is not that important.* Since components are separated in gas chromatography, peaks corresponding to the pure substance are known. Many of the other methods discussed are affected greatly by sample purity.

2. *Very small quantities of samples are needed.* Only a few milligrams of each substance are needed for gas chromatography. Many of the other methods required multiple grams of each substance to make the measurements.

3. *Experimental duration is relatively short.* The c-GC experiments require only several hours to complete (once proper experimental conditions are worked out). Some of the other methods may take up to several weeks to complete the measurements.

4. *It is possible to make hypothetical thermochemical measurements.* Since many of the compounds studied are solids at 298 K, it is possible to use this method to measure those substances' hypothetical sub-cooled liquid vapor pressures and vaporization enthalpies at 298 K. Also, if the fusion enthalpy for a given substance is known as well, it can be combined with the hypothetical vaporization enthalpy to estimate the sublimation enthalpy for that substance.

5. *It is possible to obtain low vapor pressures.* Most measurement methods described above have measured vapor pressures greater than 0.01Pa. Very few if any techniques other than c-GC are capable of providing vapor pressures at much lower pressures.

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Chapter II: Valproic Acid

2.1 Introduction

Valproic acid, 2-propylpentanoic acid, Figure 2-1, has been used clinically in the treatment of bipolar disorder, epilepsy, other mood disorders, as well as for neuropathic pain and fibromyalgia.[1,2] Valproic acid and its sodium salt are marketed under various trade names including Valparin, Depakote, Depakote ER, Depacon, and Stavzor. It has also been of recent interest in HIV treatment[3] although
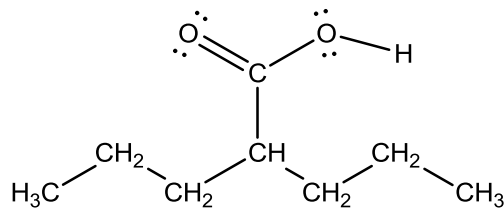
Figure 2-1. Valproic Acid

further studies found no long-term benefits from its use.[4] Valproic acid may also have implications in the treatment of various cancers.[5,6] Despite the fact that valproic acid has been in use in various therapies for over 30 years, there is very little information available regarding its thermochemical properties in the literature. The Environmental Protection Agency (EPA), for example, cites a vapor pressure of 6.1 Pa at T/K = 298, and this is an estimated value.[7] Similarly, for its vaporization enthalpy, an estimated value of (50.3 ± 6.0) kJ·mol^{-1} is predicted by ACD Laboratories software as cited by SciFinder Scholar.[8] No temperature is associated with this estimation. Another simple equation for the estimation of vaporization enthalpies of singly substituted alkanes such as valproic acid is given by equation 2-1:

$$\Delta H_{vap}(298K) \,/\, kJ \bullet mol^{-1} = 4.69(n_C - n_Q) + 1.3n_Q + 3 + b_i \qquad (2\text{-}1)$$

where n_C identifies the total number of carbon atoms, n_Q refers to the number of quaternary sp^3 carbons atoms, and b_i is the contribution of the functional group, in this case the carboxylic acid.[9] Using the group value for a carboxylic acid, 38.8, results in a

vaporization enthalpy of (79.3 ± 4.0) kJ·mol^{-1} at T/K $=$ 298.15 for valproic acid - a significantly different estimation than was predicted by the ACD Laboratories software.

The current work used correlation-gas chromatography to measure the vaporization enthalpy at T/K = 298.15 and the vapor pressure of valproic acid from (298.15 to 492.8) K. Also, an estimate of the boiling temperature at 101,325 Pa is made. For these experiments, the n-alkanoic acids from n-pentanoic to n-undecanoic acid were used as standards.

2.2 Vaporization Enthalpies and Vapor Pressures of the Standards

The vaporization enthalpies of the acid standards (n-pentanoic, n-hexanoic, n-octanoic, n-decanoic, and n-undecanoic) have been reported numerous times.[10] This work uses the values of DeKruif, *et al*,[11] who have reviewed literature vapor pressure data and have reported both vaporization enthalpies and vapor pressures of all the acids used as standards in this work with the exception of n-pentanoic acid. The vaporization enthalpy reported by Verevkin[12] was used for n-pentanoic acid. Since not all of the vaporization enthalpies are available at a common temperature, equation 2-2 was used to adjust these values to T/K = 298.15.[13]

$$\Delta H_{vap}(298.15 \text{ K})/(\text{kJ·mol}^{-1}) = \Delta H_{vap}(T_m) +$$
$$[(10.58 + 0.26*C_p(l)/(\text{J·mol}^{-1}\cdot\text{K}^{-1}))(T_m/\text{K} - 298.15 \text{ K})]/1000 \qquad (2\text{-}2)$$

The $C_p(l, 298 \text{ K})$ term in equation 2-2 refers to the heat capacity of the liquid and was estimated by group additivity.[14] The vaporization enthalpies of the standards and their adjustment to a common temperature, T/K = 298.15, are reported in Table 2-1.

Table 2-1. Vaporization Enthalpies of the Standards and Their Temperature Adjustment to
$T = 298.15$ K

	$\Delta H_{vap}(T_m)$ kJ·mol^{-1}	T_m/K	C_p(l) J·mol^{-1}·K^{-1}	$\Delta C_p \Delta T$[a] kJ·mol^{-1}	ΔH_{vap}(298.15) kJ·mol^{-1}	Ref
n-pentanoic acid	63.0±0.5	298.15	218		63.0±0.5	12
n-hexanoic acid	69.2±0.9	298.15	249.9		69.2±0.9[b]	12
n-hexanoic acid	64.9±0.1	352.4	249.9	4.10±0.9	69.0±0.9[b]	11
n-octanoic acid	81.0±0.6	298.15	313.7		81.0±0.6[c]	12
n-octanoic acid	80.0±0.2	290	313.7	-0.75±0.1	79.3±0.2[c]	11
n-decanoic acid	88.6±2.0	313.8	377.5	1.70±0.3	90.3±2.0	11
n-undecanoic acid	90.7±1.3	322.8	409.4	2.88±0.4	93.6±1.4	11

[a] Calculated using the second term of equation 2-2.
[b] An average value of (69.1±0.9) was used in subsequent correlations.
[c] An average value of (80.1±0.9) was used in subsequent correlations.

Because the vapor pressure of n-pentanoic acid is available over only a narrow temperature range that is near ambient temperature,[12] this acid was also treated as an unknown and used as a test subject to evaluate the reliability of the correlations in these experiments. The vapor pressures of the acid standards (n-hexanoic, n-octanoic, n-decanoic, and n-undecanoic) in the literature evaluated by De Kruif *et al.*[11] were fit to the equation of Clarke and Glew,[15] equation 2-3 below.

$$R \cdot \ln(p/p_o) = -\Delta G°(\theta)/\theta + \Delta H°(\theta)(1/\theta - 1/T) + \Delta C_p(\theta)\{\theta/T - 1 + \ln(T/\theta)\} \qquad (2\text{-}3)$$

The term θ is the average temperature of the experimental results while p_o is a reference pressure, 1 Pa, and R is the gas constant. Values for the thermodynamic parameters[11] used in equation 2-3 are provided in Table 2-2.

Table 2-2. Thermodynamic Properties of the Acid Standards Used in Equation 2-3

	θ K	$\Delta G°(\theta)$ J·mol^{-1}	$\Delta H°(\theta)$ J·mol^{-1}	$\Delta C_p(\theta)$ J·mol^{-1}·K^{-1}	$p(\theta)$/Pa
n-hexanoic acid	352.36	-17740±20	64890±50	75±3	427±3
n-octanoic acid	370.18	-17070±20	72300±60	96±3	256±2
n-decanoic acid	389.39	-17160±20	78920±40	111±2	200±1
n-undecanoic acid	395.80	-16660±10	82180±30	122±1	158±1

Prior to use, the vapor pressures calculated from equation 2-3 for each standard were first converted to atmosphere units by dividing each of them by p_{atm} where $p_{atm} = 101325$ Pa and then converted to the natural logarithm, $\ln(p/p_{atm})$.

2.3 Experimental Conditions

The origin of the carboxylic acids used in this study and their purities are described in Table 2-3. Each carboxylic acid standard was analyzed by gas chromatography and the purities were consistent with those values listed in Table 2-3. One of the benefits of the correlation gas chromatography method is that, unlike other studies where thermochemical properties are highly dependent on sample purity, purity of the individual compounds is not an issue since each component is separated by the chromatography.

Table 2-3. Suppliers and Purities of the Carboxylic Acids Used in This Experiment

	Supplier	Purity
valproic acid	Sigma, St. Louis, MO	Pharmaceutical grade
n-pentanoic acid	SAFC, St. Louis, MO	99%
n-hexanoic acid	SAFC, St. Louis, MO	98%
n-octanoic acid	Sigma, St. Louis, MO	98+%
n-decanoic acid	SAFC, St. Louis, MO	98+%
n-undecanoic acid	Eastman White Label	99%

All experiments were performed on an HP 5890 Gas Chromatograph equipped with a flame ionization detector and run at a split ratio of approximately 100/1. Retention times were recorded on an HP ChemStation. The compounds were run isothermally on a 0.32 mm ID, 30 m J&W FFAP column. Column temperatures were monitored independently using a Fluke digital thermometer. The temperature maintained by the gas chromatograph was constant to ± 0.1 K. Helium was used as the carrier gas.

Methylene chloride was used as the solvent, and at the temperatures of these experiments, it also served as the non-retained reference. The non-retained reference can be identified since its retention time increases slightly with temperature due to an increase in the viscosity of the carrier gas. The enthalpies of transfer measured depend both on the nature of the column and various instrumental parameters used such as flow rate and temperature. The results following the correlation with the vaporization enthalpies, however, remain independent of the experimental conditions.

Adjusted retention times, t_a, were calculated by the difference between the retention time of the analyte and that of the non-retained reference. This was repeated over a 30 K range at 5 K intervals from $435 - 465$ K. The slope of the line was obtained and multiplied by the gas constant to give the enthalpy of transfer at the mean temperature of the experiments $(-\Delta H_{trn}(T_m))$.

Correlation of the vaporization enthalpies of the standards with the enthalpies of transfer resulted in a linear relationship from which the vaporization enthalpy of the target could be evaluated. In a similar fashion, the vapor pressures of the standards, $\ln(p/p_o)$, were correlated with $\ln(t_o/t_a)$ where $t_o/\text{min} = 1$. This also resulted in a linear relationship from which $\ln(p/p_o)$ of the target was evaluated as described below. This procedure was repeated at 10 K intervals from T/K = 298.15 to the boiling temperature of the most volatile standard.

An uncertainty of 16 J·mol⁻¹·K⁻¹ was used for the uncertainty in the $C_p(l)$ term of equation 2-2.[10] The standard deviation associated with the slope (u_1) and intercept (u_2) of the equations listed at the bottom of each respective run were used to calculate the values

listed in the last column of Table 2-4 in the next section as $(u_1^2 + u_2^2)^{0.5}$. These uncertainties are a measure of the precision of the measurements.

2.4 Results and Discussion

The experimental retention times for the duplicate runs of this study are reported in Appendices A-1 and A-2 of Appendix A. Both runs were conducted at a mean temperature of $T_m/K = 450$. The results of the correlations between $\ln(t_o/t_a)$ vs $1/T$ are provided in Table 2-4 for both runs 1 and 2.

Table 2-4. Results of the Correlations between ΔH_{trn} and Vaporization Enthalpies

Run 1	slope T/K	intercept	ΔH_{trn} (450K) kJ·mol^{-1}	ΔH_{vap} (298 K) kJ·mol^{-1} (lit)	ΔH_{vap} (298 K) kJ·mol^{-1} (calc)
n-pentanoic acid	-5674.8	12.972	47.177	63.0	63.1±2.4
n-hexanoic acid	-6178.1	13.684	51.362	69.1	69.2±2.4
valproic Acid	-6640.2	14.369	55.204		74.7±2.5
n-octanoic acid	-7076.1	14.886	58.828	80.1	79.9±2.6
n-decanoic acid	-7881.5	15.904	65.524	90.3	89.6±2.7
n-undecanoic acid	-8269.9	16.393	68.753	93.6	94.3±2.8

$$\Delta H_{vap}(298.15 \text{ K})/\text{kJ·mol}^{-1} = (1.44\pm0.03)\Delta H_{trn}(450 \text{ K}) - (4.97\pm1.83) \quad r^2 = 0.9986 \quad (2\text{-}4)$$

Run 2	slope T/K	intercept	ΔH_{trn} (450 K) kJ·mol^{-1}	ΔH_{vap} (298 K) kJ·mol^{-1} (lit)	ΔH_{vap} (298 K) kJ·mol^{-1} (calc)
n-pentanoic acid	-5287.1	12.092	43.95	63.0	62.8±2.0
n-hexanoic acid	-5885.8	13.021	48.93	69.1	69.4±2.1
valproic Acid	-6381.4	13.781	53.05		74.9±2.2
n-octanoic acid	-6867.5	14.413	57.09	80.1	80.3±2.2
n-decanoic acid	-7703.9	15.503	64.05	90.3	89.6±2.4
n-undecanoic acid	-8106.1	16.024	67.39	93.6	94.0±2.5

$$\Delta H_{vap}(298.15 \text{ K})/\text{kJ·mol}^{-1} = (1.33\pm0.03)\Delta H_{trn}(450 \text{ K}) - (4.12\pm1.6) \quad r^2 = 0.9987 \quad (2\text{-}5)$$

Equations 2-4 and 2-5 located below each run in Table 4 define the equation of the line obtained by correlating the vaporization enthalpies of the standards at $T_m/K = 298.15$ with their corresponding enthalpies of transfer measured at $T_m/K = 450$ by linear regression. Figure 2-2 below also provides a visual assessment of the quality of the correlation for run 1.
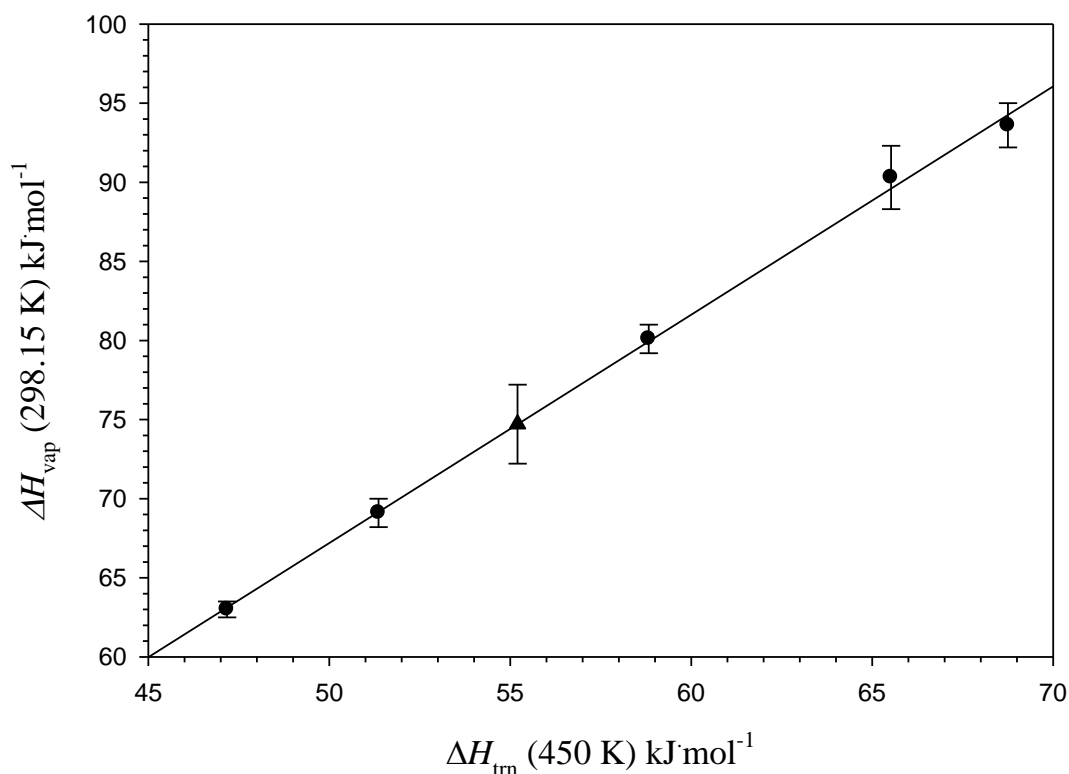
Figure 2-2. A plot of ΔH_{vap} (298.15 K) against ΔH_{trn} (450 K) of the standards (•). Uncertainties of the standards are experimental values. The line was calculated by a linear regression from equation 2-4. The triangle (▲) represents the value and uncertainty associated with valproic acid calculated from the correlation.

Using the slopes and intercepts from Table 2-4, run 1, calculated values of $\ln(p/p_{atm})$ of the standards were correlated against $\ln(t_o/t_a)_{std}$, both at $T_m/K = 298.15$. These results are shown below in Table 2-5. Figure 2-3 illustrates the results of these correlations.

Table 2-5. Correlation of $\ln(t_o/t_a)$ with Experimental $\ln(p/p_{atm})$ Values at T = 298.15 K

	slope T/K	intercept	$\ln(t_o/t_a)$	$\ln(p/p_{atm})$ lit	$\ln(p/p_{atm})$ calc
n-pentanoic acid	-5674.77	12.972	-6.062		-8.32
n-hexanoic acid	-6178.12	13.684	-7.038	-9.631	-9.54
valproic acid	-7076.13	14.886	-7.902		-10.70
n-octanoic acid	-7881.54	15.904	-8.848	-11.946	-11.96
n-decanoic acid	-8269.92	16.393	-10.53	-14.207	-14.21
n-undecanoic acid	-6640.23	14.369	-11.345	-15.292	-15.30

$$\ln(p/p_{atm})_{calc} = (1.316\pm0.011)\ln(t_o/t_a) - (0.344\pm0.107) \quad r^2 = 0.9999 \qquad (2\text{-}6)$$
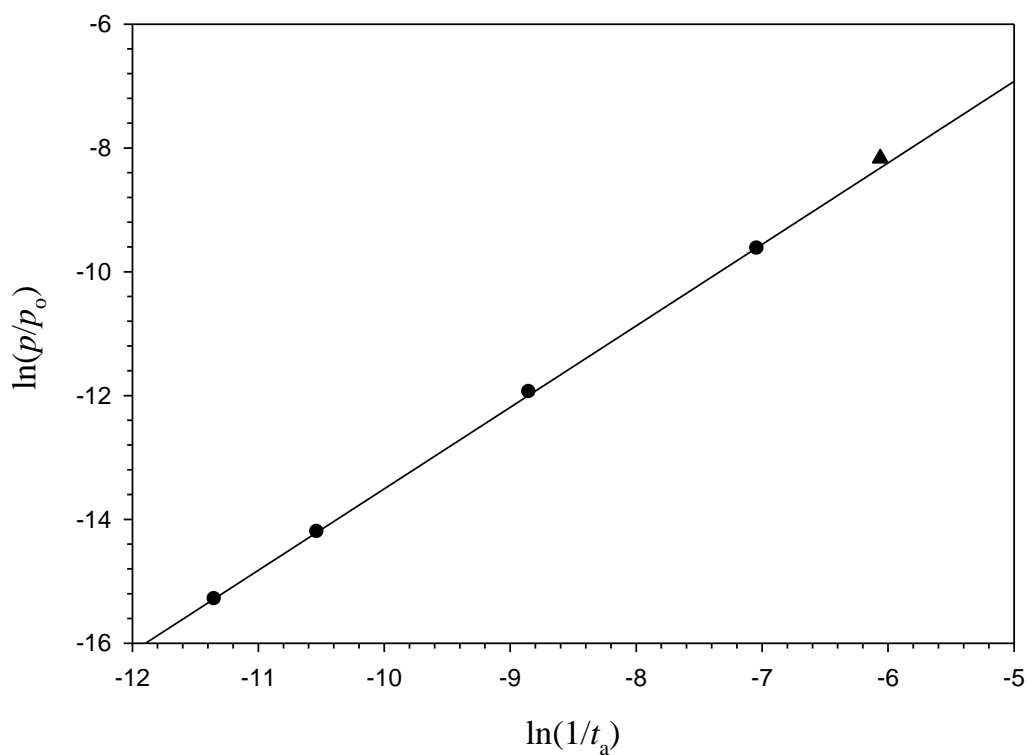
Figure 2-3. A plot of $\ln(p/p_o)$ against $\ln(t_o/t_a)$ of the standards (•) at T/K = 298.15. The literature value of pentanoic acid (▲) at T/K = 298.15[11] was not used in evaluating the line obtained by linear regression.

Correlation equation 2-6 (shown below Table 2-5) was used to evaluate the vapor pressures of both n-pentanoic acid and valproic acid at this temperature. Similar correlations between $\ln(p/p_{atm})_{std}$ and $\ln(t_o/t_a)_{std}$ were repeated at 10 K intervals from T/K =

(298.15 to 480), the boiling temperature of the lowest standard, n-hexanoic acid. This set of correlations was also repeated using the results of the second run. The correlation coefficient, r^2, exceeded 0.999 over the entire range of temperature for all correlations between $\ln(p/p_{atm})_{std}$ and $\ln(t_o/t_a)_{std}$ for both runs. The resulting $\ln(p/p_{atm})$ values for both pentanoic and valproic acid calculated from the correlation equations of the standards were then fit to a third order polynomial, equation 2-7 below. The coefficients of equation 2-7 for both acids treated as unknowns are provided in Table 2-6 below.

$$\ln(p/p_{atm})_{calc} = AT^{-3} + BT^{-2} + CT^{-1} + D \quad\quad\quad (2\text{-}7)$$

Table 2-6. Coefficients of Equation 2-7 for Pentanoic and Valproic Acids
from Runs 1 and 2

	Run	$A \times 10^8$	$B \times 10^6$	$C \times 10^2$	D
Pentanoic acid	1	1.406	-1.698	-8.885	8.454
	2	1.506	-1.782	-5.536	8.012
Valproic acid	1	2.840	-2.943	1.481	6.739
	2	1.655	-2.048	-7.518	8.577

The coefficients reported in Table 2-6 for pentanoic acid were derived by using calculated data from $T/K = (298.15 \text{ to } 460)$, 460 K being the highest 10 K interval at which $\ln(p/p_{atm})$ remained negative. For valproic acid, vapor pressures calculated up to $T/K = 480$ were used, the highest temperature at which $\ln(p/p_{atm})_{std}$ of all the standards remained negative. The boiling temperature was then calculated by extrapolating equation 2-6 until $\ln(p/p_{atm})$ for valproic acid changed signs. A summary of these results is shown in Table 2-7 below.

Table 2-7. Summary of the Calculated Vapor Pressures and Boiling Temperatures

| | Run | Boiling temperature/K | | p(298.15 K)/Pa | |
		calc	exp[a]	calc	lit
Pentanoic acid	1	461.9	459-61	21.2±4	27.3 [11]
	2	462.3		27.5±2	
Valproic acid	1	492.8	494-5	2.2±0.4	6.1 [6]
	2	492.7		2.2±0.1	

[a] Experimental boiling temperatures from SciFinder Scholar.

2.5 Summary

This study used correlation gas chromatography to measure the vaporization enthalpy of valproic acid. The average value obtained from these experiments is 74.8 ±2.4 kJ/mol. This value varies substantially from the estimated value of 50.29 ± 6.0 kJ·mol^{-1} using the ACD Laboratories software as cited by SciFinder Scholar.[8] The value obtained in this study much more closely resembles the value obtained by using the simple estimation method, (79.3±4.0) kJ·mol^{-1}, outlined in the first section of this chapter.

Both *n*-pentanoic acid and valproic acid were treated as unknowns for the purpose of estimating both the vapor pressure at T/K = 298.15 and boiling temperature. The boiling temperatures calculated for both *n*-pentanoic acid and valproic acid are in agreement with the various experimental boiling temperatures. Similarly, the vapor pressure evaluated for pentanoic acid at T/K = 298.15 is within a few Pascals of the literature value reported for pentanoic acid[12] and the value derived for valproic acid agrees well with the EPA estimate.[7]

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Chapter III: Long Chain Fatty Acids

3.1 Introduction

Fatty acids belong to a class of compounds comprised of long-chain aliphatic carboxylic acids. These acids may be either saturated or unsaturated. The naturally-occurring fatty acids have a chain length between 4 and 28 carbons. Long-chain fatty acids have chain lengths greater than 12 carbons, but generally have at most 22 carbons.

The linear fatty acids are of immense industrial and biological importance. Large-scale production of these materials from both anthropogenic and biogenic sources also pose environmental concerns.[1,2] A number of the carboxylic acids that are studied in this research have been associated with secondary ambient aerosols.[3]

Despite the fact that these compounds have been studied for well over a century, most of the thermochemical data that has been accumulated has been on the saturated fatty acids, many of which are solids at room temperature. Much less information is available on the corresponding unsaturated acids, many of which tend to be liquids at room temperature. This research measured the vaporization enthalpies and evaluated the vapor pressures of several mono- and poly-unsaturated fatty acids as well as the vaporization enthalpies and vapor pressures of n-heneicosanoic acid and n-docosanoic acid, both of which are saturated fatty acids.

The vaporization enthalpies were evaluated by correlation-gas chromatography by taking advantage of the critically reviewed vapor pressure and vaporization enthalpy data that has been reported by De Kruif, *et al*,[4] on the saturated C_{14}–C_{20} fatty acids. The vaporization enthalpy data that are available have been adjusted to $T/K = 298.15$ and used as such. Vapor pressures also obtained through correlations were assessed by comparison to

experimental boiling temperatures whenever possible. The fusion enthalpy of n-docosanoic acid was also measured, and recent fusion enthalpies reported in the literature for the C_{14}–C_{21} carboxylic acids are used to calculate sublimation enthalpies.

The compounds investigated include α-linolenic acid ($C_{18}H_{30}O_2$, *cis,cis,cis*-9,12,15-octadecatrienoic acid), γ-linolenic acid ($C_{18}H_{30}O_2$, *cis,cis,cis*-6,9,12-octadecatrienoic acid), linoleic acid ($C_{18}H_{32}O_2$, *cis,cis*-9,12-octadecadienoic acid), elaidic acid ($C_{18}H_{34}O_2$, *trans*-9-octadecenoic acid), n-heneicosanoic acid ($C_{21}H_{42}O_2$), erucic acid ($C_{22}H_{42}O_2$, *cis*-13-docosenoic acid), and n-docosanoic acid ($C_{22}H_{44}O_2$). The structures of the target acids are shown in Figure 3-1. Vapor pressures of both the sub-cooled liquid and of the solid state at $T/K = 298.15$ are also calculated for the saturated C_{14}–C_{22} fatty acids and compared to available data.

3.2 Vaporization Enthalpies, Vapor Pressures, and Fusion Enthalpies of the Standards

The vaporization enthalpies reported by De Kruif, *et al*,[4] for the saturated fatty acids are available at different temperatures. Temperature adjustments to $T/K = 298.15$ were achieved by using equation 3-1 below which has generally proven to be satisfactory.[5] The

$$\Delta H_{vap}(298.15 \text{ K})/(\text{kJ·mol}^{-1}) = \Delta H_{vap}(T_m) +$$
$$[(10.58 + 0.26*C_p(l)/(\text{J·mol}^{-1}\text{·K}^{-1}))(T_m/K - 298.15 \text{ K})]/1000 \qquad (3\text{-}1)$$

$C_p(l)$ term in equation 3-1 refers to the heat capacity at $T/K = 298.15$ and was estimated by group additivity.[6] An uncertainty of 16 J·mol^{-1}·K^{-1} has been associated with the temperature independent term of this equation. The temperature adjustments from temperature T_m to $T/K = 298.15$ are reported in Table 3-1. Since all of these acids are

solids at this temperature, the vaporization enthalpies calculated are for the sub-cooled liquid.

α-linolenic acid (cis,cis,cis-9,12,15-octadecatrienoic acid)

γ-linolenic acid (cis,cis,cis-6,9,12-octadecatrienoic acid)

linoleic acid (cis,cis-9,12-octadecadienoic acid)

elaidic acid (trans-9-octadecenoic acid)

n-heneicosanoic acid

erucic acid (cis-13-docosenoic acid)

n-docosanoic acid
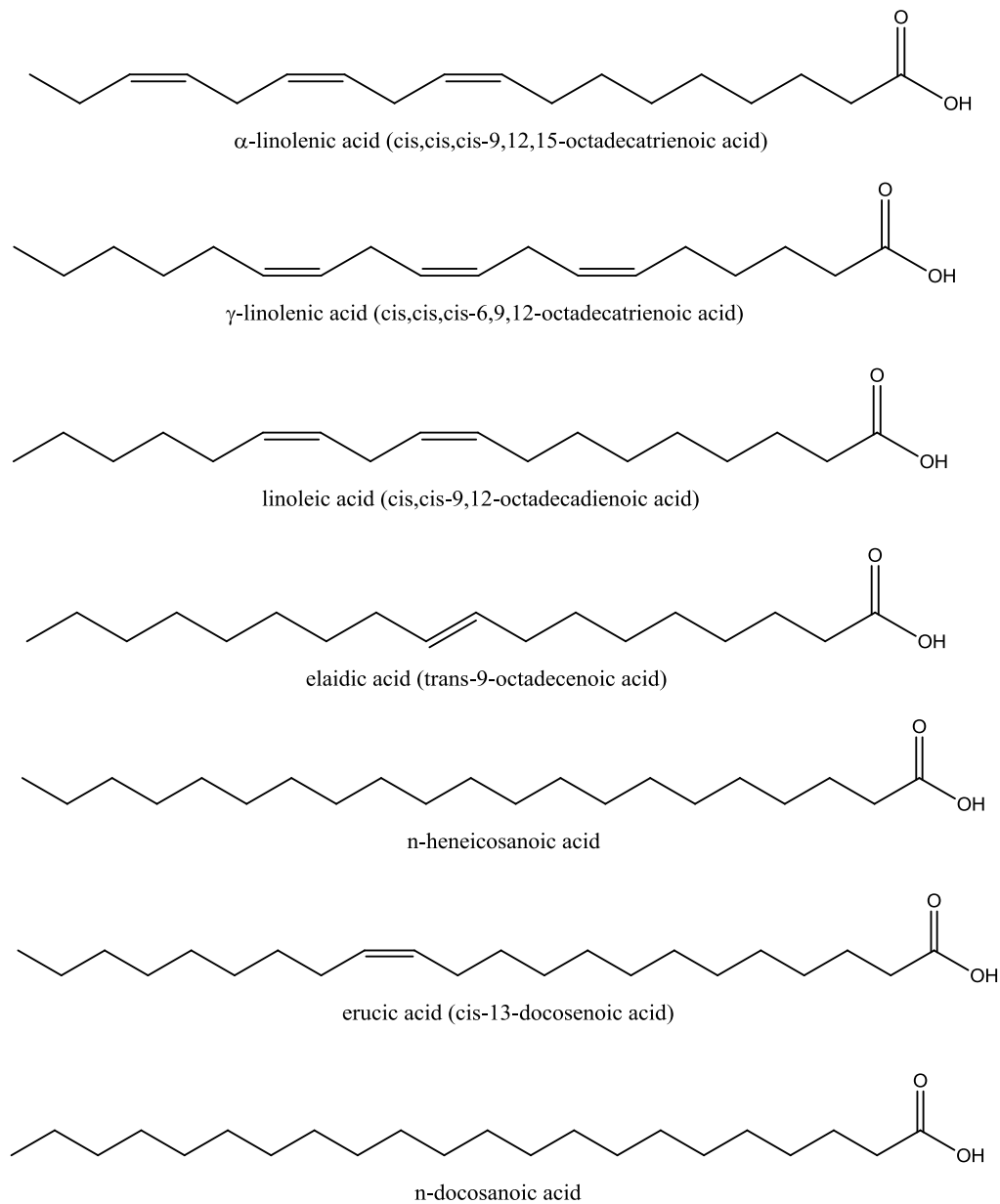
Figure 3-1: Structures of the acids being investigated in this study

Table 3-1. Vaporization Enthalpy Adjustments to $T/K = 298.15$

	$\Delta H_{vap}(T)^4$ kJ·mol^{-1} (lit)	T/K	$C_p(l)$ J·mol^{-1}·K^{-1}	$\Delta C_p \Delta T$ kJ·mol^{-1}	$\Delta H_{vap}(298\ K)$ kJ·mol^{-1}
n-tetradecanoic acid	104.1±2.0	348.6	505.1	7.2±0.8	111.3±2.2
n-pentadecanoic acid	108.4±2.0	357.1	537	8.8±0.9	117.2±2.2
n-hexadecanoic acid	110.2±2.0	364.1	568.9	10.5±1.1	120.7±2.3
n-heptadecanoic acid	112.7±2.0	372	600.8	12.3±1.2	125.0±2.3
n-octadecanoic acid	118.9±2.0	379	632.7	14.2±1.3	133.1±2.4
n-nonadecanoic acid	121.8±2.0	386.1	664.6	16.1±1.4	137.9±2.4
n-eicosanoic acid	125.5±2.0	392.5	696.5	18.1±1.5	143.6±2.5

Vapor pressures of the saturated fatty acids in Table 3-2 below are available in the form of equation 3-2 from Clark and Glew.[7] This equation has been shown to extrapolate well with temperature. Values for the appropriate terms identified in equation 3-2 are provided in Table 3-2. The reference pressure p_o in equation 3-2 is 1 Pa.

$$R \cdot \ln(p/p_o) = -\Delta G°(\theta)/\theta + \Delta H°(\theta)(1/\theta - 1/T) + \Delta C_p(\theta)\{\theta/T - 1 + \ln(T/\theta)\} \qquad (3\text{-}2)$$

Table 3-2. Thermodynamic Properties of the Carboxylic Acid Standards

	θ/K	$-\Delta G°(\theta)$ J·mol^{-1}	$\Delta H°(\theta)$ J·mol^{-1}	$-\Delta C_p(\theta)$ J·mol^{-1}·K^{-1}	$p(\theta)/Pa$
n-tetradecanoic acid	417.43	15970	91360	151	100
n-pentadecanoic acid	426.59	16410	94570	170	102
n-hexadecanoic acid	426.59	14430	97710	159	59
n-heptadecanoic acid	435.04	14760	100720	173	59
n-octadecanoic acid	443.15	15080	102810	181	60

The fusion enthalpies associated with the solid to liquid phase transition of the fatty acids is complicated by the occurrence of polymorphism. The various transitions associated with these acids have been studied by X-ray and powder pattern studies as well as by thermal analysis.[8,9] Table 3-3 below summarizes some of the recent measurements reported on the fatty acids related to this study.

Table 3-3. Recent Literature Enthalpies of Solid-Solid and Solid Liquid Phase Transitions of Some Fatty Acids

	T_t/K	$\Delta H_t(T_t)^a$ kJ·mol^{-1}	T_{fus}/K	$\Delta H_{fus}(T_{fus})$ kJ·mol^{-1}	ΔH_{tpce} kJ·mol^{-1}	Ref
n-tetradecanoic acid			327.3	45.1±0.1		10
			327.4	44.7±1.8		27
	315	1.8±0.4	326.6	45.0±1.3		8
	325.3	6.4±0.7	326.6	45.0±1.3		8
n-pentadecanoic acid	318.7	8.1±0.1	325.7	41.5±0.1	49.6±0.1[b]	11
	321.9	8.2±0.6	325.5	40.4±0.6	48.6±0.8[b]	9
	295.5	0.3±0.1	325.5	40.4±0.6	40.7±0.6[b]	9
	319.3	7.3±0.3	325.9	42.7±1.7	50.0±1.7[b]	27
n-hexadecanoic acid			335.7	53.7±0.1		10
			335.8	53.4±2.1		27
	324.7	2.6±0.7	334.7	53.0±1.0	55.6±1.2	8
	331	7.6±0.5	334.7	53.0±1.0	60.6±1.1	8
	316.7	3.1±0.2	334.7	53.0±1.0	56.1±1.0	8
	317.5	4.9±0.4	334.7	53.0±1.0	57.9±1.1	8
n-heptadecanoic acid	329.2	7.4±0.1	334.3	51.3±0.1	58.7±0.1[b]	11
	329.6	7.3±0.3	334.4	51.5±2.1	58.8±2.1[b]	27
	331.2	7.5±0.9	333.5	46.5±0.9	54.0±1.3[b]	9
trans 9-octadecenoic acid			317	58.6		28
octadecanoic acid			342.5	61.2±0.2		10
			342.6	63.0±2.5	63.0±2.5	27
			344	61.5	61.5	28
	331.6	2.8±0.3	342.4	63.2±1.4	66.0±1.7	8
	327.4	4.3±0.3	342.4	63.2±1.4	67.5±1.4	8
	324.4	5.4±0.3	342.4	63.2±1.4	68.6±1.4	8
	325.9	5.7±0.3	342.4	63.2±1.4	68.9±1.4	8
n-nonadecanoic acid	338	9.2±0.2	341.2	57.6±0.3	66.8±0.3[b]	11
	339	7.4±0.6	340.4	57.0±0.1	64.4±0.6[b]	9
	337.6	9.9±0.4	341.3	57.8±2.3	67.7±2.3[b]	28
n-eicosanoic acid			348.2	69.2±0.4		10
			348.4	72.0±2.9	72.0±2.9	27
	333.3	6.1±0.2	347.6	71.6±1.6	77.7±1.6	8
	332.8	4.1±0.3	347.6	71.6±1.6	75.7±1.6	8
	332.6	5.9±0.2	347.6	71.6±1.6	75.5±1.6	8
n-heneicosanoic acid	344.6	5.0±1.0	346.7	63.0±3.0	68.0±3.2[b]	9
n-docosanoic acid	340.9	3.6±0.2	352.3	66.3±0.2	69.9±0.4[b]	tw[c]

[a] Enthalpy of transition at the transition temperature T_t; values from the same reference refer to different polymorphic forms.
[b] Total phase transitions from T/K = (298.15 to T_{fus}) ; in cases with multiple phase transitions, all uncertainties are combined values.
[c] This work.

For the even carboxylic acids of this study, the actual solid to liquid transition appears to occur from the same structural form, referred to as the orthorhombic (C) structure.[8,10] This does not appear to be the case for the odd fatty acids.[9] Fusion enthalpies at T/K = 298.15 are required to evaluate sublimation enthalpies according to the themochemical cycle described by equation 3-3.

$$\Delta H_{\text{sub}}(298.15 \text{ K}) = \Delta H_{\text{vap}}(298.15 \text{ K}) + \Delta H_{\text{fus}}(298.15 \text{ K}) \qquad (3\text{-}3)$$

In view of the complexity and confusion in the literature[8] associated with the number of different polymorphic forms and their accompanying transition and fusion enthalpies, only a single entry for each fatty acid has been adjusted to T/K = 298.15. The fusion enthalpies of Schaake et al.[10,11] for most of the odd and all of the even series carboxylic acids were chosen since the experimental vaporization enthalpies that are available, and used in this work, were also measured by the same research group.[4,10,11] The fusion enthalpy for n-heneicosanoic acid was taken from the work of Gbabode et al.[9] Solid−solid phase transitions reported by Schaake et al. occurring at T/K > 298.15 for the odd carbon series have been included in calculating the total phase transition enthalpy, ΔH_{tpce}, since the transitions were measured on the same materials. For the even carbon series (excluding n-docosanoic acid), only the fusion enthalpies were adjusted for temperature for comparison with experimental sublimation enthalpies that were previously measured on the orthorhombic, or C, form. The temperature adjustments of fusion enthalpies have been achieved using equation 3-4.[5]

$$\begin{aligned}
\Delta H_{\text{tpce}}(298.15 \text{ K})/(\text{kJ·mol}^{-1}) = &\ \Delta H_{\text{fus}}(T_{\text{fus}}) + \Delta H_{\text{t}}(T_{\text{t}}) + \\
&\ [(0.15\ C_p(\text{cr}) - 0.26\ C_p(\text{l}))/(\text{J·mol}^{-1}\text{·K}^{-1}) - 9.83)] \text{ x} \\
&\ [T_{\text{fus}}/\text{K} - 298.15]/1000; \qquad T_{\text{t}}/\text{K} > 298
\end{aligned} \qquad (3\text{-}4)$$

The heat capacities of both the solid and the liquid phase at $T/K = 298.15$ were estimated.[5]

Experimental heat capacities of the solid phase at this temperature are available for many of the acids.[10,11] Table 3-4 below illustrates the comparison between estimated and experimental values.

Table 3-4. Comparison of Estimated[6] and Experimental C_p(cr) Values[10,11]

	C_p(cr) J·mol-1·K-1 (est)	C_p(cr) J·mol-1·K-1(exp)
n-tetradecanoic acid	412.5	432.0
n-pentadecanoic acid	439.4	443.3
n-hexadecanoic acid	466.3	463.4
n-heptadecanoic acid	493.2	475.7
n-octadecanoic acid	520.1	501.6
n-nonadecanoic acid	547	525.4
n-eicosanoic acid	573.9	545.1

Group values: CH_3: 36.6; CH_2, 26.9; CO_2H: 53.1 J·mol^{-1}·K^{-1}

The estimated C_p(cr) values deviated from the experimental by an absolute average deviation of 3.2 %. A 30 % uncertainty has been associated with the use of equation 3-4.[5] Estimated C_p(cr) values were used in place of experimental ones since equation 3-4 and equations 3-14 and 3-15 described below were derived in this manner. Experimental heat capacities of the liquid phase (C_p(l)) are not available. The results of the temperature adjustments using equation 3-4 are provided in Table 3-5 below.

Table 3-5. Temperature Adjustments of Fusion or Total Phase Change Enthalpy[10,11]

	T_{tp}/K	$\Delta H_{tpce}(T_{tp})^a$ kJ·mol^{-1}	$C_p(l)/C_p(cr)$ J·mol^{-1}·K^{-1}	$\Delta C_p \Delta T$ kJ·mol^{-1}	$\Delta H_{tpce}(298\ K)^a$ kJ·mol^{-1}
n-tetradecanoic acid	327.3[b]	45.1±0.1	505.1/412.5	-2.3±0.7	42.8±0.7[b]
n-pentadecanoic acid	325.7	49.6±0.1	537/439.4	-2.3±0.7	47.3±0.7
n-hexadecanoic acid	335.7[b]	53.7±0.1	568.9/466.3	-3.3±1.0	50.4±1.0[b]
n-heptadecanoic acid	334.3	58. 7±0.1	600.8/493.2	-3.3±1.0	55.4±1.0
elaidic acid	317[c]	58.6	624.5/509.1	-1.8±0.5	56.8±0.5
n-octadecanoic acid	342.5[b]	61.2±0.1	632.7/520.1	-4.3±1.3	56.9±1.3[b]
n-nonadecanoic acid	341.2	66.8±0.3	664.6/547	-4.3±1.3	62.5±1.3
n-eicosanoic acid	348.2[b]	69.2±0.4	696.5/573.9	-5.2±1.6	64.0±1.6[b]
n-heneicosanoic acid	346.7	68.0±3.2	728.4/600.8	-5.3±1.6	62.7±3.6
n-docosanoic acid	352.3[d]	69.9±0.4[e]	760.3/627.7	-6.1±1.8	63.8 ±1.8

[a] Total phase change enthalpy, solid-solid and solid-liquid; T_{tp}: triple point temperature; all uncertainties are combined values.
[b] Fusion enthalpy.
[c] Melting temperature.
[d] Onset temperature.
[e] Includes the enthalpy of a shoulder observed at approximately T/K= 338, this work.

3.3 Experimental Conditions

The fatty acids were obtained in kit form from Supelco. The compounds are identified and characterized in Table 3-6. The liquid samples were provided in sealed ampules by the supplier. The purities of the samples are generally not important since these experiments are conducted as dilute mixtures and the chromatography separates most other components present. All of the samples were analyzed by gas chromatography before use. Their analysis is reported in Table 3-6.

Table 3-6. Description of the Chemical Samples[a]

CAS #	Chemical Name	Supplier	mass fraction
544-63-8	n-tetradecanoic acid (myristic acid, (c))	Supelco	0.996
1002-84-2	n-pentadecanoic acid (c)	Supelco	0.991
57-10-3	n-hexadecanoic acid (palmitic acid, (c))	Supelco	0.984
506-12-7	n-heptadecanoic acid (margaric acid, (c))	Supelco	0.986
506-26-3	*cis,cis,cis*-6,9,12-octadecatrienoic acid (γ-linolenic acid, (l))	Supelco	0.992
463-40-1	*cis,cis,cis*-9,12,15-octadecatrienoic acid (α-linolenic acid, (l))	Supelco	0.997
60-33-3	*cis,cis*-9,12-octadecadienoic acid (linoleic acid, (l))	Supelco	0.997
112-79-8	*trans*-9-octadecenoic acid (elaidic acid, (c))	Supelco	0.97
57-11-4	n-octadecanoic acid (stearic acid, (c))	Supelco	0.951
646-30-0	n-nonadecanoic acid, (c)	Supelco	0.963
506-30-9	n-eicosanoic acid (arachidic acid, (c))	Supelco	0.985
2363-71-5	n-heneicosanoic acid, (c)	Supelco	0.954
112-86-7	*cis*-13-docosenoic acid (erucic acid, (c))	Supelco	0.997
112-85-6	n-docosanoic acid (behenic acid, (c))	Supelco	0.991

[a] The chemicals that were used were all commercial samples and all were analyzed by gas chromatography; chemical purities from the supplier were not available; (c): crystalline; (l): liquid at $T/K = 298$.

Two separate sets of experiments were carried out for this study. The first set of experiments (Runs 1 and 2) used n-tetradecanoic acid through n-octadecanoic acid as the standards and elaidic, linoleic, and α-linolenic acids as the target compounds with a mean experimental temperature of $T/K = 490$. The second set of experiments (Runs 3 and 4) used n-hexadecanoic acid through n-eicosanoic acid as the standards and all seven of the target compounds with a mean experimental temperature of $T/K = 500$.

All experiments were performed on an HP 5890 Series II Gas Chromatograph equipped with a flame ionization detector and run at a split ratio of approximately 100/1. Retention times were recorded on an HP ChemStation. The compounds were run isothermally on a 0.32 mm ID, 30 m J&W FFAP column. Column temperatures were monitored independently using a Fluke digital thermometer. The temperature maintained by the gas chromatograph was constant to ± 0.1 K. Helium was used as the carrier gas.

Methylene chloride was used as the solvent, and at the temperatures of these experiments, it also served as the non-retained reference. The non-retained reference can be identified since its retention time increases slightly with temperature due to an increase in the viscosity of the carrier gas. The enthalpies of transfer measured depend both on the nature of the column and various instrumental parameters used such as flow rate and temperature. The results following the correlation with the vaporization enthalpies, however, remain independent of the experimental conditions.

Adjusted retention times, t_a, were calculated for each analyte from the difference between the retention time of the given analyte and that of the non-retained reference. This was repeated over a 30 K range at 5 K intervals from $T/K = 475 - 505$ for the first set of experiments and from $T/K = 485 - 515$ for the second set of experiments. The slope of the line was obtained for each run and multiplied by the gas constant to give the enthalpy of transfer at the mean temperature of each of the experiments as $-\Delta H_{trn}(T_m)$.

Correlation of the vaporization enthalpies of the standards with the enthalpies of transfer resulted in a linear relationship from which the vaporization enthalpies of the target compounds could be evaluated. In a similar fashion, the vapor pressures of the standards, $\ln(p/p_o)$ where $p_o /Pa = 1$, were correlated with $\ln(t_o/t_a)$ at $T_m/K = 298.15$ where $t_o/min = 1$. This also resulted in a linear relationship from which $\ln(p/p_o)$ of the target compounds were evaluated as described below. This procedure was repeated at 15 K intervals from $T/K = 298.15$ to the boiling temperature of the most volatile standard for each set of experiments.

All plots were characterized by correlation coefficients, r^2, of >0.99. The enthalpy of transfer, $\Delta H_{trn}(T_m)$, is thermodynamically related to the corresponding vaporization enthalpy, $\Delta H_{vap}(T_m)$, by equation 3-5 below where the term $\Delta H_{intr}(T_m)$ refers to the enthalpy of interaction of the analyte with the column.[12]

$$\Delta H_{trn}(T_m) = \Delta H_{vap}(T_m) + \Delta H_{intr}(T_m) \tag{3-5}$$

All combined uncertainties in the tables were calculated as $(u_1^2 + u_2^2 + ...)^{0.5}$. Uncertainties for values derived from linear correlations were calculated from both the uncertainties in the slope and intercept of the correlation equations derived between the vaporization enthalpies of the standards and the enthalpies of transfer.

The fusion enthalpy of n-docosanoic acid was measured on a Perkin-Elmer DSC-7 using the Pyris Series Thermal Analysis software under a flow of nitrogen gas at a rate of 5 $K \cdot min^{-1}$ in hermetically sealed aluminum pans. The pans were weighed before and after each experiment. No mass loss was detected. The instrument is a power compensated model. The instrument was calibrated using an indium standard, $w = 0.99999$, ($J \cdot g^{-1}$, T/K: 28.5, 429.8) provided by the manufacturer and the heat calibration checked using Gold Label scintillation grade naphthalene, $w = > 0.99$ (Aldrich) by comparing with recommended values [$kJ \cdot mol^{-1}$, T/K: (19.1 ± 0.1) kJ, (353.3 ± 0.1); lit.13 (19.06 ± 0.08), (353.4 ± 0.04)]. These results were within the experimental uncertainties. Naphthalene was chosen because of the proximity of its melting temperature to that of n-docosanoic acid.

Measurements for the solid acid are reported in Table 3-7 and Figure 3-2 provides a representative differential scanning calorimetry (DSC) scan.

Table 3-7. A Summary of the Fusion Enthalpy Measurements for n-Docosanoic Acid

	Sample mg	T_t/K	$\Delta H_t(T_t)$ kJ·mol^{-1}	T_{fus}/K[a]	$\Delta H_{fus}(T_{fus})$ kJ·mol^{-1}
n-docosanoic acid					
	13.9	340.8	3.84	352.3	66.3
	11.55	340.7	3.53	352.3	66.2
	11.06	341.2	3.34	352.4	66.5
	Avg	340.9±0.2	3.57±0.3	352.3±0.1	66.3±0.2

[a] Reported as onset temperatures (lit.[13] ; mp 353.1 K);
all uncertainties are standard deviations.
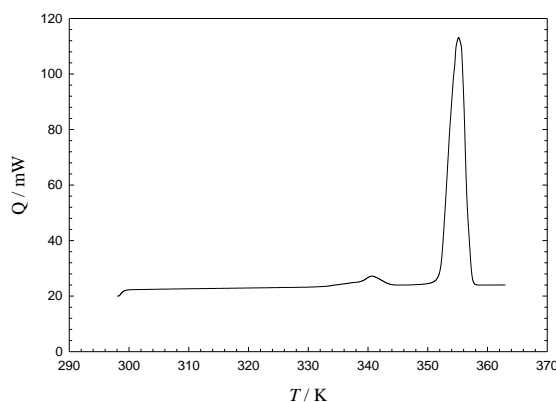
Figure 3-2. The DSC plot of endothermic heat flow, Q, as a function
of temperature for n-docosanoic acid.

In addition to fusion, n-docosanoic acid exhibited an additional phase transition that appeared as two overlapping transitions, a broad one and a larger, sharper transition exhibiting a peak at T/K = (338 ± 0.2). Due to peak overlap and broadness of the peaks, the uncertainty in the peak position and enthalpy of the phase transitions is probably of the order of T/K = ± 0.5 and ± 0.5 kJ·mol^{-1}. The fusion enthalpy reported is for the sum of both transitions obtained by integration of the peaks by the software. An onset temperature of T/K = (352.3 ± 0.1) for fusion compares very favorably with the literature value[13] T/K = (353.1 ± 0.1). To eliminate the possibility that the broad peak was due to the loss of water,

not detected by the FID detector, the fusion of a sample was measured in an open capsule and heated by the DSC to $T/\text{K} = 373$. No mass loss was detected upon cooling.

3.4 Results and Discussion

The experimental retention times for the duplicate runs of this study are reported in Appendices B-1 through B-4 of Appendix B. Table 3-8 on the next page summarizes the results of four correlations between the enthalpy of transfer measured by gas chromatography and literature vaporization enthalpies. Equations 3-6 through 3-9 below each correlation define the quality of the linear relationship observed between $\Delta_{trn}H_m(T_m)$ and $\Delta H_{vap}(298\ \text{K})$ for each run.

Since the vaporization enthalpies evaluated are quite large, the uncertainties associated with the intercept are likewise larger in magnitude than normally observed. As a means of evaluating how well the vaporization enthalpies can be reproduced by these correlations, n-heptadecanoic acid was also used as an unknown in the first two correlations using the saturated C_{14}–C_{16} and C_{18} carboxylic acids as standards. The resulting value agrees with the literature value within 2.5 kJ·mol^{-1}. The results suggest that the uncertainties in these measurements are likely more in the range of ± 5 kJ·mol^{-1} (2σ). The vaporization enthalpies of elaidic, linoleic, and α-linolenic acids were also evaluated in the first two runs, and their values were then used as additional standards in runs 3 and 4. The vaporization enthalpy value of n-heptadecanoic acid evaluated in the first two runs was also used as a standard in subsequent correlations.

Table 3-8. Correlation of Vaporization Enthalpies with Enthalpies of Transfer.

Run 1	slope T/K	intercept	$\Delta_{trn}H_m$ (490 K) kJ·mol^{-1}	ΔH_{vap} (298 K) kJ·mol^{-1} (lit)[a]	ΔH_{vap} (298 K) kJ·mol^{-1} (calc)
n-tetradecanoic acid	-8716.6	16.577	72.47	111.3±2.2	111.2±8.6
n-pentadecanoic acid	-9061.6	16.977	75.33	117.2±2.2	116.5±9.0
n-hexadecanoic acid	-9421.5	17.404	78.33	120.7±2.3	121.9±9.3
n-heptadecanoic acid	-9776.8	17.824	81.28	125.0±2.3[b]	127.3±9.7
n-octadecanoic acid	-10134.2	18.251	84.25	133.1±2.4	132.7±10.1
elaidic acid	-10183.4	18.259	84.66		133.4±10.1
linoleic acid	-10268.2	18.264	85.37		134.7±10.2
α-linolenic acid	-10424.2	18.394	86.66		137.1±10.3

$$\Delta_l^g H_m \text{ (298.15 K)/kJ·mol}^{-1} = (1.82 \pm 0.12)\, \Delta_{trn}H_m \text{ (490 K)} - (20.5\pm9.3);\ r^2 = 0.9915 \qquad (3\text{-}6)$$

Run 2	slope T/K	intercept	$\Delta_{trn}H_m$ (490 K) kJ·mol^{-1}	ΔH_{vap} (298 K) kJ·mol^{-1} (lit)[a]	ΔH_{vap} (298 K) kJ·mol^{-1} (calc)
n-tetradecanoic acid	-8631.3	16.401	71.76	111.3±2.2	111.1±9.0
n-pentadecanoic acid	-8969.6	16.787	74.57	117.2±2.2	116.6±9.3
n-hexadecanoic acid	-9301.0	17.155	77.33	120.7±2.3	121.9±9.7
n-heptadecanoic acid	-9635.4	17.532	80.1	125.0±2.3[b]	127.3±10.0
n-octadecanoic acid	-9967.0	17.905	82.86	133.1±2.4	132.6±10.4
elaidic acid	-9966.3	17.811	82.86		132.6±10.4
linoleic acid	-10021.6	17.756	83.32		133.5±10.4
α-linolenic acid	-10219.0	17.972	84.96		136.7±10.6

$$\Delta_l^g H_m \text{ (298.15 K)/kJ·mol}^{-1} = (1.94 \pm 0.13)\, \Delta_{trn}H_m \text{ (490 K)} - (27.8\pm9.6);\ r^2 = 0.9917 \qquad (3\text{-}7)$$

Run 3	slope T/K	intercept	$\Delta_{trn}H_m$ (500 K) kJ·mol^{-1}	ΔH_{vap} (298 K)[a] kJ·mol^{-1} (lit)	ΔH_{vap} (298 K) kJ·mol^{-1} (calc)
n-hexadecanoic acid	-9074.2	16.7	75.44	120.7±2.3	121.2±5.6
n-heptadecanoic acid	-9411.7	17.1	78.25	127.3±9.9	126.7±5.7
n-octadecanoic acid	-9760.2	17.5	81.14	133.1±2.0	132.5±5.8
elaidic acid	-10085.8	17.9	83.85	133.0±10.3	133.1±5.9
linoleic acid	-9884.4	17.5	82.17	134.1±10.3	134.5±5.9
n-nonadecanoic acid	-9796.6	17.5	81.44	137.9±2.4	137.9±5.9
γ-linolenic acid	-10054.1	17.7	83.59		135.8±5.9
α-linolenic acid	-10426.8	18.3	86.68	136.9±10.4	137.3±5.9
n-eicosanoic acid	-9963.9	17.6	82.84	143.6±2.5	143.5±6.1
n-henicosanoic acid	-10753.1	18.7	89.4		148.9±6.2
n-docosanoic acid	-11089.5	19	92.19		154.4±6.3
erucic acid	-10219.0	17.972	84.96		154.4±6.3

$$\Delta_l^g H_m \text{ (298.15 K)/kJ·mol}^{-1} = (1.99 \pm 0.05)\, \Delta_{trn}H_m \text{ (500 K)} - (28.8\pm4.2);\ r^2 = 0.9961 \qquad (3\text{-}8)$$

Table 3-8. Continued

Run 4	slope T/K	intercept	$\Delta_{\text{trn}}H_{\text{m}}$ (500 K) kJ·mol^{-1}	ΔH_{vap} (298 K)[a] kJ·mol^{-1} (lit)	ΔH_{vap} (298 K) kJ·mol^{-1} (calc)
n-hexadecanoic acid	-9125.1	16.816	75.86	120.7±2.0	121.2±7.4
n-heptadecanoic acid	-9464.5	17.208	78.68	127.3±9.9	126.9±7.5
n-octadecanoic acid	-9801.2	17.591	81.48	133.1±2.0	132.6±7.7
elaidic acid	-9834.8	17.58	81.76	133.0±10.3	133.2±7.7
linoleic acid	-9909.7	17.56	82.39	134.1±10.3	134.5±7.7
n-nonadecanoic acid	-10121.5	17.944	84.15	137.9±2.4	138.0±7.8
γ-linolenic acid	-9997.6	17.631	83.12		135.9±7.7
α-linolenic acid	-10082.5	17.72	83.82	136.9±10.4	137.4±7.8
n-eicosanoic acid	-10458.8	18.336	86.95	143.6±2.5	143.8±7.9
n-henicosanoic acid	-10790.4	18.727	89.71		149.4±8.0
n-docosanoic acid	-11113.6	19.084	92.39		154.9±8.2
erucic acid	-11098.4	18.975	92.27		154.6±8.2

[a] Values used as standards unless otherwise noted.
[b] Literature value not used as a standard in the correlation, but as a test sample

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}} (298.15 \text{ K})/\text{kJ·mol}^{-1} = (2.04 \pm 0.07) \Delta_{\text{trn}}H_{\text{m}} (500 \text{ K}) - (33.5\pm5.4); \ r^2 = 0.9958 \quad (3\text{-}9)$$

The results of all the correlations are summarized and averaged in Table 3-9 below. The uncertainties reported in column six are also averages. Also included in this table in the last column are vaporization enthalpies estimated using the following simple equation:[14]

$$\Delta H_{\text{vap}}(298.15 \text{ K})/(\text{kJ·mol}^{-1}) = \ 4.69(n_{\text{C}} - n_{\text{Q}}) +1.3 \ n_{\text{Q}} + b + 3.0 \quad (3\text{-}10)$$

where n_{C} refers to the total number of carbon atoms, n_{Q} to the number of quaternary sp^3 hybridized carbon atoms, and b is the contribution of the functional group; the carboxylic acid contributes 38.8 kJ·mol^{-1}. Agreement between the experimental and estimated values is quite good. The results in Table 3-9 also suggest that as the amount of unsaturation increases, vaporization enthalpies increase as well.

Table 3.9. A Summary of Runs 1-4 and Comparison with Literature and Estimated Values

	Run 1	Run 2	Run 3	Run 4	ΔH_{vap} (298 K) kJ·mol^{-1}		
					avg[a]	lit	est[b]
n-tetradecanoic acid	111.2±8.6	111.1±9.0			111.2±8.8	111.3±2.2	107.5
n-pentadecanoic acid	116.5±9.0	116.6±9.3			116.6±9.2	117.2±2.2	112.2
n-hexadecanoic acid	121.9±9.3	121.9±9.7	121.2±5.6	121.2±7.4	121.6±8.0	120.7±2.3	116.8
n-heptadecanoic acid	127.3±9.7	127.3±10.0	126.7±5.7	126.9±7.5	127.3±9.9[c]	125.0±2.3	121.5
n-octadecanoic acid	132.7±10.1	132.6±10.4	132.5±5.8	132.6±7.7	132.6±8.6	133.1±2.4	126.2
elaidic acid	133.4±10.1	132.6±10.4	133.1±5.9	133.2±7.7	133.0±10.3[c]		126.2
linoleic acid	134.7±10.2	133.5±10.4	134.5±5.9	134.5±7.7	134.1±10.3[c]		126.2
n-nonadecanoic acid			137.9±5.9	138.0±7.8	138.0±6.8	137.9±2.4	130.9
γ-linolenic acid			135.8±5.9	135.9±7.7	135.9±6.8		126.2
α-linolenic acid	137.1±10.3	136.7±10.6	137.3±5.9	137.4±7.8	136.9±10.4[c]		126.2
n-eicosanoic acid			143.5±6.1	143.8±7.9	143.7±8.0	143.6±2.5	135.6
n-henicosanoic acid			148.9±6.2	149.4±8.0	149.2±7.1		140.3
n-docosanoic acid			154.4±6.3	154.9±8.2	154.7±7.3		145.0
erucic acid			154.4±6.3	154.6±8.2	154.5±7.3		146.0

[a] Uncertainties are average values.
[b] Estimated value using equation 3-8.
[c] Average based only on Runs 1 and 2.

Using the slopes and intercepts from Table 3-8, calculated values of $\ln(p/p_{atm})$ of the standards were correlated against $\ln(t_o/t_a)_{std}$, both at $T_m/K = 298.15$. These results are shown in Table 3-10 on the next page.

The retention times of the n-tetradecanoic acid through n-octadecanoic acid standards at $T/K = 298.15$ were calculated from the slopes and intercepts of runs 1 and 2 and runs 3 and 4 of Table 3-8 and the two sets averaged separately. The resulting values of $\ln(t_o/t_a)_{av}$ were correlated against the corresponding $\ln(p/p_{atm})$ values of the standards calculated by equation 3-2. In these correlations, the term p_{atm} refers to the reference pressure, $p/Pa = 101,325$.

Table 3-10. Correlation of $\ln(t_o/t_a)$ with Experimental $\ln(p/p_{atm})$ Values at $T/K = 298.15$

Set 1:

Runs 1and 2	slope/K (1)	intercept (1)	slope/K (2)	intercept (2)	$\ln(t_o/t_a)_{av}$	$\ln(p/p_{atm})^a$ lit	$\ln(p/p_{atm})$ calc
n-tetradecanoic acid	-8716.6	16.577	-8631.3	16.401	-12.60	-18.61	-18.7±0.8
n-pentadecanoic acid	-9061.6	16.977	-8969.6	16.787	-13.35	-19.87	-19.7±0.8
n-hexadecanoic acid	-9421.5	17.404	-9301.0	17.155	-14.12	-20.71	-20.8±0.9
n-heptadecanoic acid	-9776.8	17.824	-9635.4	17.532	-14.87	-21.92	-21.9±0.9
n-octadecanoic acid	-10134.2	18.251	-9967.0	17.905	-15.63	-22.96	-23.0±0.9
elaidic acid	-10183.4	18.259	-9966.3	17.811	-15.75		-23.1±0.9
linoleic acid	-10268.2	18.264	-10021.6	17.756	-16.00		-23.5±0.9
α-linolenic acid	-10424.2	18.394	-10219.0	17.972	-16.43		-24.1±0.9

$$\ln(p/p_{atm})_{calc} = (1.422\pm0.044)\ln(t_o/t_a) - (0.74\pm0.617) \qquad r^2 = 0.9972 \qquad (3\text{-}11)$$

Set 2:

Runs 3 and 4	slope/K (3)	intercept (3)	slope/K (4)	intercept (4)	$\ln(t_o/t_a)_{av}$	$\ln(p/p_{atm})^a$ lit	$\ln(p/p_{atm})$ calc
n-hexadecanoic acid	-9074.2	16.816	-9125.1	16.816	-13.75	-20.71	-20.8±0.6
n-heptadecanoic acid	-9411.7	17.208	-9464.5	17.208	-14.5	-21.92	-21.9±0.6
n-octadecanoic acid	-9760.2	17.591	-9801.2	17.591	-15.25	-22.96	-22.9±0.6
elaidic acid	-10085.8	17.58	-9834.8	17.58	-15.38	-23.13[b]	-23.1±0.6
linoleic acid	-9796.6	17.944	-10121.5	17.944	-15.66	-23.49[b]	-23.5±0.6
n-nonadecanoic acid	-10054.1	17.631	-9997.6	17.631	-15.98		-24.0±0.6
γ-linolenic acid	-9963.9	18.336	-10458.8	18.336	-15.88		-23.8±0.6
α-linolenic acid	-10426.8	17.56	-9909.7	17.56	-16.08	-24.09[b]	-24.1±0.6
n-eicosanoic acid	-9884.4	17.72	-10082.5	17.72	-16.72		-25.1±0.7
n-henicosanoic acid	-10753.1	18.727	-10790.4	18.727	-17.44		-26.1±0.7
n-docosanoic acid	-11089.5	19.084	-11113.6	19.084	-18.17		-27.1±0.7
erucic acid	-10219.0	18.975	-11098.4	18.975	-18.24		-27.2±0.7

[a] Values used as standards.
[b] Calculated using the constants of equation 3-11 from runs 1 &2.

$$\ln(p/p_{atm})_{calc} = (1.441\pm0.029)\ln(t_o/t_a) - (0.948\pm0.437) \qquad r^2 = 0.9984 \qquad (3\text{-}12)$$

The resulting equations obtained from each correlation, equations 3-11 and 3-12 obtained at $T/K = 298.15$, were used to calculate the corresponding $\ln(p/p_{atm})$ values of the remaining acids in the mixture. This process was repeated over 15 K intervals from $T/K = (298.15$ to $600)$ for set 1 consisting of runs 1 and 2 and $T/K = (298.15$ to $630)$ for set 2 consisting of runs 3 and 4. The values of $\ln(p/p_{atm})$ as a function of temperature calculated from each correlation were tabulated and fit to the third-order polynomial, equation 3-13.

In Table 3-10 (Set 2), values of $\ln(p/p_{atm})$ for n-hexadecanoic through n-octadecanoic acid were calculated using equation 3-2, and the remaining acids that were evaluated in Table 3-10 (Set 1) and used as standards in runs 3 and 4 were calculated using equation 3-13. The constants of equation 3-13 obtained from both sets of runs are tabulated in Table 3-11 on the next page. In all correlations performed as a function of temperature, the correlation coefficient at each temperature, r^2, exceeded 0.99. The upper temperature limits for combined correlations from runs 1 and 2, and runs 3 and 4 were chosen so as not to exceed the boiling temperature of the most volatile component.

$$\ln(p/p_{atm})_{calc} = AT^{-3} + BT^{-2} + CT^{-1} + D \qquad (3\text{-}13)$$

Normal boiling temperatures are available for the standards and for n-nonadecanoic acid. Boiling temperatures for n-tetradecanoic through n-octadecanoic acid, compounds used as vapor pressure standards and calculated from the correlations, are also included in Table 3-11 to illustrate the quality of both the $\ln(p/p_{atm})$ vs $\ln(t_o/t_a)$ correlations and that of the estimates generated by extrapolations of equation 3-13.

While, unlike the equation of Clark and Glew, equation 3-2, the constants A to D of equation 3-13 have no physical significance. However, vapor pressures calculated by equation 3-13 extrapolate well with temperature as indicated by how well the experimental boiling temperatures for n-heptadecanoic acid and n-octadecanoic acid, calculated by extrapolations of approximately 40 K, are predicted by runs 1 and 2. The boiling temperature for n-nonadecanoic acid, calculated from runs 3 and 4 by extrapolation of approximately 50 K, is also in good agreement with the experimental value.

Table 3-11. Coefficients of Equation 3-13 for the Fatty Acids from Runs 1 to 4 and Calculated and Experimental Boiling Temperatures

	Runs	$A*10^{-8}$	$B*10^{-6}$	$C*10^{-3}$	D	BT/K calc	BT/K lit[4]
n-tetradecanoic acid	1 and 2	4.348	-4.830	4.645	3.697	598.4	599
n-pentadecanoic acid	1 and 2	4.526	-5.029	4.813	3.623	610.3	612.3
n-hexadecanoic acid	1 and 2	4.707	-5.228	4.978	3.552	622.1	622.3
	3 and 4	4.995	-5.405	5.332	3.317	622.2	622.3
n-heptadecanoic acid	1 and 2	4.883	-5.424	5.134	3.493	633.3	634.7
	3 and 4	5.080	-5.549	5.403	3.293	633.8	634.7
n-octadecanoic acid	1 and 2	5.056	-5.617	5.282	3.443	644.2	648.1
	3 and 4	5.165	-5.693	5.473	3.273	645.1	648.1
elaidic acid	1 and 2	5.204	-5.742	5.587	3.088	650.5	
	3 and 4	5.275	-5.794	5.716	2.996	650.1	
linoleic acid	1 and 2	5.440	-5.946	6.061	2.549	661.4	
	3 and 4	5.437	-5.955	6.091	2.528	661.1	
α-linolenic acid	1 and 2	5.587	-6.099	6.288	2.345	669.9	
	3 and 4	5.633	-6.153	6.459	2.175	670.9	
n-nonadecanoic acid	3 and 4	5.279	-5.858	5.615	3.167	656.8	659.2[a]
γ-linolenic acid	3 and 4	5.597	-6.104	6.409	2.218	667.3	
n-eicosanoic acid	3 and 4	5.488	-6.097	5.926	2.954	670.9	
n-henicosanoic acid	3 and 4	5.422	-6.120	5.696	3.189	677.1	
n-docosanoic acid	3 and 4	5.524	-6.276	5.809	3.115	688.2	
erucic acid	3 and 4	5.699	-6.424	6.223	2.630	695.9	

[a] Reference [15].

A comparison of the results of duplicate runs 1 and 2 and runs 3 and 4 in Table 3-11 for six of the acids resulted in an average precision of ± 0.4 K. When appropriate standards are chosen for the correlations, the accuracy in predicting boiling temperature by this method has usually been within ± 5 K.[16,17,18] Boiling temperatures for a few of the other acids of this study are available at reduced pressures.[19,20,21,21] Boiling temperatures at reduced pressures generally tend to be less reliable. These results are summarized in Table 3-12 below.

Table 3-12. A Summary of Various Literature Boiling Temperatures (BT) at Reduced Pressures

	$\ln(p/p_o)$	BT/K Runs 3&4 calc	BT/K lit	Ref
linoleic acid	-7.33	450.9	450.2	19
n-nonadecanoic acid	-4.33	510.8	503.2, 511	20, 21
α-linolenic acid	-8.47	437.7	420.2	22

Interest in the vapor pressures of the sub-cooled liquid form arises from the fact that fatty acids are one of many components present in aerosols and as such are not necessarily present in crystalline form. Partitioning between the gas and condensed phase has been modeled by an empirical relationship using the vapor pressure of the sub-cooled liquid.[23] Column 3 of Table 3-13 on the next page lists the sub-cooled vapor pressures evaluated in this study at T/K = 298.15 and compares them to either an EPA database or estimates, generated from the EPI Suite.[24] The uncertainties in these values were calculated from the uncertainties reported in the last column of Table 3-10. This resulted in vapor pressures that vary by a factor of approximately (1.8 to 2.5) of the value reported in Table 3-13. As indicated in this table, the vapor pressures of the sub-cooled liquid are quite low.

Agreement for n-tetradecanoic acid through n-octadecanoic acid is reasonably good considering the vapor pressures reported are in micro-Pascals. Agreement between this work and the estimated values is considerably worse. As the last two columns of Table 3-13 indicate, the EPI Suite estimates[24] do not show the trend in vapor pressure observed in this work with increasing molecular size.

Table 3-13. Predicted Vapor Pressures at T/K= 298.15 of the Sub-cooled Liquid

	Runs	$p*10^{-6}$/Pa		MW^b
		tw^a	lit	
n-tetradecanoic acid	1 and 2	800	340^c 360^d	228.4
n-pentadecanoic acid	1 and 2	274	108^e	242.4
n-hexadecanoic acid	1 and 2, 3 and 4	93, 98	117^e, 14^c	256.4
n-heptadecanoic acid	1 and 2, 3 and 4	31, 33	19^e	270.5
n-octadecanoic acid	1 and 2, 3 and 4	11, 11	261^e, 2.2^c	284.5
elaidic acid	1 and 2, 3 and 4	9.2, 9.3	288^e	282.5
linoleic acid	1 and 2, 3 and 4	6.4, 6.2	116^e	280.5
α-linolenic acid	1 and 2, 3 and 4	3.5, 3.4	72^e	278.4
n-nonadecanoic acid	3 and 4	3.9	$26*10^{4\ d}$	298.5
γ-linolenic acid	3 and 4	4.5	na^f	278.4
n-eicosanoic acid	3 and 4	1.3	0.76^d	312.5
n-heneicosanoic acid	3 and 4	0.5	430^d	326.6
n-docosanoic acid	3 and 4	0.2	223^d	340.6
erucic acid	3 and 4	0.1	182^d	338.6

[a] This work.
[b] Molecular weight used as a rough measure of molecular size.
[c] Measured by temperature – programmed desorption, ref [1].
[d] Estimated using EPI Suite, reference [24].
[e] Experimental database, EPI Suite, reference [24].
[f] Not available.

Sublimation enthalpies can be evaluated from the available fusion and vaporization enthalpies at the melting temperature according to equation 3-3. The presence of the numerous polymorphic forms reported in Table 3-3 obviously complicates the calculation of sublimation enthalpy. Table 3-14 below summarizes the sublimation enthalpies calculated using the vaporization and fusion enthalpies or total phase change enthalpies reported in articles by De Kruif et al.[4] and Schaake et al.[10,11] whose measurements were made on the same samples.[4]

Table 3-14. Sublimation Enthalpies of the Fatty Acids in This Study

	ΔH_{tpce}(298 K) kJ·mol^{-1}	$\Delta H_{\text{vap}}(T)^a$ kJ·mol^{-1}	ΔH_{vap}(298 K)^b kJ·mol^{-1}	ΔH_{sub}(298 K)^c kJ·mol^{-1}	ΔH_{sub}(298 K)^d kJ·mol^{-1} (lit.)
n-tetradecanoic acid	42.8±0.7^e	107.1/105.6	111.3±2.2	154.0±2.3^f	148.8±3.9
n-pentadecanoic acid	47.3±0.7	113.2/110.3	117.3±2.2	164.5±2.3	
n-hexadecanoic acid	50.4±1.0^e	114.7/112.9	120.7±2.3	169.3±2.7^f	166.7±4.4
n-heptadecanoic acid	55.4±1.0	119.0/117.7	125.0±2.3	180.4±2.5	
elaidic acid	56.8±0.5	129.7/125.6	133.0±10.3	189.7±10.3	
n-octadecanoic acid	56.9±1.3^e	125.3/121.1	133.1±2.4	190.0±2.7^f	172.2±4.5
n-nonadecanoic acid	62.5±1.3	130.0/125.7	137.9±2.4	200.4±2.7	
n-eicosanoic acid	64.0±1.6^e	134.0/129.0	143.6±2.5	207.6±3.0^f	206.5±7.8
n-heneicosanoic acid	62.7±3.6	139.6^g/133.7	149.2±7.1	211.9±8.0	
n-docosanoic acid	63.8±1.8	143.4^g/137.0	154.7±7.3	218.5±7.5	201.8±8.3

[a] The first value corresponds to ΔH_{vap} adjusted to T_{tp} or T_{fus} using equation 3-14 and the second value was calculated by extrapolating the vapor pressures calculated using equation 3-13 over a T/K= 30 temperature range centered at either at T_{tp} or T_{fus}; T_{tp}: triple point.
[b] Temperature adjustments from T/K= (T_{m} to 298.15) using equation 3-14.
[c] The sum of columns 2 and 4; uncertainties are combined values.
[d] From Davies and Malpass;[25] temperature adjustments from T/K= (T_{m} to 298.15) using equation 3-15.
[e] Fusion enthalpy.
[f] Sublimation enthalpy for the orthorhombic (C)[10] form of the acid.
[g] This work, adjusted to T_{fus} from T/K = 298.15 using equation 3-15.

Fusion enthalpies for n-heneicosanoic acid are from Gbabode *et al*.[9] and results for n-docosanoic acid are from this work. Vaporization enthalpies are included at both T/K = 298.15 and at the triple point (T_{tp}) or the melting temperature (T_{fus}). The first set of vaporization enthalpies listed at $T = T_{\text{tp}}$, column 3 of Table 3-14, are results from De Kruif *et al*.[4] adjusted to this temperature using equation 3-14.

$$\Delta H_{\text{vap}}(298.15 \text{ K})/(\text{kJ·mol}^{-1}) = \Delta H_{\text{vap}}(T_{\text{m}}) +$$

$$[(10.58 + 0.26*C_p(\text{l})/(\text{J·mol}^{-1}\cdot\text{K}^{-1}))(T_{\text{m}}/\text{K} - 298.15 \text{ K})]/1000 \qquad (3\text{-}14)$$

The second set of vaporization enthalpies were obtained from vapor pressures calculated using equation 3-13, the constants listed in Table 3-11, and the Clausius−Clapeyron

equation for liquids at a temperature centered at the triple point. Agreement between the two sets of values in column 3 is within the combined uncertainties associated with both the measurements and their temperature adjustments. The sublimation enthalpies calculated in column 5 of Table 3-14 using equation 3-3 are the sum of vaporization and fusion enthalpies evaluated at $T/\text{K} = 298.15$ for the orthorhombic, or C, form. They are, for the most part, in good agreement with the literature values of Davies and Malpass[25] obtained by Knudsen effusion. The measurements conducted on the even carboxylic acids reported by Davies and Malpass used samples that were melted and re-solidified near their melting temperature to ensure that their measurements were performed on acids in their C form.[8] Only the results reported for n-octadecanoic acid are in strong disagreement.

Direct experimental measurement of subcooled vapor pressures is possible for only a few compounds. Consequently, current interest on atmospherically relevant compounds found in aerosols has focused on vapor pressure measurements of the solid state. Experimental techniques employed include the use of a tandem differential mobility analyzer,[3] and more recently, thermal desorption mass spectrometry studies have been reported.[1,2] Also available are the vapor pressure data of Davies and Malpass from Knudsen effusion studies.[25] The calculation of sublimation vapor pressures is also possible using a combination of gas chromatography and computation.[26] The latter method relies on using available vapor pressure measurements from the literature either evaluated at or extrapolated to the fusion temperature or triple point. Vaporization enthalpies obtained by gas chromatography and adjusted to the triple point temperature (or T_{fus}) when combined with experimental fusion enthalpies provide access to both the sublimation enthalpy and the vapor pressure common to both the solid and liquid at this temperature. If the melting

temperature is near room temperature, adjusting the sublimation enthalpy to the mean temperature, $(T_{fus} + 298.15)/2$, by inclusion of a heat capacity adjustment term, equation 3-15, and using the Clausius−Clapeyron equation for solids, equation 3-16, provides a value for the vapor pressure at $T/K = 298.15$.

$$\Delta C_p(cr)\Delta T = (0.75 + 0.15\ C_p(cr))((T_{fus/tp}/K\ \text{-}298.15\ K)/2) \tag{3-15}$$

$$\ln(p_{(298)}) = [\Delta H_{sub}(T_{fus/tp}) + \Delta C_p(cr)\Delta T]\ \text{x}$$

$$[1/T_{fus/tp}/K - 1/298.15]/R + \ln(p_{(Tfus/tp)}) \tag{3-16}$$

Equation 3-15 has previously been shown to provide reasonable enthalpic temperature adjustments for solids.[5] For those substances with additional solid−solid phase transitions, the calculations need to be performed in steps. Equation 3-16 is used to calculate the vapor pressure at the transition temperature. Addition of the phase transition enthalpy to the sublimation enthalpy along with a second heat capacity adjustment followed by a second calculation performed from the transition temperature to $T/K = 298.15$ provides a vapor pressure at $T/K = 298.15$. The vapor pressure evaluated at the transition temperature, T_t, from the first calculation is then used in equation 3-16. A similar protocol can be used for compounds whose melting temperature is further removed from $T/K = 298.15$. This protocol has been shown previously to reproduce experimental sublimation vapor pressures measured by experimental methods to within a factor of 3.[26] Table 3-15 summarizes the vapor pressures calculated using this protocol (equation 3-16) and the sublimation enthalpies of Table 3-14 and compares the results to available vapor pressures and sublimation enthalpies from the recent literature.

Table 3-15. A Comparison of Vapor Pressures (Pa) and Sublimation Enthalpies (kJ·mol^{-1}) at T/K= 298.15

Reference	tw[a]	[1]	[2]	[3]	[25][b]	[24]
n-tetradecanoic acid						
p_s(298 K)/Pa	(1.6±0.1)E-04	3.15E-04	0.7E-04	2.0E-04	2.58E-04	3.46E-02
ΔH_{sub}(298 K)	154.1±2.3	123.1	168.6	163.8	148.8±3.9	
n-pentadecanoic acid						
p_s(298 K)/Pa	(5.4±0.4)E-05	17.5E-05		10.5E-05		1.8E-02
ΔH_{sub}(298 K)	164.5±2.3	142.0		163.7		
n-hexadecanoic acid						
p_s(298 K)/Pa	(9.1±0.1)E-06	26.6E-06	0.13E-06	10.6E-06	19.0E-06	7.4E-03
ΔH_{sub}(298 K)	169.3±2.7	132.8	193.8±11	177.4	166.7±4.4	
n-heptadecanoic acid						
p_s(298 K)/Pa	(2.8±0.1)E-06	21.0E-06		11.6E-06		8.31E-06
ΔH_{sub}(298 K)	180.4±2.5	150.0		178.0		
elaidic acid						
p_s(298 K)/Pa	(2.2±0.2)E-06					6.84E-03
ΔH_{sub}(298 K)	189.7±10.3					
n-octadecanoic acid						
p_s(298 K)/Pa	(4.5±0.7)E-07	28.3E-07	1.0E-07	5.6E-07	13.8E-07	1.1E-03
ΔH_{sub}(298 K)	190.0±2.7	158.8	204.1±9	190.9	172.2±4.5	
n-nonadecanoic acid						
p_s(298 K)/Pa	(4.8±0.4)E-07	17.8E-07				9.94E-02
ΔH_{sub}(298 K)	200.4±2.7	145.0				
n-eicosanoic acid						
p_s(298 K)/Pa	(2.4±0.5)E-08	32.5E-08			4.13E-08	1.93E-02
ΔH_{sub}(298 K)	207.6±3.0	151.0			206.5±7.8	
n-heneicosanoic acid						
p_s(298 K)/Pa	(1.0±0.2)E-08	21.8E-08				2.25E-05
ΔH_{sub}(298 K)	208.1±7.3	147.9				
n-docosanoic acid						
p_s(298 K)/Pa	(2.3±0.6)E-09	48.9E-09			7.04E-09	6.52E-05
ΔH_{sub}(298 K)	218.4±7.5	153.0			205.3±8.3	

[a] This work. The vapor pressures are believed known to within a factor of three of the value reported.[26] The uncertainty reported provides a simple measure of the vapor pressure differences calculated using the two enthalpy values reported in column 3 of Table 3-14.

[b] The results assume the absence of any phase transitions occurring between the temperature of measurement and T/K = 298.15.

The second column in Table 3-15 includes the results of this work taking into account the solid−solid phase transitions as measured by Schaake *et al.*[11] for the carboxylic acids with an odd number of carbon atoms. The vapor pressures reported in column 2 of Table 3-15

are an average calculated using the two vaporization enthalpies cited in column 3 of Table

3-14 to calculate the sublimation enthalpy. The uncertainty in the vapor pressure cited

reflects the numerical differences in vapor pressure obtained using the two different

vaporization enthalpies in Table 3-14 as discussed above. For example, the two vapor

pressures calculated for n-tetradecanoic acid were (1.5 and 1.7)$\cdot 10^{-4}$ Pa. As noted

previously, this method of obtaining vapor pressures of the solid phase is only capable of

reproducing experimental vapor pressures within a factor of 3.[26] A third calculation (not

included) that totally ignored the enthalpies associated with the phase transitions of the

fatty acids studied did not have a very large impact on the vapor pressures calculated.

Column 3 lists the sublimation enthalpies reported by Chattopadhyay and Ziemann[1] on

organic aerosol particles as measured by thermal desorption methods. All were measured

at temperatures below any of the solid−solid phase transitions listed in Table 3-3.

Sublimation enthalpies reported by these workers were adjusted to T/K = 298.15 using

equation 3-15 to account for the heat capacity differences between the solid and gas phase.

As noted in the table, these sublimation enthalpies are considerably smaller than those

listed in column 2 and the vapor pressures greater than the results reported by the others.

The sublimation enthalpies and vapor pressures reported by Cappa $et\ al.$[2] in column 4 also

on organic aerosol particles by thermal desorption methods were provided at T/K = 298.15

by the authors. Measurements were conducted over a range of temperatures up to the

melting temperature of the acids. Details on how the properties reported at T/K = 298.15

were obtained are not available.[2] The sublimation enthalpy values reported by these

workers are considerably larger than calculated using equation 3-3, while the reported

vapor pressures are smaller in magnitude.

The vapor pressures and vaporization enthalpies reported by Tao and McMurry[3] using a tandem differential mobility analyzer are provided in column 5. Both vapor pressure and sublimation enthalpies were calculated using the equations cited in their text. Since additional details are not reported, it is difficult to evaluate the data. Their results however are generally in good agreement with this work.

The experimental results reported by Davies and Malpass[25] obtained by Knudsen effusion are reported in column 6. As noted above, their measurements on the even acids were performed on samples in their C form.[8] The sublimation enthalpies reported are generally consistent with the results of this work as are the vapor pressures calculated by extrapolating their equations describing the temperature dependence of sublimation pressure. It is surprising that despite the large difference in sublimation enthalpy reported for n-octadecanoic acid between their work and this work, the vapor pressures calculated by the two methods are within the experimental uncertainty noted above.

The last column lists the values available from the EPI Suite.[24] The trend in vapor pressure as a function of the number of carbon atoms observed in this work is obviously not reproduced. A qualitative evaluation of these results is summarized by Figure 3-3 below where the vapor pressures of the saturated fatty acids are reported in logarithmic terms and compared as a function of the number of carbon atoms. With the exception of n-nonadecanoic acid, the results from this work (solid circles) appear remarkably linear with carbon number. The relationship between $\ln(p_{298})$ and carbon number is provided in the caption under the figure.
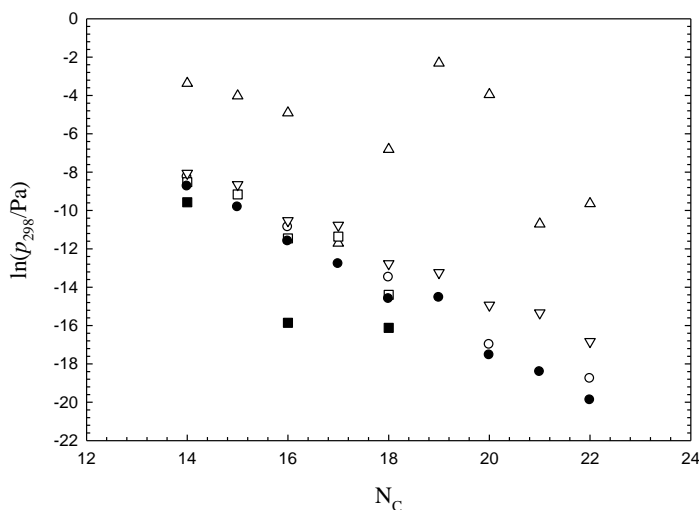
Figure 3.3. A plot of $\ln(p_{298}/\text{Pa})$ against the number of carbon atoms of the solid saturated fatty acids; ●, this work; ■, Cappa *et al.*;[2] □, Tao and McMurry;[3] ▽, Chattopadhyay and Ziemann;[1] ○, Davies and Malpass;[25] △, EPI Suite.[24] The results of this work are reasonably well-described by the linear relationship: $\ln(p_{298}/\text{Pa}) = -(1.4 \pm 0.06)N_C + (10.99 \pm 1.15)$; $r^2 = 0.9860$.

Finally, comparing the vapor pressures of the subcooled liquid (Table 3-13) to the solid at $T/\text{K} = 298.15$ (Table 3-15) reveals a difference of roughly a factor of 4 for n-tetradecanoic acid based on this work. This increases to a factor of roughly 100 for n-docosanoic acid.

3.5 Summary

This study used correlation gas chromatography to measure the vaporization enthalpies of several long-chain fatty acids. The measured values agree reasonably well with the literature values for the standards. Vaporization enthalpies for the target compounds were measured to be, respectively ($\Delta H_{vap}(298.15 \text{ K}) \text{ kJ·mol}^{-1}$): α-linolenic acid, (136.9 ± 10.4); γ-linolenic acid, (135.9 ± 6.8); linoleic acid, (134.1 ± 10.3); elaidic acid, (133.0 ± 10.3); n-

heneicosanoic acid, (149.2 ± 7.1); erucic acid, (149.2 ± 7.1); and n-docosanoic acid (154.7 ± 7.3).

Literature and measured vaporization, sublimation, and fusion enthalpies were combined and used to predict vapor pressures of both the solid and sub-cooled liquid state of a series of saturated and unsaturated fatty acids. The results were compared to similar properties reported in studies aimed at the development of estimations useful for predicting vapor pressures of compounds with low volatility typically found in atmospheric aerosols. While significant differences are observed in sublimation enthalpies as reported by different workers and techniques, the calculated vapor pressures, given their magnitude, appear to be generally in qualitative agreement with the estimations.

3.6 References

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Chapter IV: More Long Chain Fatty Acids

4.1 Introduction

As stated in the previous chapter, fatty acids are aliphatic carboxylic acids that may be either saturated or unsaturated. Naturally occurring fatty acids have chain lengths from 4 to 28 carbons. For this study, some thermodynamic properties of several additional long chain fatty acids, all with chain lengths between 18 and 26 carbons, were studied.

The importance of the long chain fatty acids has been described in the previous chapter. The very long chain fatty acids occur naturally in the outer coverings of fruits and vegetables as well as in human tissues such as the myelin sheath membranes.[1] Many of the compounds in this study are of interest for use as industrial oils[2] and as nutritional supplements.[3]

This chapter describes measurement of the vaporization enthalpies and evaluation of the vapor pressures of several mono-unsaturated fatty acids and one poly-unsaturated fatty acid as well as the vaporization enthalpies and vapor pressures of n-tetracosanoic acid and n-hexacosanoic acid, both of which are saturated fatty acids. The vaporization enthalpies were measured by correlation-gas chromatography and adjusted to $T/K = 298.15$ by taking advantage of the published research from the previous chapter of this work[4]. Vapor pressures also were obtained through correlations using gas chromatographic retention time data.

The compounds investigated in this study include petroselinic acid ($C_{18}H_{34}O_2$, *cis*-6-octadecenoic acid), gondoic acid ($C_{20}H_{36}O_2$, *trans*-11-eicosenoic acid), n-tetracosanoic acid ($C_{24}H_{48}O_2$), nervonic acid ($C_{24}H_{46}O_2$, *cis*-15-tetracosenoic acid), cervonic acid ($C_{26}H_{40}O_2$, *cis,cis,cis,cis,cis,cis*-4,7,10,13,16,19-docosahexaenoic acid), and n-

hexacosanoic acid ($C_{26}H_{52}O_2$). The structures of these target acids are shown in Figure 4-1.

petroselinic acid (cis-6-octadecenoic acid

gondoic acid (trans-11-eicosenoic acid)

n-tetracosanoic acid

nervonic acid (cis-15-tetracosenoic acid)

n-hexacosanoic acid

cervonic acid ((cis,cis,cis,cis,cis,cis)-4,7,10,13,16,19-docosahexaenoic acid)
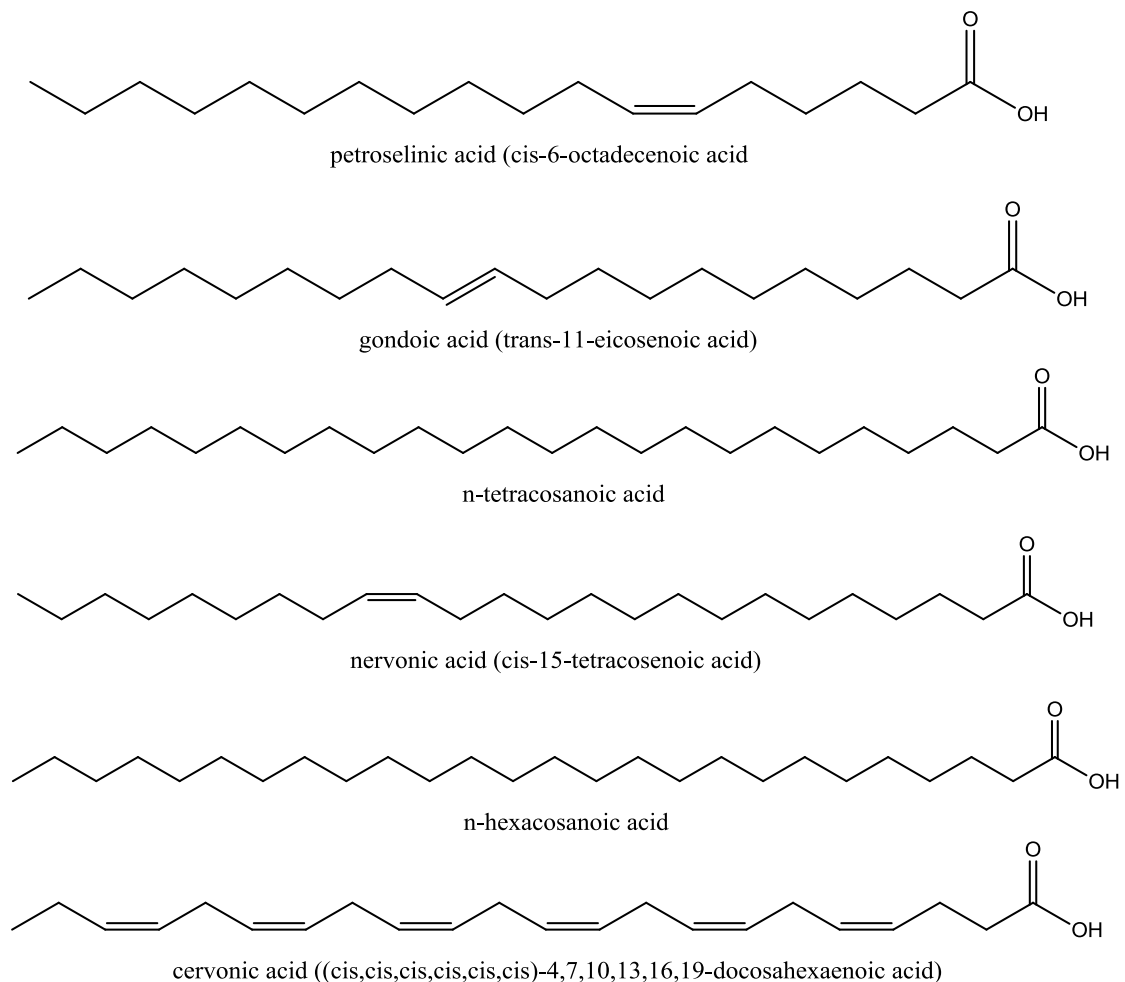
Figure 4-1: Structures of the acids being investigated in this study

4.2 Vaporization Enthalpies and Vapor Pressures of the Standards

Vaporization enthalpies and vapor pressures of the standards used in this study are taken from the previous chapter's published research[4]. For the acids that are solids at T/K = 298.15, the vaporization enthalpies reported are for the sub-cooled liquid. Tables 4-1 and

4-2 provide the vaporization enthalpy and vapor pressure values respectively for the standards used in this study.

Table 4-1. Vaporization Enthalpies of the Standards at T/K = 298.15

	ΔH_{vap}(298 K) kJ·mol^{-1}
n-hexadecanoic acid	120.7
linoleic acid	134.1
n-eicosanoic acid	143.6
erucic acid	154.5

Table 4-2. Vapor Pressures of the Standards at T/K = 298.15

	p(298 K)/Pa
n-hexadecanoic acid	$9.6*10^{-5}$
linoleic acid	$6.3*10^{-6}$
n-eicosanoic acid	$1.3*10^{-6}$
erucic acid	$1.5*10^{-7}$

These four compounds were selected to serve as standards for this study because they eluted separately from the target compounds across the entire 30 degree temperature range of the experiments. Two of the standards are saturated (n-hexadecanoic acid and n-eicosanoic acid), one of the standards is mono-unsaturated (erucic acid), and the remaining standard is di-unsaturated (linoleic acid), thus structurally closely related to the target compounds.

4.3 Experimental Conditions

The fatty acids were obtained in kit form from Supelco. The compounds are identified and characterized in Table 4-3. The liquid samples were provided in sealed ampules by the supplier. The purities of the samples are generally not important since these experiments are conducted as dilute mixtures and the chromatography separates most other

components present. All of the samples were analyzed by gas chromatography before use.

Their analysis is reported in Table 4-3.

Table 4-3. Description of the Chemical Samples[a]

CAS #	Chemical Name	Supplier	mass fraction
57-10-3	n-hexadecanoic acid (palmitic acid, (c))	Supelco	0.984
60-33-3	*cis,cis*-9,12-octadecadienoic acid (linoleic acid, (l))	Supelco	0.997
506-30-9	n-eicosanoic acid (arachidic acid, (c))	Supelco	0.985
112-86-7	*cis*-13-docosenoic acid (erucic acid, (c))	Supelco	0.997
593-39-5	*cis*-6-octadecenoic acid (petroselinic acid, (c))	Supelco	0.982
5561-99-9	*trans*-11-eicosenoic acid (gondoic acid, (c))	Supelco	0.974
557-59-5	n-tetracosanoic acid (lignoceric acid, (c))	Supelco	0.993
506-37-6	*cis*-15-tetracosenoic acid (nervonic acid, (c))	Supelco	0.991
6217-54-5	*cis,cis,cis,cis,cis,cis*-4,7,10,13,16,19-docosahexaenoic acid (cervonic acid, (l))	Supelco	0.982
506-46-7	n-hexacosanoic acid (cerotic acid, (c))	Supelco	0.992

[a] The chemicals that were used were all commercial samples and all were analyzed by gas chromatography; chemical purities from the supplier were not available; (c): crystalline; (l): liquid at $T/K = 298$.

All experiments were performed on an HP 5890 Series II Gas Chromatograph equipped with a flame ionization detector and run at a split ratio of approximately 100/1. Retention times were recorded on an HP ChemStation. The compounds were run isothermally on a 0.32 mm ID, 15 m J&W FFAP column. Column temperatures were monitored independently using a Fluke digital thermometer. The temperature maintained by the gas chromatograph was constant to ± 0.1 K. Helium was used as the carrier gas.

Methylene chloride was again used as the solvent, and at the temperatures of these experiments, it also served as the non-retained reference. The non-retained reference can be identified since its retention time increases slightly with temperature due to an increase in the viscosity of the carrier gas. The enthalpies of transfer measured depend both on the nature of the column and various instrumental parameters used such as flow rate and

temperature. The results following the correlation with the vaporization enthalpies of the standards, however, remain independent of the experimental conditions.

Adjusted retention times, t_a, were calculated for each analyte as the difference between the retention time of the given analyte and that of the non-retained reference. This was repeated over a 30 K range at 5 K intervals from $T/K = 485 - 515$. The slope of the line was obtained for each run and multiplied by the gas constant to give the enthalpy of transfer at the mean temperature of each of the experiments as $-\Delta H_{trn}(T_m)$.

Correlation of the vaporization enthalpies of the standards with the enthalpies of transfer resulted in a linear relationship from which the vaporization enthalpies of the target compounds could be evaluated. In a similar fashion, the vapor pressures of the standards, $\ln(p/p_o)$ where $p_o/Pa = 1$, were correlated with $\ln(t_o/t_a)$ where $t_o/min = 1$. This also resulted in a linear relationship from which $\ln(p/p_o)$ of the target compounds were evaluated as described below. This procedure was repeated at 15 K intervals from $T/K = 298.15$ to the boiling temperature of the most volatile standard, in this case n-hexadecanoic acid.

All plots were characterized by correlation coefficients, r^2, of >0.99. The enthalpy of transfer, $\Delta H_{trn}(T_m)$, is thermodynamically related to the corresponding vaporization enthalpy, $\Delta H_{vap}(T_m)$, by equation 4-1 below where the term $\Delta H_{intr}(T_m)$ refers to the enthalpy of interaction of the analyte with the column.[5]

$$\Delta H_{trn}(T_m) = \Delta H_{vap}(T_m) + \Delta H_{intr}(T_m) \qquad (4\text{-}1)$$

All combined uncertainties in the tables were calculated as $(u_1^2 + u_2^2 + ...)^{0.5}$. Uncertainties for values derived from linear correlations were calculated from both the uncertainties in

the slope and intercept of the correlation equations derived between the vaporization enthalpies of the standards and the enthalpies of transfer.

4.4 Results and Discussion

The experimental retention times for the duplicate runs of this study are reported in Appendices C-1 and C-2 of Appendix C. Table 4-4 below summarizes the results of correlations between the enthalpy of transfer measured by gas chromatography and literature vaporization enthalpies. Equations 4-2 and 4-3 below each correlation define the quality of the linear relationship observed between $\Delta_{trn}H_m(T_m)$ and $\Delta H_{vap}(298\ K)$ for each run.

Table 4-4. Correlation of Vaporization Enthlpies with Enthalpies of Transfer of Some Fatty Acids.

Run 1	slope T/K	intercept	ΔH_{trn} (500 K) kJ·mol^{-1}	ΔH_{vap}(298 K) kJ·mol^{-1} (lit)	ΔH_{vap}(298 K) kJ·mol^{-1} (calc)
n-hexadecanoic acid	-9239.19	18.29264	76.81	120.7	120.7 ± 2.3
petroselininc acid	-9842.61	18.84836	81.83		130.9 ± 2.4
linoleic acid	-10043.8	19.08636	83.50	134.1	134.3 ± 2.4
n-eicosanoic acid	-10578.9	19.82859	87.95	143.6	143.4 ± 2.5
gondoic acid	-10589.8	19.76039	88.04		143.6 ± 2.3
erucic acid	-11245.4	20.51184	93.49	154.5	154.7 ± 2.4
n-tetracosanoic acid	-12266.8	22.04201	101.98		172.0 ± 2.6
nervonic acid	-12260.4	21.9412	101.93		171.9 ± 2.6
cervonic acid	-11745.5	20.85715	97.65		163.2 ± 2.6
n-hexacosanoic acid	-12570.9	22.13374	104.51		177.1 ± 2.7

$\Delta_l^g H_m(298.15\ K)/kJ·mol^{-1} = (2.04 \pm 0.02)\ \Delta H_{trn}\ (500\ K) - (36.0 \pm 1.6);\ r^2 = 0.9998$ (4-2)

Run 2	slope T/K	intercept	$\Delta H_{trn}(490\ K)$ $kJ{\cdot}mol^{-1}$	$\Delta H_{vap}(298\ K)$ $kJ{\cdot}mol^{-1}$ (lit)	$\Delta H_{vap}(298\ K)$ $kJ{\cdot}mol^{-1}$ (calc)
n-hexadecanoic acid	-9380.49	18.64092	77.99	120.7	120.8 ± 1.7
petroselininc acid	-10019.6	19.27452	83.30		131.4 ± 1.8
linoleic acid	-10179	19.42671	84.62	134.1	134.0 ± 1.9
n-eicosanoic acid	-10753	20.25069	89.40	143.6	143.5 ± 1.9
gondoic acid	-10747.8	20.14849	89.35		143.4 ± 1.8
erucic acid	-11431.7	20.96144	95.04	154.5	154.7 ± 1.9
n-tetracosanoic acid	-12332.9	22.24524	102.53		169.6 ± 2.0
nervonic acid	-12323.8	22.14001	102.46		169.5 ± 2.0
cervonic acid	-11917	21.28137	99.07		162.7 ± 2.0
n-hexacosanoic acid	-12803.1	22.68197	106.44		177.4 ± 2.0

$$\Delta_l^g H_m(298.15\ K)/kJ{\cdot}mol^{-1} = (1.99 \pm 0.01)\ \Delta H_{trn}\ (500\ K) - (34.3 \pm 1.0);\ \ r^2 = 0.9999 \quad (4\text{-}3)$$

Using the slopes and intercepts from Table 4-4, calculated values of $\ln(p/p_{atm})$ of the standards were correlated against $\ln(t_o/t_a)_{av}$, both at $T_m/K = 298.15$. These results are shown in Table 4-5 below.

Table 4-5. Correlation of $\ln(t_o/t_a)$ with Experimental $\ln(p/p_{atm})$ Values at $T/K = 298.15$

Runs 1and 2	slope/K (1)	intercept (1)	slope/K (2)	intercept (2)	$\ln(t_o/t_a)_{av}$	$\ln(p/p_{atm})$ lit	$\ln(p/p_{atm})$ calc
n-hexadecanoic acid	-9239.2	18.293	-9380.5	18.641	-12.76	-20.76	-20.8±0.1
petroselininc acid	-9842.6	18.848	-10019.6	19.275	-14.24		-22.9±0.2
linoleic acid	-10043.8	19.086	-10179.0	19.427	-14.66	-23.52	-23.5±0.2
n-eicosanoic acid	-10578.9	19.829	-10753.0	20.251	-15.73	-25.05	-25.0±0.2
gondoic acid	-10589.8	19.760	-10747.8	20.148	-15.83		-25.2±0.2
erucic acid	-11245.4	20.512	-11431.7	20.961	-17.29	-27.26	-27.3±0.2
n-tetracosanoic acid	-12266.8	22.042	-12332.9	22.245	-19.11		-29.9±0.2
nervonic acid	-12260.4	21.941	-12323.8	22.140	-19.19		-30.0±0.2
cervonic acid	-11745.5	20.857	-11917.0	21.281	-18.61		-29.2±0.2
n-hexacosanoic acid	-12570.9	22.134	-12803.1	22.682	-20.14		-31.4±0.2

$$\ln(p/p_{atm})_{calc} = (1.434\pm0.075)\ \ln(t_o/t_a) - (2.48\pm0.114) \qquad r^2 = 0.9999 \qquad (4\text{-}6)$$

The resulting equation obtained from the correlation in Table 4-5, equation 4-6 obtained at $T/K = 298.15$, was used to calculate the corresponding $\ln(p/p_{atm})$ values of the acids in the mixture. This process was repeated over 15 K intervals from $T/K = (298.15\ to\ 630)$. The

values of $\ln(p/p_{atm})$ as a function of temperature calculated from each correlation were tabulated and fit to the third-order polynomial, equation 4-7.

$$\ln(p/p_{atm})_{calc} = AT^{-3} + BT^{-2} + CT^{-1} + D \tag{4-7}$$

The constants of equation 4-7 obtained are tabulated in Table 4-6 below. In all correlations performed as a function of temperature, the correlation coefficient at each temperature, r^2, exceeded 0.99. The upper temperature limit was chosen so as not to exceed the boiling temperature of the most volatile component, n-hexadecanoic acid.

Table 4-6. Coefficients of Equation 4-7 for the Fatty Acids and Calculated and Estimated[b] Boiling Temperatures

	$A*10^8$	$B*10^6$	$C*10^3$	D	BT/K calc	BT/K lit
n-hexadecanoic acid	5.148	-5.510	5.558	3.155	622.6	622.2[a]
petroselininc acid	5.539	-6.032	6.289	2.369	654.0	672.2[b]
linoleic acid	5.292	-5.948	5.560	3.248	661.4	661.4[a]
n-eicosanoic acid	5.545	-6.320	5.991	2.798	667.2	670.9[a]
gondoic acid	5.488	-5.944	6.203	2.455	675.2	699.5[b]
erucic acid	5.486	-6.115	6.022	2.715	696.1	695.9[a]
n-tetracosanoic acid	5.014	-6.095	4.522	4.562	697.8	679.1[b]
nervonic acid	5.218	-6.268	5.008	4.001	706.0	752.4[b]
cervonic acid	6.118	-6.927	7.232	1.400	738.1	N/A[c]
n-hexacosanoic acid	5.455	-6.554	5.432	3.536	725.6	691.9[b]

[a] From previous chapter published research, reference [4]
[b] Estimate, ACD labs, SciFinder Scholar, substance identifier, thermal properties, reference [6]
[c] Not Available

When appropriate standards are chosen for the correlations, the accuracy in predicting boiling temperature by this method has usually been within ± 5 K.[7,8,9]

Interest in the vapor pressures of the sub-cooled liquid form arises from the fact that fatty acids are one of many components present in aerosols and as such are not necessarily present in crystalline form. Partitioning between the gas and condensed phase has been

modeled by an empirical relationship using the vapor pressure of the sub-cooled liquid.[10]

Column 2 of Table 4-7 below lists the sub-cooled vapor pressures evaluated in this study

at T/K = 298.15 and compares them in column 3 to either an EPA database or estimates,

generated from the EPI Suite.[11] As indicated in this table, the vapor pressures of the sub-

cooled liquid are quite low.

Table 4-7. Predicted Vapor Pressures at T/K= 298.15 of the Sub-cooled Liquid

	p/Pa		MW[b]
	tw[a]	lit	
n-hexadecanoic acid	$9.8*10^{-5}$	$1.17*10^{-4}$ [e], $1.4*10^{-5}$ [c]	256.4
petroselinic acid	$1.2*10^{-5}$	$2.3*10^{-5}$ [f]	282.5
linoleic acid	$6.3*10^{-6}$	$1.16*10^{-4}$ [e]	280.5
n-eicosanoic acid	$1.3*10^{-6}$	$7.6*10^{-7}$ [d]	312.5
gondoic acid	$1.2*10^{-6}$	$2.5*10^{-6}$ [f]	310.5
erucic acid	$1.4*10^{-7}$	$1.82*10^{-4}$ [d]	338.6
n-tetracosanoic acid	$1.0*10^{-8}$	$3.4*10^{-5}$ [f]	368.3
nervonic acid	$9.3*10^{-9}$	$2.2*10^{-8}$ [f]	366.6
cervonic acid	$2.1*10^{-8}$	N/A[g]	328.5
n-hexacosanoic acid	$2.4*10^{-9}$	$1.2*10^{-5}$ [f]	396.7

[a] This work.
[b] Molecular weight used as a rough measure of molecular size.
[c] Measured by temperature – programmed desorption, reference [12].
[d] Estimated using EPI Suite, reference [11].
[e] Experimental database, EPI Suite, reference [11].
[f] Estimate, ACD labs, SciFinder Scholar, substance identifier, thermal properties, reference [6]
[g] Not Available

Agreement for n-hexadecanoic acid, linoleic acid, and n-eicosanoic acid is reasonably

good considering the vapor pressures reported are in micro-Pascals. Agreement between

this work and the estimated value of erucic acid is considerably worse. As the last two

columns of Table 4-7 indicate, the EPI Suite estimates[11] do not show the trend in vapor

pressure observed in this work expected with increasing molecular size.

The trend in vapor pressure as a function of the number of carbon atoms observed in this work is obviously not reproduced in the estimates from the EPI Suite.[11] A qualitative evaluation of these results is summarized by Figure 4-2 below where the vapor pressures of the fatty acids in this study are reported in logarithmic terms and compared as a function of the number of carbon atoms. With the exception of cervonic acid, the results from this work (solid circles) appear reasonably linear with carbon number.
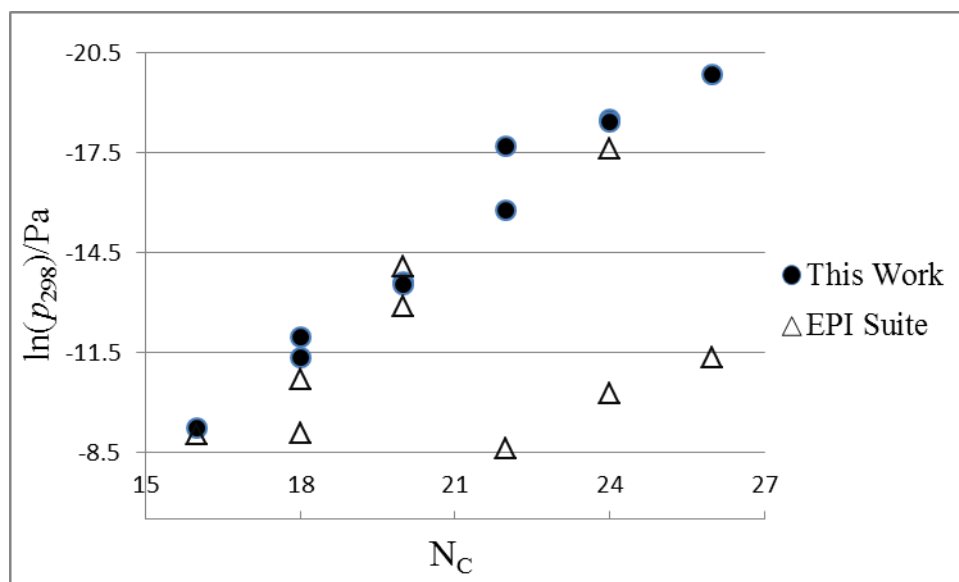
Figure 4.2. A plot of $\ln(p_{298}/\text{Pa})$ against the number of carbon atoms of the fatty acids in this study; ●, this work; △, EPI Suite.[11]

The results of this work are described by the linear relationship:

$$\ln(p_{298}/\text{Pa}) = -(1.113 \pm 0.07)N_C + (8.382 \pm 1.49); \; r^2 = 0.9693 \qquad (4\text{-}8)$$

When cervonic acid is omitted from the plotted data, the r^2 rises to 0.9930.

4.5 Summary

This study used correlation gas chromatography to measure the vaporization enthalpies of several long chain and very long chain fatty acids. The measured values agree reasonably well with the literature values for the standards. Vaporization enthalpies for the target compounds were measured to be, respectively (ΔH_{vap}(298.15 K) kJ·mol^{-1}): petroselinic acid, (131.2 ± 2.1); gondoic acid, (143.5 ± 2.1); n-tetracosanoic acid, (170.8 ± 2.3); nervonic acid, (170.7 ± 2.3); cervonic acid, (163.0 ± 2.3); and n-hexacosanoic acid (177.3 ± 2.4).

These retention times were also then used to predict vapor pressures of the target compounds. Vapor pressures for the target compounds were calculated to be, respectively (p(298.15 K) Pa): petroselinic acid, (($1.2 ± 0.01$)*10^{-5}); gondoic acid, (($1.2 ± 0.02$)*10^{-6}); n-tetracosanoic acid, (($1.1 ± 0.02$)*10^{-8}); nervonic acid, (($9.7 ± 0.2$)*10^{-9}); cervonic acid, (($2.2 ± 0.04$)*10^{-8}); and n-hexacosanoic acid (($2.5 ± 0.04$)*10^{-9}). Boiling temperatures are estimated to be, respectively (T, K): petroselinic acid, (654.0); gondoic acid, (675.2); n-tetracosanoic acid, (697.8); nervonic acid, (706.0); cervonic acid, (738.1); and n-hexacosanoic acid (725.6).

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Chapter V: Synthesis of 3-Hydroxydodecanedioic Acid and
3-Hydroxy-2,2-dideuterododecanedioic Acid

5.1 Introduction

There are many inheritable metabolic disorders and among the most prevalent of these are the ones that result in deficiencies of enzymes that catalyze the beta oxidation of fatty acids.[1] Discovery of these metabolic disorders is not easy since symptoms tend to be episodic in nature. Within the past several decades, diagnostic tests have been developed to detect these disorders. These tests include the measurement of acylcarnitine species in plasma,[2] the quantitation of acylglycine conjugates in urine,[3] and activity measurements of the oxidation of radiolabeled fatty acids by fibroblasts or cellular homogenates.[4]

Commonly, diagnosis of fatty acid metabolic disorders is accomplished through the analysis of organic acids in urine. When a patient is exhibiting symptoms of this type of metabolic disorder, a characteristic pattern of fatty acid metabolites (elevated dicarboxylic acids, with little or no 3-hydroxybutyric acid) will frequently be observed. However, the presence of dicarboxylic acids in urine is a nonspecific marker, with elevations occurring in prolonged fasting or when the diet contains a high percentage of calories as triglycerides. Moreover, several of the fatty acid disorders lead to elevation of dicarboxylic acids, and further testing is needed to distinguish between the possible specific deficiencies.

Deficiency of long-chain hydroxyacyl CoA-dehydrogenase (LCHAD) is among the most common of the fatty acid oxidation defects.[5] Children with this deficiency develop symptoms in the first 2 years of life; hypoglycemia (with little or no ketosis), cardiomyopathy, muscle hypotonia, and hepatomegaly are the most important symptoms.[6] Most patients have large amounts of dicarboxylic acids, including 3-hydroxysebacic acid, in their urine when they are symptomatic, but the qualitative pattern of urinary metabolites

is variable and difficult to distinguish from those seen in other fatty acid metabolic defects.

A good approach for the diagnosis of LCHAD deficiency is to quantitate the excretion of 3-hydroxydicarboxylic acids, which are alternative metabolic products of fatty acid metabolism. These metabolites likely accumulate in large quantities in LCHAD deficiency because of the inability of affected children to metabolize 3-hydroxy fatty acids, which are known to accumulate in the blood of LCHAD-deficient children.[7] In order to quantitate the excretion of 3-hydroxy long-chain dicarboxylic acids, suitable standards must be available.

This project involved the synthesis of 3-hydroxydodecanedioic acid and its di-deuterated analog. This compound possesses properties that may facilitate its quantitation as a metabolite in the urine of LCHAD-deficient children. The synthesis of the dideutero analog was performed by James Laird and the actual use of this compound and its di-deuterated analog as a diagnostic tool was performed by Dr. Michael Landt, Department of Pediatrics, Washington University School of Medicne at St. Louis Children's Hospital.

5.2 Analytical Methods

Unless otherwise indicated, ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were obtained in CDCl$_3$ solution on a Varian XL-300 (Varian, Palo Alto, CA) mHz NMR spectrometer. The ^{1}H chemical shifts are reported in δ units downfield from tetramethylsilane (TMS), while carbon spectra are referenced to the center line of the chloroform-d triplet at 77.00 ppm. Nuclear magnetic

data are reported as follows: chemical shift; multiplicities abbreviated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; and number of protons. All melting points were determined on a Thomas Hoover capillary melting point apparatus (Philadelphia, PA) and are not corrected. Infrared spectra, reported as υ_{max} wavelengths, were obtained with a Perkin Elmer 1600 FTIR (Shelton, CT).

Gas chromatographic-mass spectrometric analyses of the principal compounds were performed with both electron impact and positive chemical ionization devices. Electron impact analysis was performed on a Varian 3700 chromatograph and an ion-trap detector (Finnigan, San Jose, CA) fitted with an XP-1 0.32 mm x 15 m column (0.5 m coating of dimethylpolysiloxane (P.J. Cobert, Assoc., St. Louis, MO)), and a split/splitless injector. Separation was obtained using temperature programming from 80–280°C (ramped at 6°C/min). Some spectra were obtained with a Hewlett-Packard 5890 gas chromatograph/mass detector (Hewlett-Packard, Wilmington, DE). Positive chemical ionization analysis was performed on a Hewlett-Packard 5890 gas chromatograph fitted with an HP-1 column (0.31 mm x 15 m), using the same elution program as above. Eluted compounds were detected with a Hewlett-Packard 5988 detector, with the source temperature at 200°C.

5.3 Synthetic Procedures

The synthesis of 3-hydroxydodecanedioic acid was achieved in a four-step process. 3-Hydroxy-2,2-dideuterododecanedioic acid was synthesized in a six-step process. The schemes for these synthetic strategies are contained in Figures 5.1 and Figure 5.2 below.
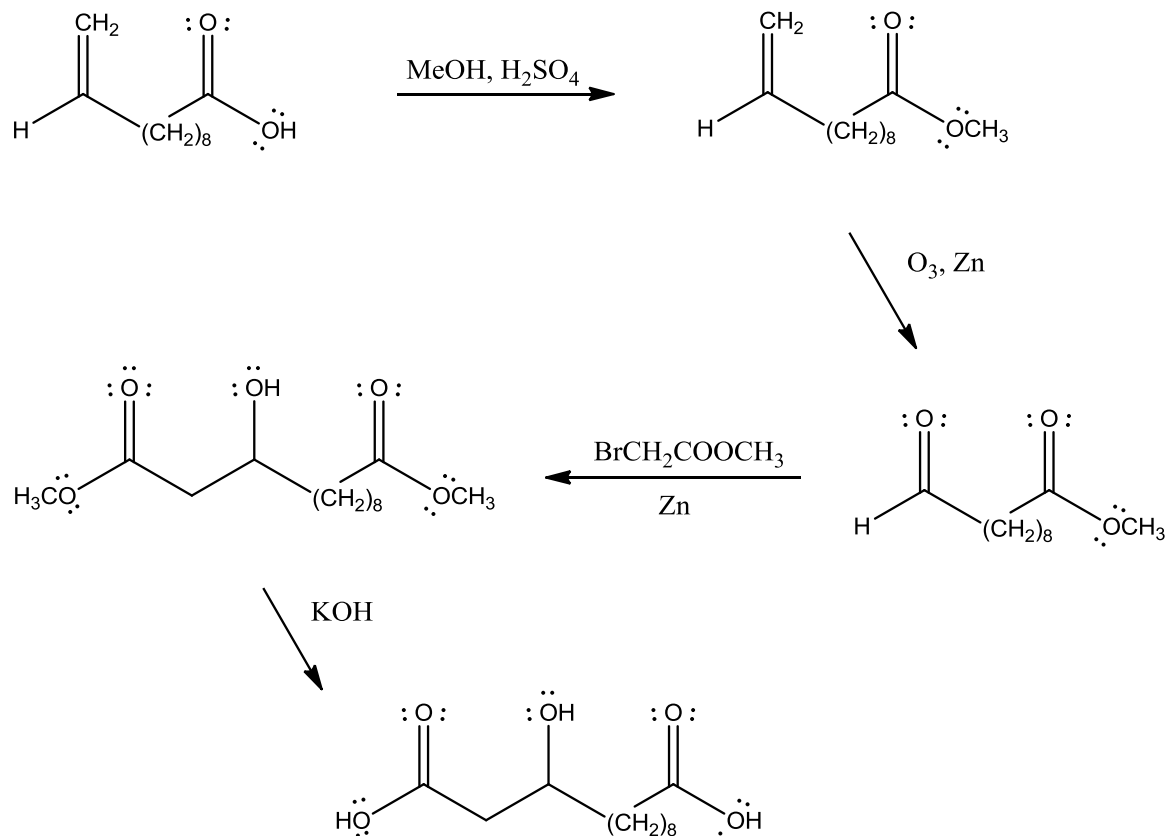
Figure 5.1. Synthetic Strategy for 3-Hydroxydodecanedioic Acid

5.3.1 Preparation of Methyl-10-Undecylenate

10-Undecylenic acid (29.0 g (0.157 mol); Aldrich Chemical Co., Milwaukee, WI) was

placed in a 500-ml round-bottomed flask equipped with magnetic stirrer, heating mantle,

and condenser. Methanol (132 mL) and concentrated sulfuric acid (5 mL) were added and

the mixture was then allowed to reflux gently for 24 hours. The reaction mixture was

cooled to room temperature and the solvent was removed on a rotatory evaporator. Ether

(200 mL) was added and the mixture was extracted with saturated sodium bicarbonate.
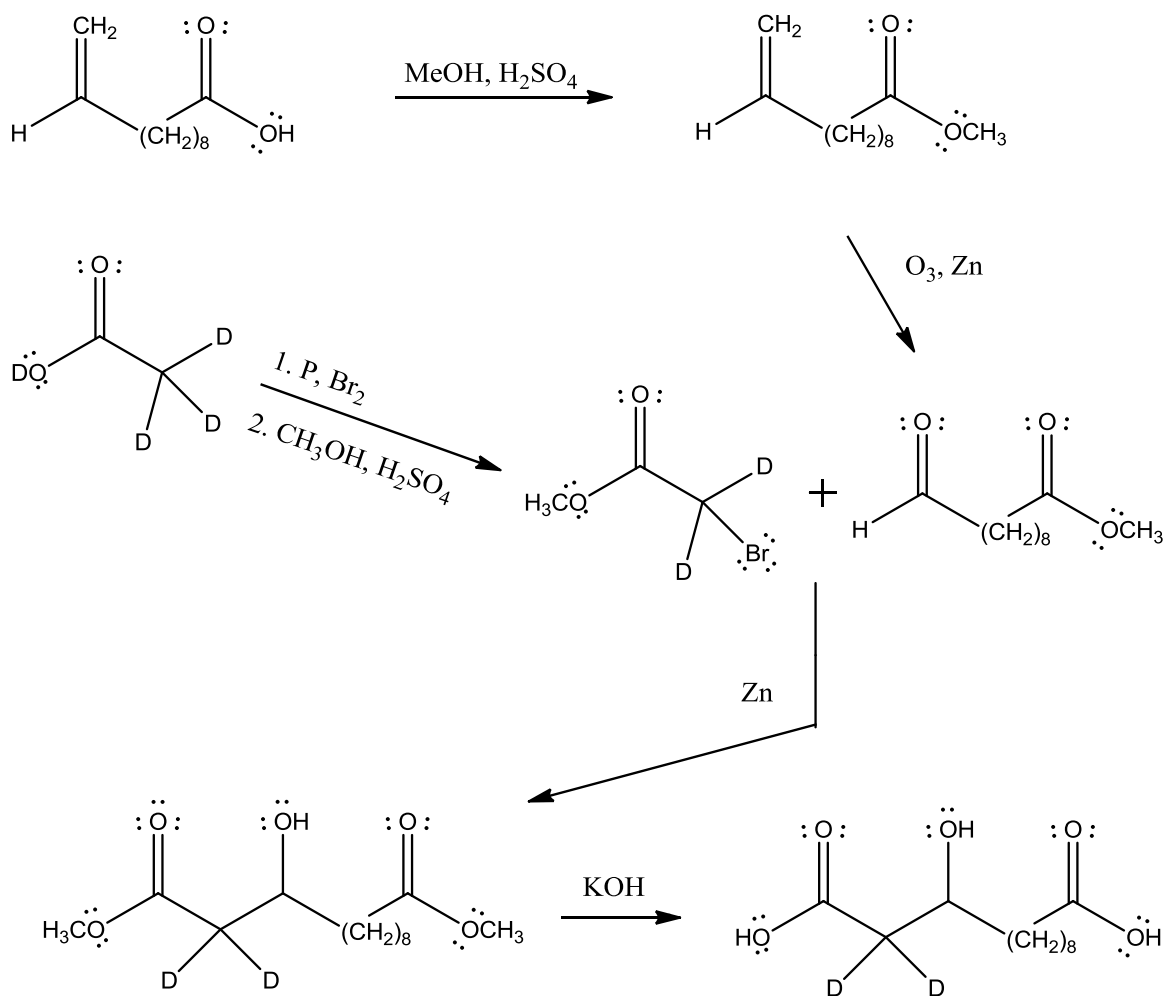
Figure 5.2. Synthetic Strategy for 3-Hydroxy-2,2-dideuterododecanedioic Acid

Evaporation of the ether and vacuum distillation of the residue at 80°C (10 Pa) afforded

the methyl ester of 10-undecylenic acid (29.8 g, 95.5% yield). ^{1}H NMR: 5.7–5.9 (m, 1H),

4.8–5.0 (m, 2 H), 3.6 (s, 3 H), 2.25 (t, 2H), 1.95 (m, 2H), 1.5–1.65 (m, 2H), 1.2–1.4 (m,

10H). ^{13}C NMR: 174.1, 138.1, 114.2, 52.5, 34.2, 34.0, 29.5, 29.4, 29.3, 29.2, 29.1, 25.1.

IR: υ_{max} (neat): 3100, 2926, 2854, 1743, 1640 cm^{-1}.

5.3.2 Preparation of Methyl ω-Aldehydo-Nonanoate

The procedure used for this preparation was similar to that reported by Noller and Adams.[8] A commercial laboratory ozone generator (OZONOSAN PM80, Dr. J. Häsler, Gmbh, Iffezheim, Germany) was used to generate ozone, which was immediately bubbled through an inlet tube into a three-neck, 100-mL round-bottomed flask containing methyl-10-undecylenate (10.0 g (0.05 mol)), glacial acetic acid (50 mL), a magnetic stirrer, and a reflux condenser connected to a trap containing a saturated solution of KI. Ozone was gently bubbled through the solution until a sample no longer decolorized a solution of bromine in glacial acetic acid. A cool-water bath was used to prevent the reaction flask from overheating. The reaction mixture liquid was diluted with ether (100 mL) and transferred to a 500-mL round-bottomed flask fitted with a magnetic stirrer and reflux condenser. Zinc dust (25.0 g) was added to the stirred solution in small portions over a period of 1 hour. A vigorous reaction occurred upon the addition of the zinc dust. The zinc acetate sludge was then filtered through a Buchner funnel and washed thoroughly with ether. Suction was turned off and water was added to the funnel to prevent ignition of the excess zinc dust. The filtrate was then extracted with two portions of water (75 mL each), followed by an extraction with 10% sodium carbonate solution (40 mL), then another with water, and finally dried over calcium chloride. The ether was removed under vacuum and the residue was distilled at 80–84°C (16-20 Pa) to give methyl ω-aldehydo-nonanoate (8.0 g, 78% yield). ^{1}H NMR: 9.5 (s, 1H), 3.4 (s, 3H), 2.2 (t, 2H), 2.1 (t, 2H), 1.3–1.5 (m, 4H), 1.1–1.2 (m, 8H). ^{13}C NMR: 201.7, 173.3, 50.9, 43.4, 33.6, 28.8, 28.7, 24.5, 21.6. IR: υ_{max} (neat) 2927.7, 2700, 1732 cm^{-1}.

5.3.3 Condensation of Methyl ω-Aldehydo-Nonanoate With Methyl Bromoacetate

Granulated zinc (4–5 g) was measured into a three-neck, 250-mL round-bottom flask containing a magnetic stir bar and equipped with an argon gas inlet, a reflux condenser connected to an oil bubbler, and an additional funnel (50 mL). Several drops of methyl bromoacetate were added to the reaction flask and heated in a hot-water bath to initiate the reaction. A solution of freshly distilled aldehyde ester (6.0 g, 0.03 mol) and methyl bromoacetate (5.5 g) in dry ether (40 mL) was added drop-wise under argon flow with rapid stirring. Vigorous bubbling and immediate reflux of the reaction mixture characterized initiation of the reaction. Once addition was complete, gentle heat was provided by a water bath, and the reaction mixture was heat at reflux for about 1 hour. Hydrochloric acid (10 drops, 6 *M*) was added next, followed by additional ether (100 mL). The mixture was extracted with 5% sodium bicarbonate (2 x 200 mL). The solution was dried and the ether removed under vacuum; the residue was vacuum distilled. The methyl 3-hydroxydodecanedioate distilled at 131°C (5 Pa) (2.1 g isolated, 30% yield; the yield varied from 30% to 60% in multiple experiments). Upon cooling, the ester solidified and had a melting point of 40°C. ^{1}H NMR: 3.9–4.05 (br-s, 1H), 3.7 (s, 3H), 3.6 (s, 3H), 2.9 (br-s, 1H), 2.35–2.5 (m, 2H), 2.25 (t, 2H), 1.1–1.7 (m, 8H), ^{13}C NMR: 174.2, 173.3, 68.1, 51.8, 51.5, 41.4, 36.7, 34.2, 29.6, 29.5, 29.3, 29.2, 25.6, 25.1 IR: υ_{max} (neat): 3503.2, 2929.4, 1739.6 cm^{-1}.

5.3.4 Hydrolysis of Methyl 3-Hydroxydodecanedioate to 3-Hydroxydodecanedioic Acid

Hydrolysis was achieved by stirring methyl 3-hydroxydodecanedioate (2.0 g) with 10% KOH (ester:KOH, 1:3 molar ratio) at room temperature. After 1 hour, only one phase remained. The solution was acidified with 6 M HCl and the compound extracted from the reaction with ether. Ether was removed under vacuum, leaving behind a white solid. The 3-hydroxydodecanedioic acid was recrystallized from ethyl acetate (1.0 g, 60% yield, mp 107-109°C). Purity, estimated from the absence of other NMR signals, was greater than 95%. ^{13}C NMR (DMSO): 174.4, 172.9, 67.1, 42.8, 37.0, 33.7, 29.1, 29.0, 28.8, 28.6, 25.1, 24.6. IR: υ_{max} (KBr): 3564, broad band from 3400–2300, 2926, 2850, 1694 cm^{-1}.

5.3.5 Preparation of Bromoacetic-d$_2$ Acid

This compound was prepared according to the published method of Goddard and Ward.[9] Acetic acid-d$_4$ (20 g), was added to a round-bottomed flask equipped with a reflux condenser, and red phosphorus (0.4 g) was added. The mixture was treated with bromine (60 g, 20 mL) and heated on a steam bath for 6 hours. The pale brown liquid was distilled. After bromine, acetic acid, and bromoacetyl bromide were removed, a clear liquid remained in the reaction flask, which solidified on cooling (mp 48–50°C). The yield was about 80% (35 g). ^{13}C NMR: 169.0 (s), 27.7 (q).

5.3.6 Preparation of Methyl Bromoacetate-d$_2$

A mixture of bromoacetic acid-d$_2$ (15 g), methanol (75 mL), and concentrated sulfuric acid (1 mL) were heated at reflux for 6 hours. The solution was cooled and then ether (100 mL) was added. The ether solution was washed with water and then extracted with 2%

sodium bicarbonate solution. After removal of the ether, the solution was heated up to 100°C at atmospheric pressure to remove any remaining ether. The methyl bromoacetate-d_2 was used without any further purification. ^{1}H NMR: 375 (s, 3H). 13C NMR: 167.8, 52.3, 25.4 (q).

5.3.7 Condensation of Methyl ω-Aldehydo-Nonanoate With Methyl Bromoacetate-d_2

The methyl bromoacetate-d_2 and methyl ω-aldehydononanoate were reacted with zinc as described above for unlabeled methyl bromoacetate. The methyl 3-hydroxy-2,2-dideuterododecanedioate that was isolated was characterized by ^{1}H NMR. The ^{1}H NMR spectrum was similar to the un-deuterated material, with the exception that the multiplet at 2.35–2.5 ppm was absent. Hydrolysis of the diester in the same manner as described above for the unlabeled ester afforded the diacid that was characterized by ^{13}C NMR in DMSO-d_6. The ^{13}C spectrum of 3-hydroxy-2,2-dideuterododecanedioic acid was identical to the un-deuterated acid, with the exception of the resonances at 42.8 ppm, which were barely observable. Purity, estimated from the absence of other NMR signals, was greater than 95%.

5.4 Results and Discussion

Schemes were developed for the synthesis of 3-hydroxydodecanedioic (3OHDD) and for a di-deuterated analog, 3-hydroxy-2,2-dideuterododecanedioic acid (3OHDD-D2). Analysis of newly synthesized or recrystallized samples of these compounds (trimethylsilyl derivative) by gas chromatography on a dimethylpolysiloxane-coated 0.53 mm x 15 m

column produced a single peak. Native 3OHDD and 3OHDD-D2 produced similar chromatograms. However, additional peaks appeared when the compound was stored for weeks at room temperature or at 4°C.

Several derivatization schemes were attempted with the goal of producing mass spectral patterns that yielded high-intensity large mass ions that incorporated the deuterated carbon, and thus were suitable for use as internal standard in stable-isotope analysis of body fluids. Derivatization with diazomethane, methyl-bis(trifluoroacetamide), N,N-dimethylformamide dimethyl acetal, and N-methyl-N-(tert-butyldimethylsilyl)trifluoro-acetamide (MTBSTFA) all appeared to be unsuccessful, resulting in no detectable volatile products (first three agents) or a reduced yield (MTBSTFA). Only N,O-bis(trimethylsilyl) trifluoroacetamide yielded apparently quantitative derivatization, based on equivalent peak area (flame ionization detection) compared with an internal standard (o-hydroxyphenylacetic acid) present at the same weight concentration. Trimethylsilyl (TMS) derivatives appeared to be stable for periods of up to a week. Mass-spectral analysis of the TMS derivative of 3OHDD with ion-trap electron impact mass spectroscopy produced a characteristic pattern of ions, but the M-15 ion (m/z 447) and other large m/z ions were obtained in low quantities. Analysis with a quadropole device yielded somewhat better abundance of larger ions, and an additional ion of m/z 233 was prominent. The spectrum of 3OHDD-D2 showed several ions increased in mass by 2, in comparison to 3OHDD – notably the M-15 ion (m/z 449) and m/z 359 (M minus CH_3-TMSOH). Analysis by a quadropole spectrometer produced a prominent additional ion of m/z 235. Analysis of 3OHDD with positive chemical ionization mass spectrometry produced spectra with a much greater yield of larger ions, with the M-15 ion (m/z 447)

and the M minus TMSO ion (m/z 373) most prominent; the molecular ion and M+15 ion were also present. The spectra for 3OHDD-D2 contained analogous ions, with mass increased by 2. The mass spectra were measured at Washington University School of Medicne at St. Louis Children's Hospital by Dr. Michael Landt and his associates.

5.5 Summary

This study produced the first synthetic scheme for synthesis of 3-hydroxydodecanedioic acid (3OHDD). The development of methods to synthesize 3-OHDD and a di-deuterated analog (3OHDD-D2) offered new opportunities to quantitate, by stable-isotope dilution mass spectroscopy, the excretion of metabolites of 3-hydroxy fatty acids (3-OHFAs), which are known to accumulate in the body fluids of children with LCHAD.[7] The principal alternative metabolic pathway for fatty acids in humans, where mitochondrial fatty acid metabolism is blocked by enzymatic deficiency, is omega-oxidation.[10] This pathway, located in microsomes, forms dicarboxylic acids which are rapidly and quantitatively excreted in urine. Because of the known accumulation of the precursor 3-OHFAs, and the documented efficiency of omega-oxidation, diagnostically important elevations in excretion of 3-OHDD will be formed by this alternative pathway, which likely offer a specific and practical means of diagnosing LCHAD deficiency.

The synthetic schemes for 3OHDD and 3OHDD-D2 are likely to be effective for shorter and longer carbon chain lengths; chain lengths can be varied by varying the chain length of the unsaturated carboxylic acid starting material. However, because the 14-carbon and 16-carbon 3-OHFAs are known to accumulate in LCHAD children at the highest magnitude in relation to normal levels,[7] and because omega-oxidation to produce

dicarboxlic acids results in chain shortening by two carbons, the 12-carbon 3-OHDD is likely to be produced in very large amounts in children with LCHAD deficiency. These facts taken together suggest that 3-OHDD will be diagnostically the most sensitive elevation in fatty acid-derived metabolites in urine from LCHAD children.

Current diagnosis of LCHAD rests on appropriate clinical history, an abnormal profile of fatty acid metabolites in urine and serum, and demonstration of impaired fatty acid metabolism in fibroblasts cultured from skin biopsy. The signs and symptoms of LCHAD can occur in other diseases, particularly other metabolic errors of the respiratory chain, fatty acid metabolism, and carnitine metabolism. Patterns of fatty acid metabolites also can be qualitatively similar in these disorders.[11,12] Oxidation of fatty acids, and specifically long-chain fatty acids, are impaired in mitochondria from LCHAD children, but the culture of fibroblasts from biopsy requires weeks, and equipment to measure fatty acid oxidation is available at only a few locations worldwide. Development of a more specific and quantitative method, using stable isotope dilution mass spectroscopy and deuterated 3OHDD, may considerably lessen the time required to make a reliable diagnosis.

5.6 References

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Appendix A

Appendix A-1: Experimental Data for Run 1 for Valproic Acid Study

Run 1	435.4	440.4	445.2	450.1	455.0	460.0	465.0
				t/min			
methylene chloride	1.219	1.223	1.227	1.242	1.226	1.254	1.243
n-pentanoic acid	2.292	2.140	2.013	1.917	1.809	1.761	1.685
n-hexanoic acid	2.890	2.637	2.427	2.265	2.100	2.007	1.895
valproic acid	3.650	3.259	2.939	2.689	2.450	2.299	2.140
n-octanoic acid	5.164	4.496	3.955	3.527	3.141	2.875	2.624
n-decanoic acid	10.274	8.589	7.252	6.202	5.309	4.652	4.089
n-undecanoic acid	14.780	12.148	10.080	8.465	7.119	6.116	5.282

Run 1	$\dfrac{\text{slope}}{T/\text{K}}$	intercept	$\dfrac{\Delta^{g}_{sln}H_{m}\,(450\ \text{K})}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta^{g}_{l}H_{m}\,(298.15)}{\text{kJ·mol}^{-1}}$ (lit)	$\dfrac{\Delta^{g}_{l}H_{m}\,(298.15)}{\text{kJ·mol}^{-1}}$ (calc)
n-pentanoic acid	-5674.8	12.972	47.178	63.00	63.1 ± 2.4
n-hexanoic acid	-6178.1	13.684	51.362	69.00	69.1 ± 2.5
valproic acid	-6640.2	14.369	55.204		74.7 ± 2.5
n-octanoic acid	-7076.1	14.886	58.828	80.10	79.9 ± 2.6
n-decanoic acid	-7881.5	15.904	65.524	90.30	89.6 ± 2.8
n-undecanoic acid	-8269.9	16.393	68.753	93.60	94.3 ± 2.8

$$\Delta^{g}_{l}H_{m}\,(298.15) = (1.445 \pm 0.031)\,\Delta^{g}_{sln}H_{m}\,(450\ \text{K}) - (5.11 \pm 1.85) \quad r^2 = 0.9986$$

n-pentanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.35	0.002297	-0.070318204
440.35	0.002271	0.08176004
445.15	0.002246	0.231135062
450.05	0.002222	0.359027596
454.95	0.002198	0.528065771
459.95	0.002174	0.613582892
464.95	0.002151	0.763289139

Slope Coefficient	-5674.77
Intercept Coefficient	12.9717
Standard Error of the Slope	131.7036
Standard Error of the Intercept	0.292815
r^2	0.997314
Standard Error of Regression	0.016943
F-test	1856.525
Degrees of Freedom	5

n-pentanoic acid

$y = -5674.8x + 12.972$
$R^2 = 0.9973$
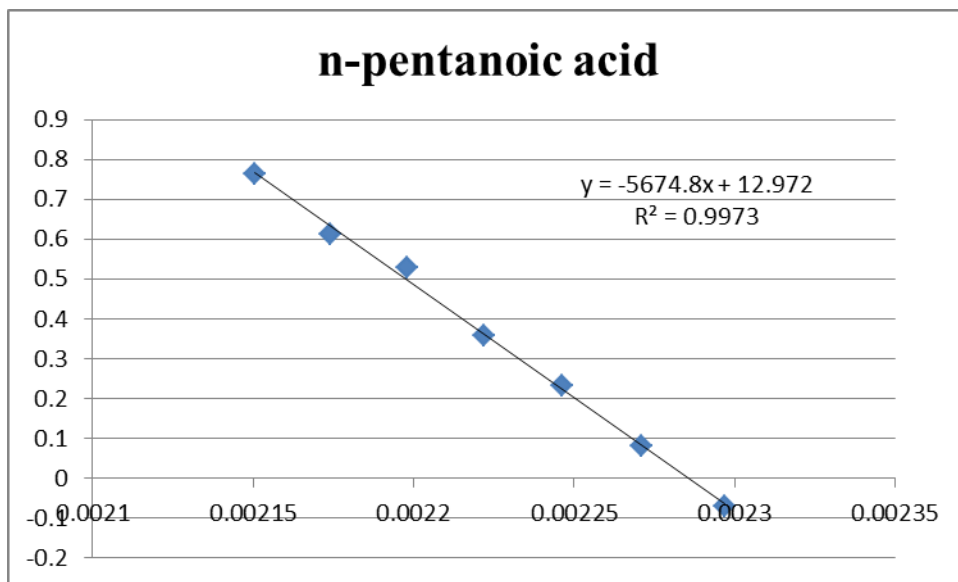
n-hexanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.35	0.002297002	-0.51314
440.35	0.002270921	-0.34919
445.15	0.002246434	-0.18894
450.05	0.002221975	-0.04475
454.95	0.002198044	0.126816
459.95	0.002174149	0.238267
464.95	0.002150769	0.391325

Slope Coefficient	-6178.118083
Intercept Coefficient	13.68393362
Standard Error of the Slope	98.33935036
Standard Error of the Intercept	0.218636706
r^2	0.998734791
Standard Error of Regression	0.012650689
F-test	3946.914691
Degrees of Freedom	5

n-hexanoic acid

$y = -6178.1x + 13.684$
$R^2 = 0.9987$
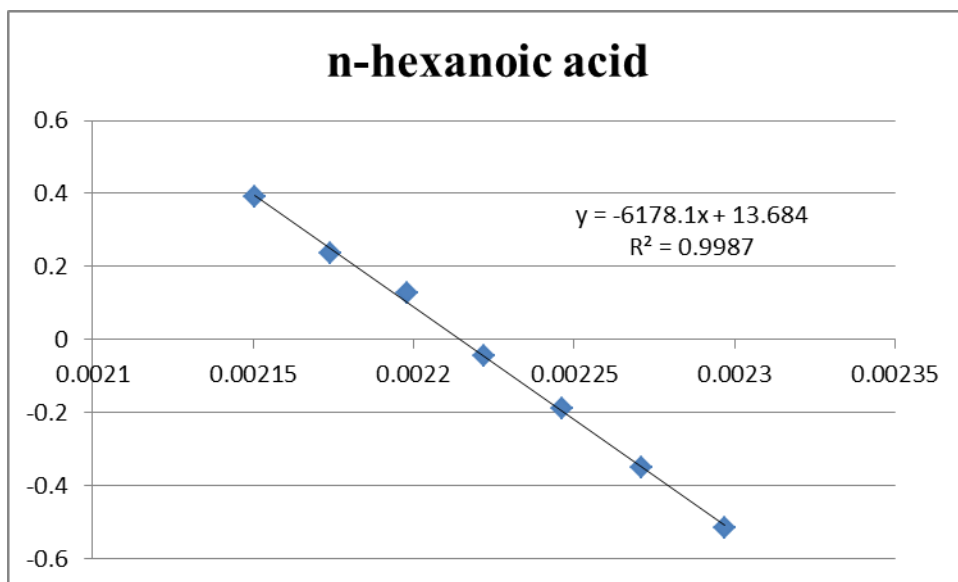
valproic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.35	0.002297	-0.888442243
440.35	0.002271	-0.713019209
445.15	0.002246	-0.542511837
450.05	0.002222	-0.385391029
454.95	0.002198	-0.207478315
459.95	0.002174	-0.077012847
464.95	0.002151	0.082104987

Slope Coefficient	-6640.23
Intercept Coefficient	14.36937
Standard Error of the Slope	80.16136
Standard Error of the Intercept	0.178222
r^2	0.999272
Standard Error of Regression	0.010312
F-test	6861.775
Degrees of Freedom	5

valproic acid

$y = -6640.2x + 14.369$

$R^2 = 0.9993$
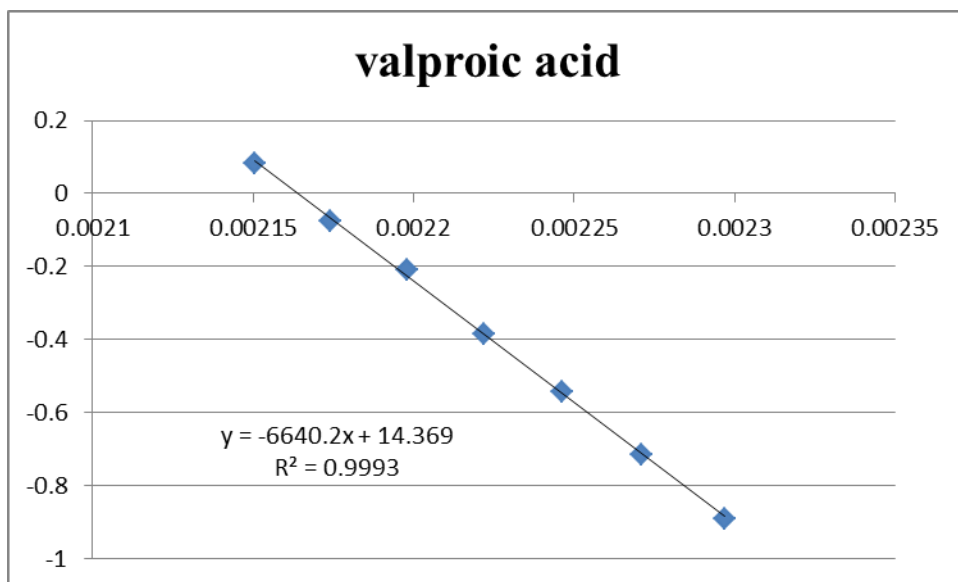
n-octanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.35	0.002297002	-1.37248
440.35	0.002270921	-1.18677
445.15	0.002246434	-1.00633
450.05	0.002221975	-0.83617
454.95	0.002198044	-0.65336
459.95	0.002174149	-0.50462
464.95	0.002150769	-0.33975

Slope Coefficient	-7076.13321
Intercept Coefficient	14.88573714
Standard Error of the Slope	63.29714778
Standard Error of the Intercept	0.140727795
r^2	0.999600081
Standard Error of Regression	0.008142748
F-test	12497.51649
Degrees of Freedom	5

n-octanoic acid

$y = -7076.1x + 14.886$
$R^2 = 0.9996$
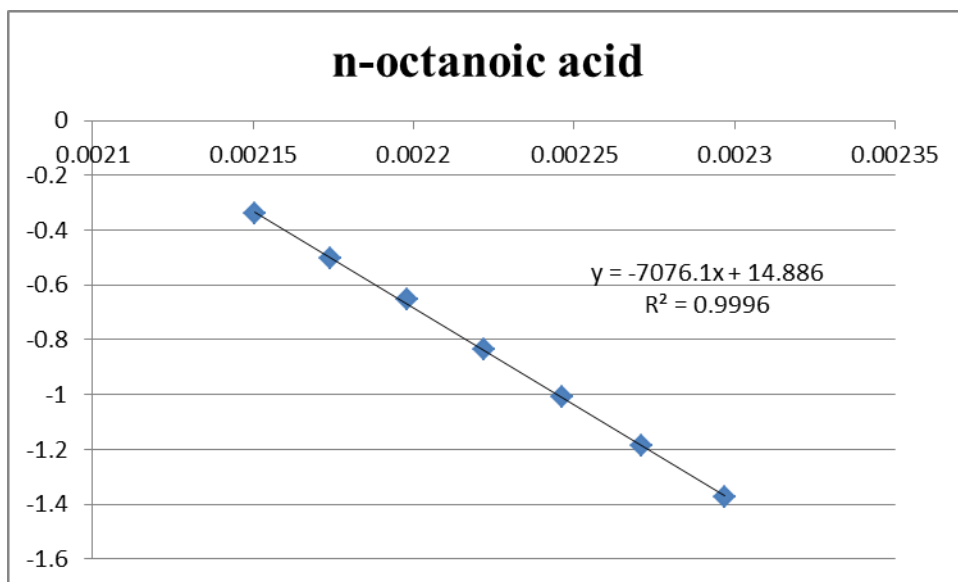
n-decanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.35	0.002297	-2.2033399
440.35	0.002271	-1.997430275
445.15	0.002246	-1.797211873
450.05	0.002222	-1.606095665
454.95	0.002198	-1.408605456
459.95	0.002174	-1.233435721
464.95	0.002151	-1.054317223

Slope Coefficient	-7881.54
Intercept Coefficient	15.90439
Standard Error of the Slope	52.04042
Standard Error of the Intercept	0.115701
r^2	0.999782
Standard Error of Regression	0.006695
F-test	22937.18
Degrees of Freedom	5

$y = -7881.5x + 15.904$
$R^2 = 0.9998$
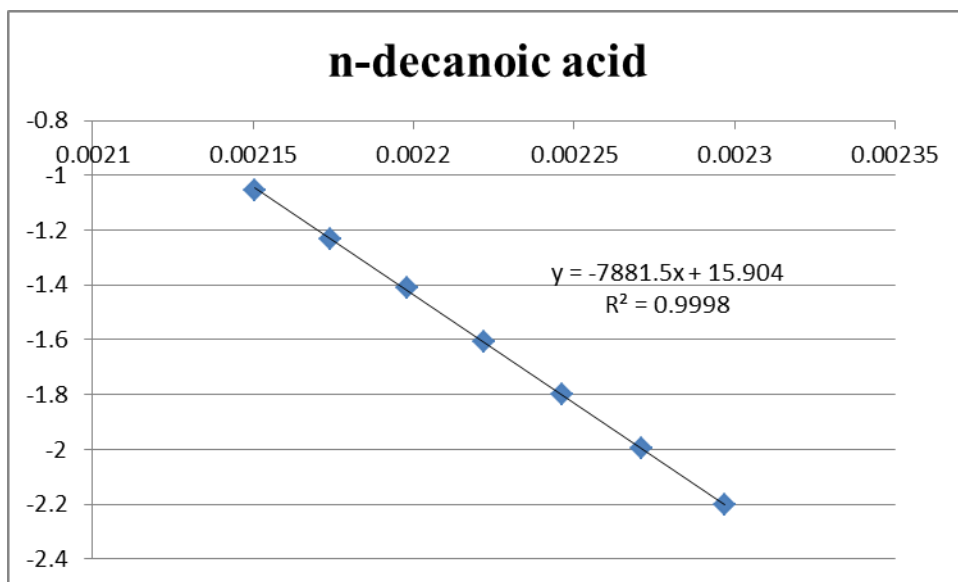
n-undecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.35	0.002297002	-2.60721
440.35	0.002270921	-2.39138
445.15	0.002246434	-2.1817
450.05	0.002221975	-1.98043
454.95	0.002198044	-1.77499
459.95	0.002174149	-1.58861
464.95	0.002150769	-1.40196

Slope Coefficient	-8269.916356
Intercept Coefficient	16.39254123
Standard Error of the Slope	50.49833155
Standard Error of the Intercept	0.112272339
r^2	0.999813602
Standard Error of Regression	0.006496267
F-test	26819.3455
Degrees of Freedom	5
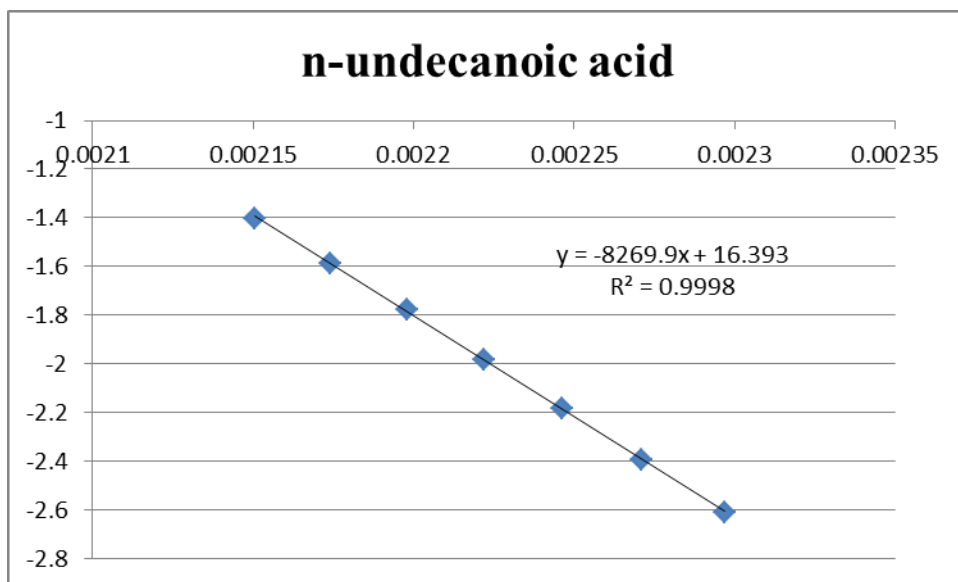
Appendix A-2: Experimental Data for Run 2 for Valproic Acid Study

Run 2	435.2	440.2	445.2	450.1	455.1	460.1	465.1
				t/min			
methylene chloride	1.203	1.218	1.220	1.231	1.242	1.249	1.254
n-pentanoic acid	2.274	2.131	2.000	1.904	1.823	1.753	1.694
n-hexanoic acid	2.874	2.629	2.415	2.251	2.116	2.001	1.904
valproic acid	3.641	3.261	2.935	2.679	2.471	2.299	2.155
n-octanoic acid	5.158	4.498	3.949	3.515	3.164	2.877	2.640
n-decanoic acid	10.28	8.606	7.256	6.188	5.342	4.669	4.121
n-undecanoic acid	14.79	12.163	10.081	8.442	7.154	6.135	5.318

Run 2	$\dfrac{\text{slope}}{T/\text{K}}$	intercept	$\dfrac{\Delta_{\text{sln}}^{\text{g}} H_{\text{m}} \,(450\ \text{K})}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta_{\text{l}}^{\text{g}} H_{\text{m}} \,(298.15)}{\text{kJ·mol}^{-1}}$ (lit)	$\dfrac{\Delta_{\text{l}}^{\text{g}} H_{\text{m}} \,(298.15)}{\text{kJ·mol}^{-1}}$ (calc)
n-pentanoic acid	-5287.1	12.092	43.955	63.00	62.7 ± 2.1
n-hexanoic acid	-5885.8	13.021	48.933	69.00	69.4 ± 2.2
valproic acid	-6381.4	13.781	53.053		74.9 ± 2.2
n-octanoic acid	-6867.5	14.413	57.094	80.10	80.3 ± 2.3
n-decanoic acid	-7703.9	15.503	64.047	90.30	89.6 ± 2.5
n-undecanoic acid	-8106.1	16.024	67.391	93.60	94.0 ± 2.5

$$\Delta_{\text{l}}^{\text{g}} H_{\text{m}}(298.15) = (1.336 \pm 0.029)\,\Delta_{\text{sln}}^{\text{g}} H_{\text{m}}(450\ \text{K}) - (3.995 \pm 1.64) \quad r^2 = 0.9986$$

n-pentanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.15	0.002298	-0.06791
440.15	0.002272	0.075129
445.15	0.002246	0.226875
450.05	0.002222	0.355576
455.05	0.002198	0.478486
460.05	0.002174	0.597991
465.05	0.00215	0.712641

Slope Coefficient	-5287.08
Intercept Coefficient	12.09223
Standard Error of the Slope	79.27333
Standard Error of the Intercept	0.176256
r^2	0.998877
Standard Error of Regression	0.010319
F-test	4448.133
Degrees of Freedom	5

n-pentanoic acid

$y = -5287.1x + 12.092$
$R^2 = 0.9989$
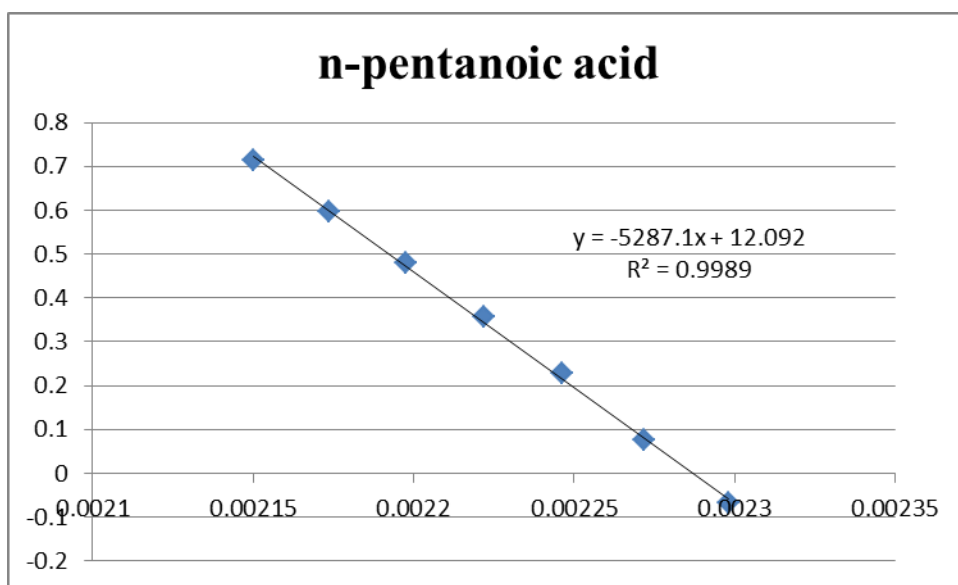
n-hexanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.15	0.002298	-0.51307
440.15	0.002272	-0.3548
445.15	0.002246	-0.19227
450.05	0.002222	-0.04684
455.05	0.002198	0.09166
460.05	0.002174	0.226517
465.05	0.00215	0.355294

Slope Coefficient	-5885.848457
Intercept Coefficient	13.02144062
Standard Error of the Slope	66.62831055
Standard Error of the Intercept	0.148141146
r^2	0.999359689
Standard Error of Regression	0.008673059
F-test	7803.699719
Degrees of Freedom	5

n-hexanoic acid

$y = -5885.8x + 13.021$
$R^2 = 0.9994$
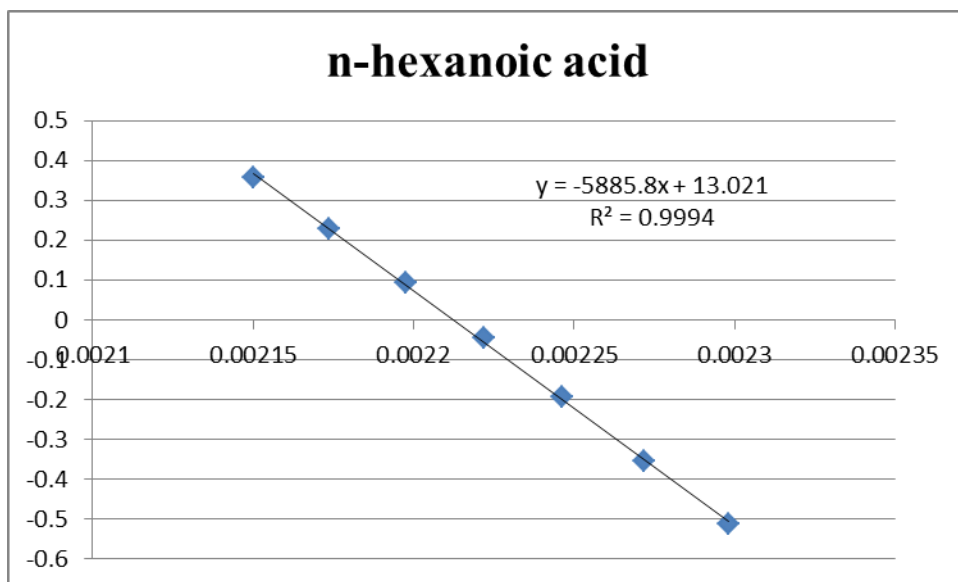
valproic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.15	0.002298	-0.89101
440.15	0.002272	-0.72176
445.15	0.002246	-0.54925
450.05	0.002222	-0.38935
455.05	0.002198	-0.23726
460.05	0.002174	-0.09163
465.05	0.00215	0.049299

Slope Coefficient	-6381.425738
Intercept Coefficient	13.78054209
Standard Error of the Slope	59.67350052
Standard Error of the Intercept	0.132677847
r^2	0.999562974
Standard Error of Regression	0.007767746
F-test	11435.95426
Degrees of Freedom	5
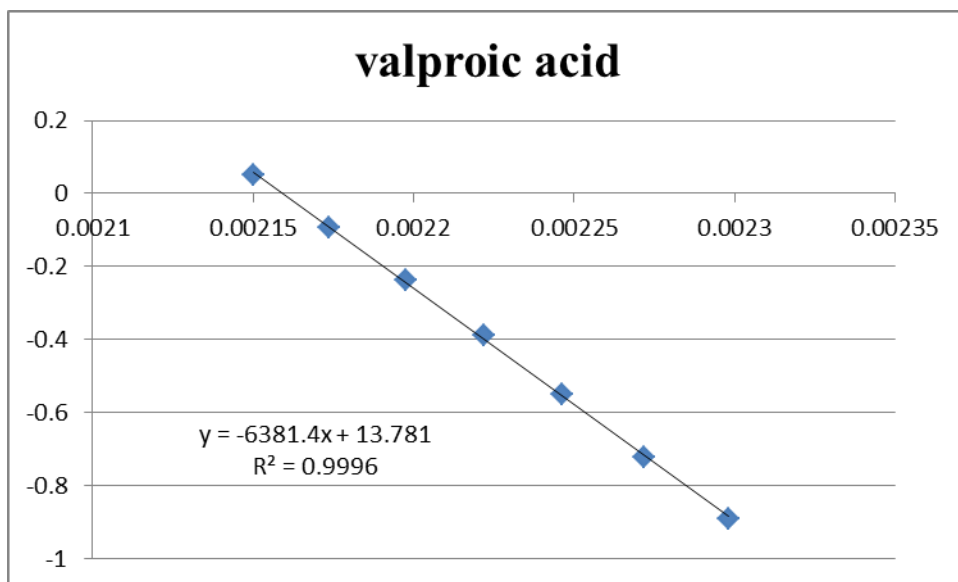
n-octanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.15	0.002298	-1.37496
440.15	0.002272	-1.19227
445.15	0.002246	-1.01002
450.05	0.002222	-0.83798
455.05	0.002198	-0.67306
460.05	0.002174	-0.51521
465.05	0.00215	-0.36261

Slope Coefficient	-6867.510006
Intercept Coefficient	14.41315672
Standard Error of the Slope	52.81312295
Standard Error of the Intercept	0.117424508
r^2	0.999704385
Standard Error of Regression	0.006874725
F-test	16908.8824
Degrees of Freedom	5

n-octanoic acid

$y = -6867.5x + 14.413$
$R^2 = 0.9997$
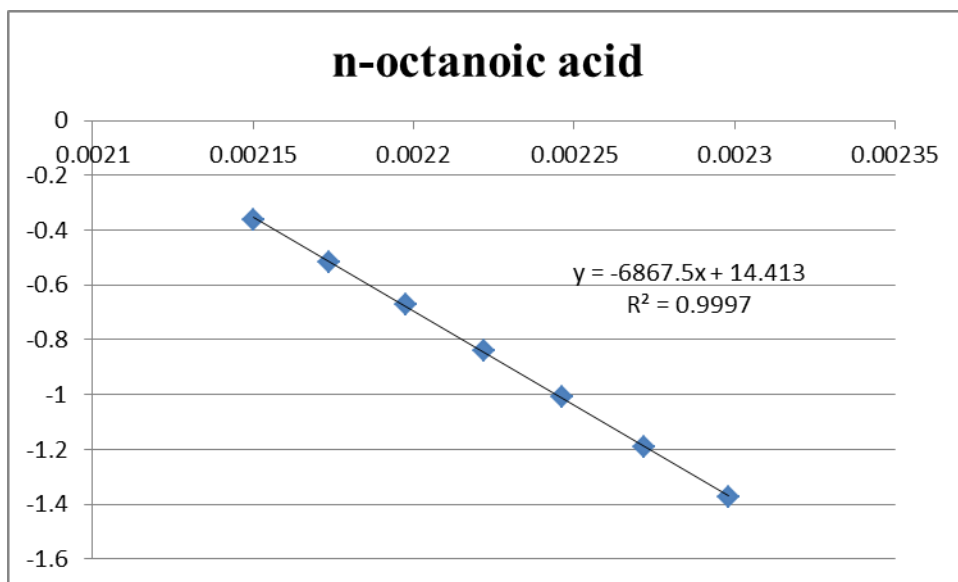
n-decanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.15	0.002298	-2.20617
440.15	0.002272	-2.00189
445.15	0.002246	-1.80046
450.05	0.002222	-1.60639
455.05	0.002198	-1.42046
460.05	0.002174	-1.24282
465.05	0.00215	-1.07081

Slope Coefficient	-7703.856892
Intercept Coefficient	15.50324776
Standard Error of the Slope	50.37271704
Standard Error of the Intercept	0.111998518
r^2	0.999786277
Standard Error of Regression	0.006557055
F-test	23389.7543
Degrees of Freedom	5

n-decanoic acid

$y = -7703.9x + 15.503$
$R^2 = 0.9998$
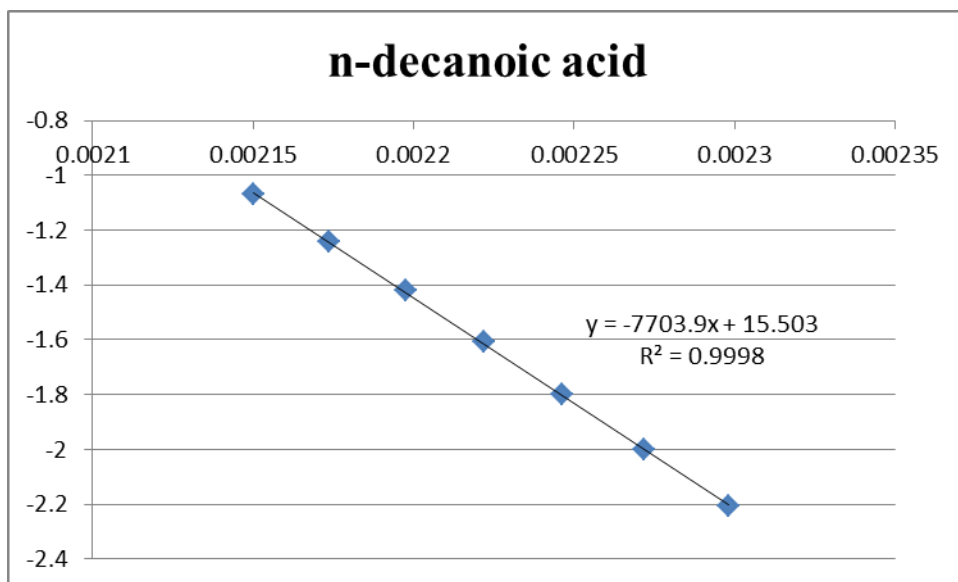
n-undecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
435.15	0.002298	-2.60925
440.15	0.002272	-2.3942
445.15	0.002246	-2.18353
450.05	0.002222	-1.97947
455.05	0.002198	-1.78345
460.05	0.002174	-1.59572
465.05	0.00215	-1.4145

Slope Coefficient	-8106.143042
Intercept Coefficient	16.02445349
Standard Error of the Slope	48.28641231
Standard Error of the Intercept	0.107359836
r^2	0.999822616
Standard Error of Regression	0.006285479
F-test	28182.44378
Degrees of Freedom	5
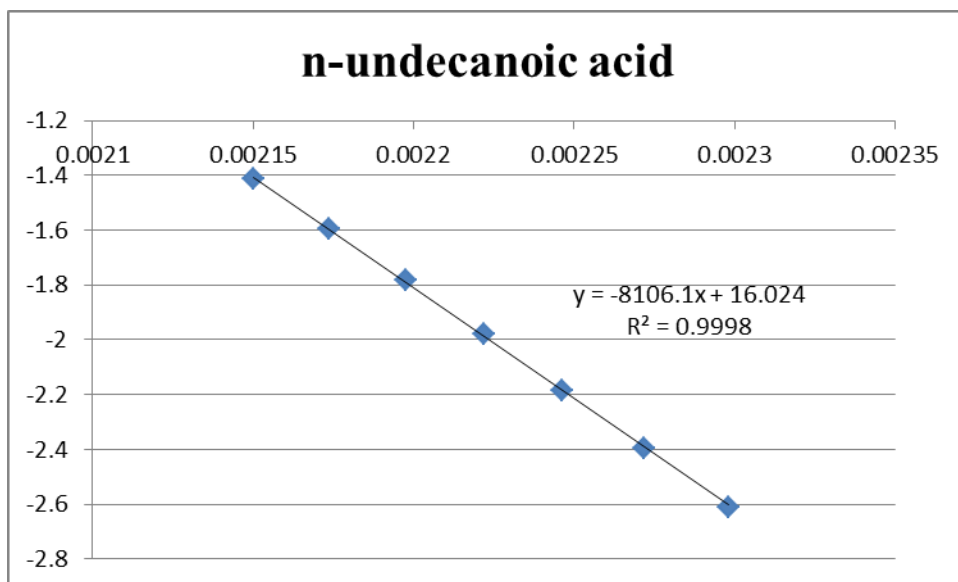
Appendix B

Appendix B-1: Experimental Data for Run 1 for Long-chain
Fatty Acids Study

Run 1	474.8	479.7	484.7	489.7	494.7	499.7	504.7
				t/min			
methylene chloride	0.963	0.969	0.959	0.99	0.991	1.004	0.993
n-tetradecanoic acid	6.941	5.895	5.045	4.386	3.825	3.388	3.006
n-pentadecanoic acid	9.252	7.75	6.542	5.596	4.806	4.193	3.668
n-hexadecanoic acid	12.496	10.335	8.621	7.259	6.14	5.278	4.554
n-heptadecanoic acid	16.966	13.866	11.44	9.497	7.921	6.719	5.721
n-octadecanoic acid	23.106	18.666	15.307	12.505	10.301	8.626	7.251
elaidic acid	25.308	20.454	16.726	13.651	11.192	9.352	7.838
linoleic acid	29.863	24.09	19.685	15.97	13.029	10.839	9.042
α-linolenic acid	36.263	29.079	23.593	19.063	15.486	12.804	10.627

Run 1	$\frac{\text{slope}}{T/\text{K}}$	intercept	$\frac{\Delta_{sln}^{g}H_{m}\,(450\text{ K})}{\text{kJ·mol}^{-1}}$	$\frac{\Delta_{l}^{g}H_{m}\,(298.15)}{\text{kJ·mol}^{-1}}$ (lit)	$\frac{\Delta_{l}^{g}H_{m}\,(298.15)}{\text{kJ·mol}^{-1}}$ (calc)
n-tetradecanoic	-8716.6	16.577	72.47	111.3±2.2	111.2 ± 8.6
n-pentadecanoic	-9061.6	16.977	75.33	117.2±2.2	116.5 ± 9.0
n-hexadecanoic	-9421.5	17.404	78.33	120.7±2.3	121.9 ± 9.3
n-heptadecanoic	-9776.8	17.824	81.28	125.0±5.2	127.3 ± 9.7
n-octadecanoic	-10134.2	18.251	84.25	133.1±2.4	132.7 ± 10.1
elaidic acid	-10183.4	18.259	84.66		133.4 ± 10.1
linoleic acid	-10268.2	18.264	85.37		134.7 ± 10.2
α-linolenic acid	-10424.2	18.394	86.66		137.1 ± 10.3

$$\Delta_{l}^{g}H_{m}\,(298.15) = (1.82 \pm 0.12)\,\Delta_{sln}^{g}H_{m}\,(490\text{ K}) - (20.5\pm9.3) \qquad r^2 = 0.9915$$

n-tetradecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-1.787941446
479.65	0.002085	-1.59458395
484.65	0.002063	-1.407357427
489.65	0.002042	-1.222528016
494.65	0.002022	-1.041577116
499.65	0.002001	-0.868999269
504.65	0.001982	-0.699794648

Slope Coefficient	-8716.63
Intercept Coefficient	16.5768
Standard Error of the Slope	30.29938
Standard Error of the Intercept	0.061916
r^2	0.99994
Standard Error of Regression	0.003339
F-test	82761.68
Degrees of Freedom	5

n-tetradecanoic acid

$y = -8716.6x + 16.577$
$R^2 = 0.9999$
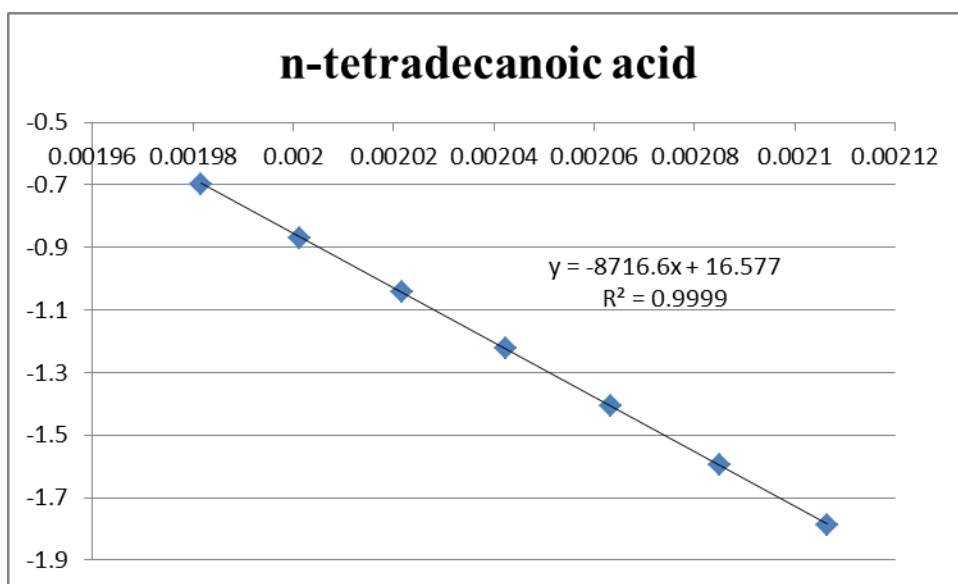
n-pentadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-2.114896361
479.65	0.002085	-1.914248499
484.65	0.002063	-1.719611482
489.65	0.002042	-1.527220422
494.65	0.002022	-1.33896049
499.65	0.002001	-1.159719391
504.65	0.001982	-0.983964759

Slope Coefficient	-9061.62
Intercept Coefficient	16.97653
Standard Error of the Slope	31.54059
Standard Error of the Intercept	0.064453
r^2	0.999939
Standard Error of Regression	0.003476
F-test	82541.5
Degrees of Freedom	5

n-pentadecanoic acid

$y = -9061.6x + 16.977$
$R^2 = 0.9999$
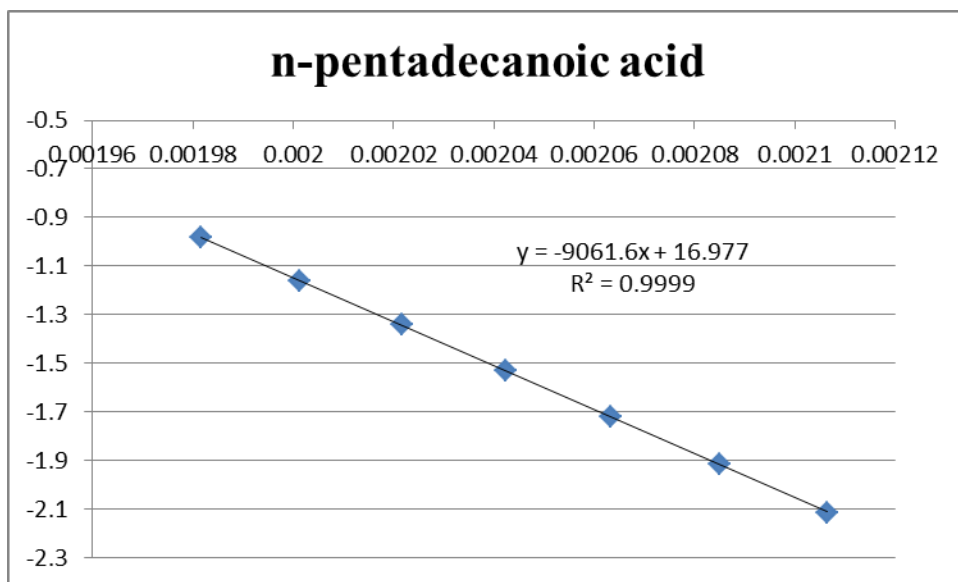
n-hexadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-2.445179321
479.65	0.002085	-2.237177104
484.65	0.002063	-2.036279402
489.65	0.002042	-1.83548959
494.65	0.002022	-1.638647933
499.65	0.002001	-1.452561018
504.65	0.001982	-1.270008544

Slope Coefficient	-9421.51
Intercept Coefficient	17.4037
Standard Error of the Slope	31.22944
Standard Error of the Intercept	0.063817
r^2	0.999945
Standard Error of Regression	0.003441
F-test	91014.88
Degrees of Freedom	5

n-hexadecanoic acid

$y = -9421.5x + 17.404$
$R^2 = 0.9999$
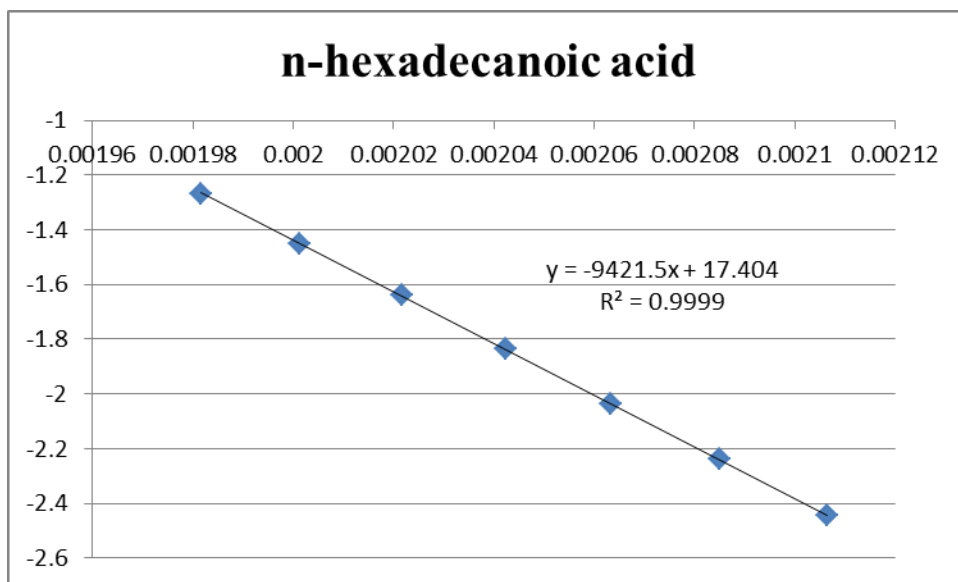
n-heptadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-2.77276787
479.65	0.002085	-2.557014752
484.65	0.002063	-2.349508344
489.65	0.002042	-2.140818435
494.65	0.002022	-1.935883905
499.65	0.002001	-1.743046514
504.65	0.001982	-1.553436039

Slope Coefficient	-9776.82
Intercept Coefficient	17.82431
Standard Error of the Slope	32.05222
Standard Error of the Intercept	0.065498
r^2	0.999946
Standard Error of Regression	0.003532
F-test	93041.88
Degrees of Freedom	5

n-heptadecanoic acid

$y = -9776.8x + 17.824$
$R^2 = 0.9999$
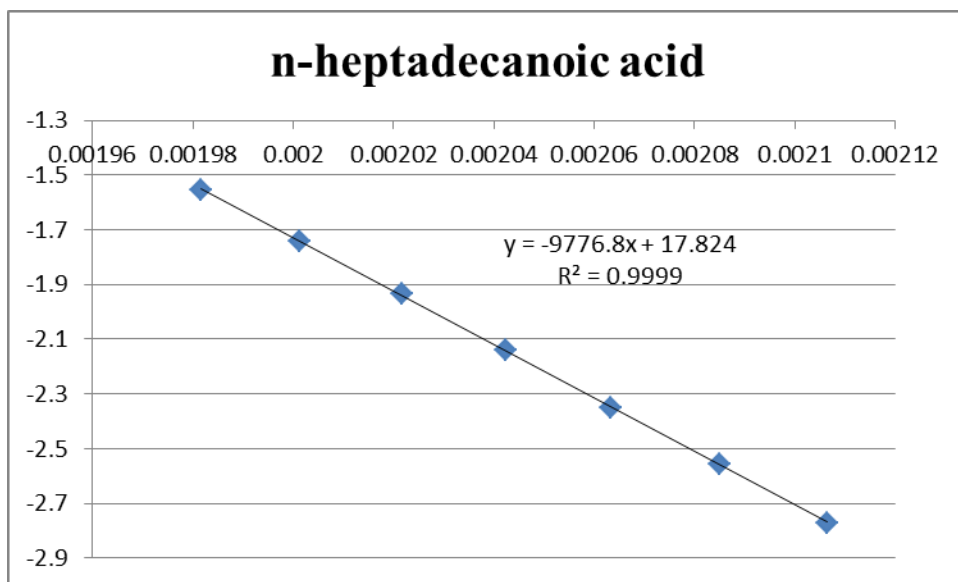
n-octadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-3.097510373
479.65	0.002085	-2.873414319
484.65	0.002063	-2.663603908
489.65	0.002042	-2.443639501
494.65	0.002022	-2.231008491
499.65	0.002001	-2.031064418
504.65	0.001982	-1.833904736

Slope Coefficient	-10134.2
Intercept Coefficient	18.25145
Standard Error of the Slope	37.21459
Standard Error of the Intercept	0.076048
r^2	0.999933
Standard Error of Regression	0.004101
F-test	74157.63
Degrees of Freedom	5

n-octadecanoic acid

$y = -10134x + 18.251$
$R^2 = 0.9999$
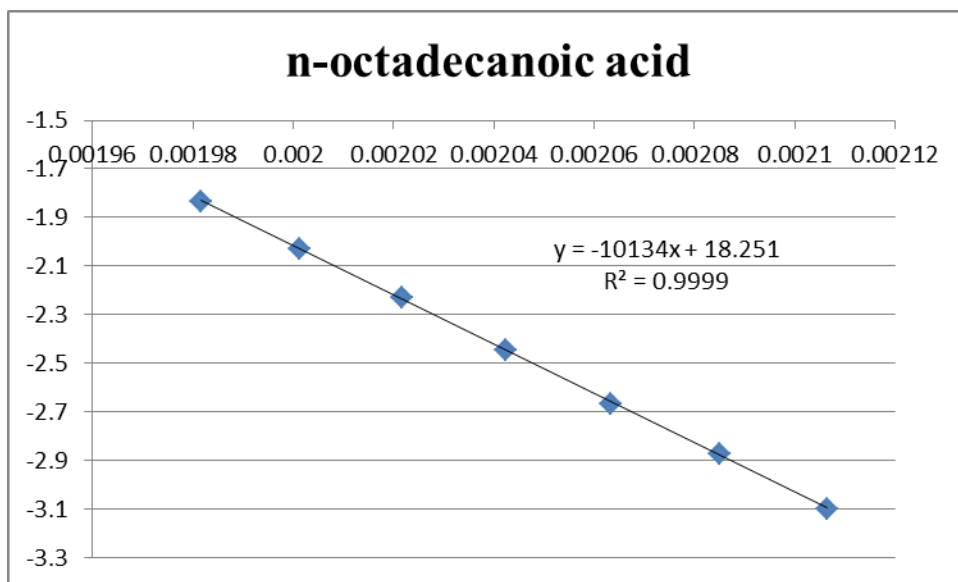
elaidic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-3.192300053
479.65	0.002085	-2.969694574
484.65	0.002063	-2.757919244
489.65	0.002042	-2.538500468
494.65	0.002022	-2.322441812
499.65	0.002001	-2.12202388
504.65	0.001982	-1.92361009

Slope Coefficient	-10183.4
Intercept Coefficient	18.25867
Standard Error of the Slope	35.22232
Standard Error of the Intercept	0.071976
r^2	0.99994
Standard Error of Regression	0.003881
F-test	83588.89
Degrees of Freedom	5

elaidic acid

$y = -10183x + 18.259$
$R^2 = 0.9999$
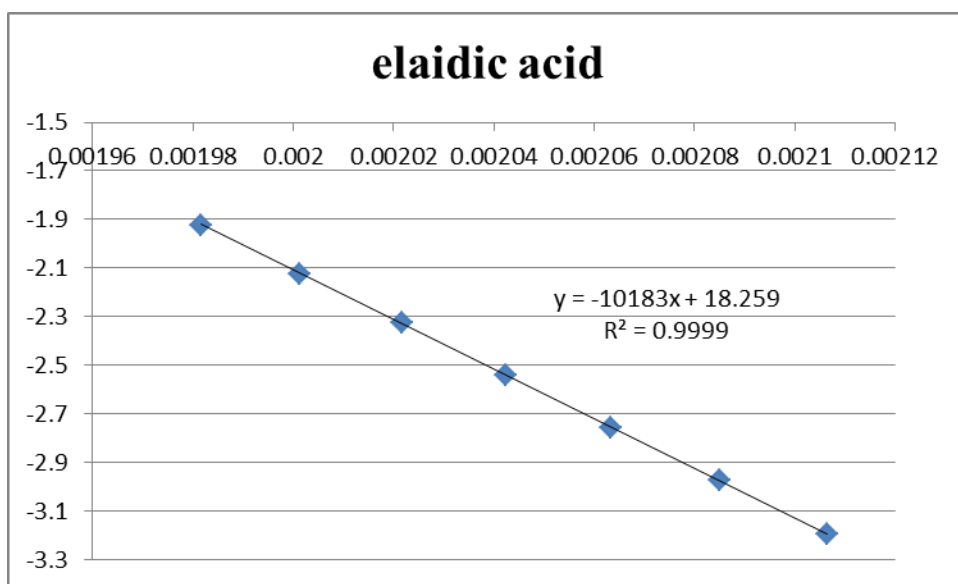
linoleic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-3.363808182
479.65	0.002085	-3.140781461
484.65	0.002063	-2.929902502
489.65	0.002042	-2.706710373
494.65	0.002022	-2.488014113
499.65	0.002001	-2.285935141
504.65	0.001982	-2.085507126

Slope Coefficient	-10268.2
Intercept Coefficient	18.26413
Standard Error of the Slope	42.04149
Standard Error of the Intercept	0.085911
r^2	0.999916
Standard Error of Regression	0.004633
F-test	59652.58
Degrees of Freedom	5

y = -10268x + 18.264
R² = 0.9999
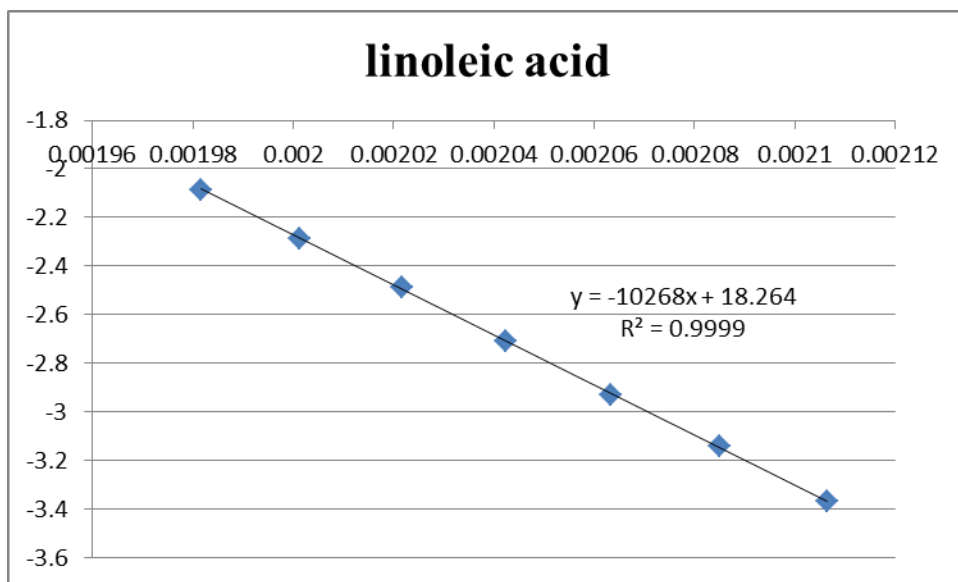
α-lenolenic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.75	0.002106	-3.563863271
479.65	0.002085	-3.336148595
484.65	0.002063	-3.119447562
489.65	0.002042	-2.894377234
494.65	0.002022	-2.673754392
499.65	0.002001	-2.468125571
504.65	0.001982	-2.26534486

Slope Coefficient	-10424.2
Intercept Coefficient	18.39435
Standard Error of the Slope	35.86233
Standard Error of the Intercept	0.073284
r^2	0.999941
Standard Error of Regression	0.003952
F-test	84491.04
Degrees of Freedom	5
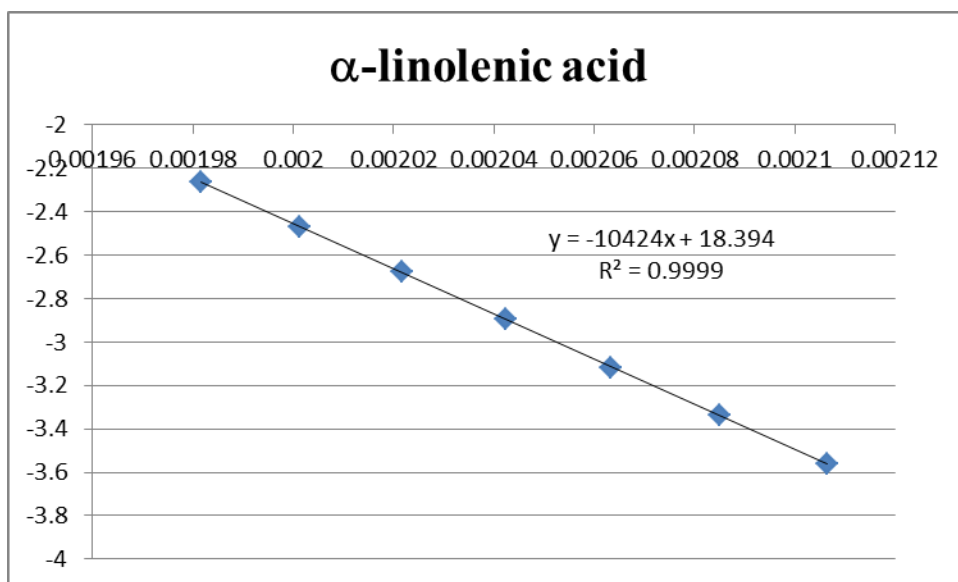
Appendix B-2: Experimental Data for Run 2 for Long-chain
Fatty Acids Study

Run 2	474.9	479.9	484.9	489.8	494.7	499.7	504.7
				t/min			
methylene chloride	0.981	0.984	0.984	0.998	1.002	1.008	0.977
n-tetradecanoic acid	6.908	5.863	5.053	4.369	3.845	3.401	3.007
n-pentadecanoic acid	9.2	7.697	6.544	5.569	4.832	4.211	3.675
n-hexadecanoic acid	12.41	10.248	8.615	7.214	6.185	5.313	4.576
n-heptadecanoic acid	16.829	13.727	11.424	9.428	7.992	6.774	5.763
n-octadecanoic acid	22.89	18.483	15.311	12.391	10.427	8.73	7.324
elaidic acid	25.047	20.176	16.693	13.508	11.365	9.486	7.938
linoleic acid	29.532	23.731	19.627	15.78	13.255	11.024	9.176
α-linolenic acid	35.875	28.655	23.493	18.838	15.706	12.978	10.757

Run 2	slope T/K	intercept	$\Delta_{sln}^{g} H_m$ (450 K) kJ·mol^{-1}	$\Delta_{l}^{g} H_m$ (298.15) kJ·mol^{-1} (lit)	$\Delta_{l}^{g} H_m$ (298.15) kJ·mol^{-1} (calc)
n-tetradecanoic	-8631.3	16.401	71.76	111.3±2.2	111.1 ± 9.0
n-pentadecanoic	-8969.6	16.787	74.57	117.2±2.2	116.6 ± 9.3
n-hexadecanoic	-9301.0	17.155	77.33	120.7±2.3	121.9 ± 9.7
n-heptadecanoic	-9635.4	17.532	80.1	125.0±2.0	127.3 ± 10.0
n-octadecanoic	-9967.0	17.905	82.86	133.1±2.4	132.6 ± 10.4
elaidic acid	-9966.3	17.811	82.86		132.6 ± 10.4
linoleic acid	-10021.6	17.756	83.32		133.5 ± 10.4
α-linolenic acid	-10219.0	17.972	84.96		136.7 ± 10.6

$$\Delta_{l}^{g} H_m (298.15) = (1.94 \pm 0.13) \Delta_{sln}^{g} H_m (490 \text{ K}) - (27.8 \pm 9.6) \qquad r^2 = 0.9917$$

n-tetradecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-1.779669046
479.85	0.002084	-1.584856852
484.85	0.002062	-1.403480822
489.75	0.002042	-1.215184962
494.65	0.002022	-1.044959432
499.65	0.002001	-0.872811751
504.65	0.001982	-0.707990619

Slope Coefficient	-8631.29
Intercept Coefficient	16.40125
Standard Error of the Slope	45.43274
Standard Error of the Intercept	0.092824
r^2	0.999861
Standard Error of Regression	0.004973
F-test	36092.22
Degrees of Freedom	5

n-tetradecanoic acid

$y = -8631.3x + 16.401$
$R^2 = 0.9999$
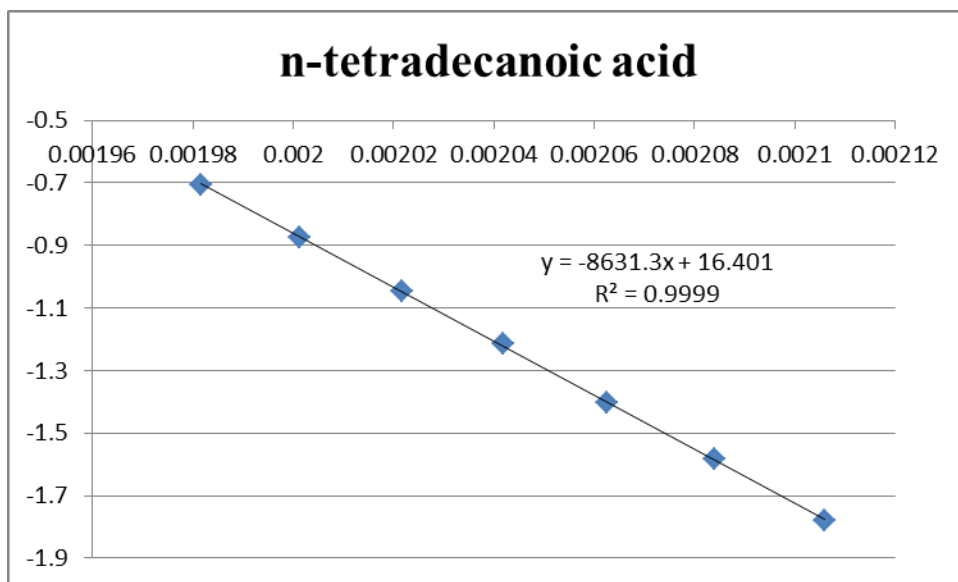
n-pentadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-2.106477959
479.85	0.002084	-1.904125187
484.85	0.002062	-1.715627814
489.75	0.002042	-1.519684386
494.65	0.002022	-1.342929584
499.65	0.002001	-1.164222612
504.65	0.001982	-0.992799355

Slope Coefficient	-8969.62
Intercept Coefficient	16.78707
Standard Error of the Slope	47.78591
Standard Error of the Intercept	0.097632
r^2	0.999858
Standard Error of Regression	0.005231
F-test	35232.89
Degrees of Freedom	5
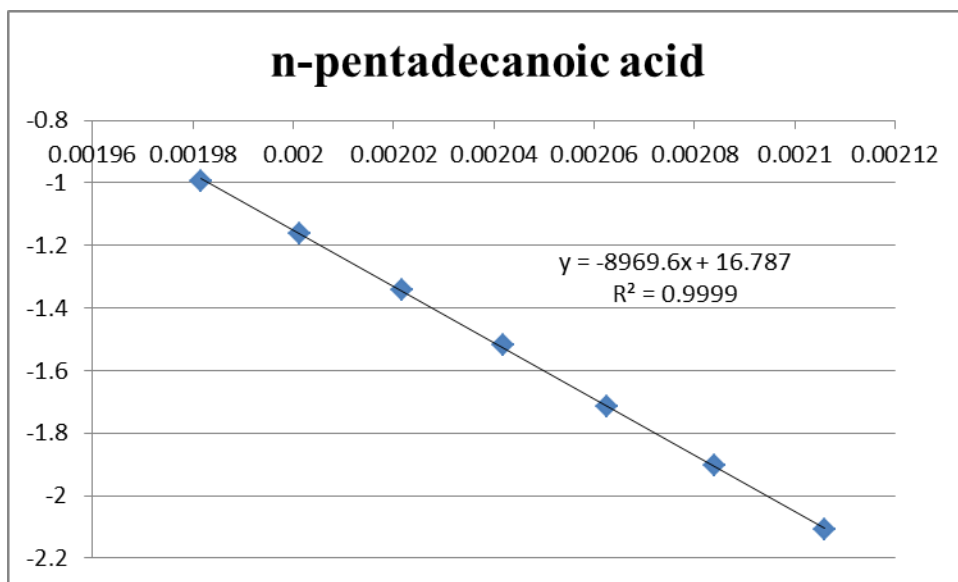
n-hexadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-2.436190743
479.85	0.002084	-2.226133804
484.85	0.002062	-2.032200751
489.75	0.002042	-1.827136704
494.65	0.002022	-1.64551409
499.65	0.002001	-1.459923406
504.65	0.001982	-1.280723426

Slope Coefficient	-9301.03
Intercept Coefficient	17.1552
Standard Error of the Slope	50.53307
Standard Error of the Intercept	0.103245
r^2	0.999852
Standard Error of Regression	0.005531
F-test	33877.46
Degrees of Freedom	5

n-hexadecanoic acid

$y = -9301x + 17.155$
$R^2 = 0.9999$
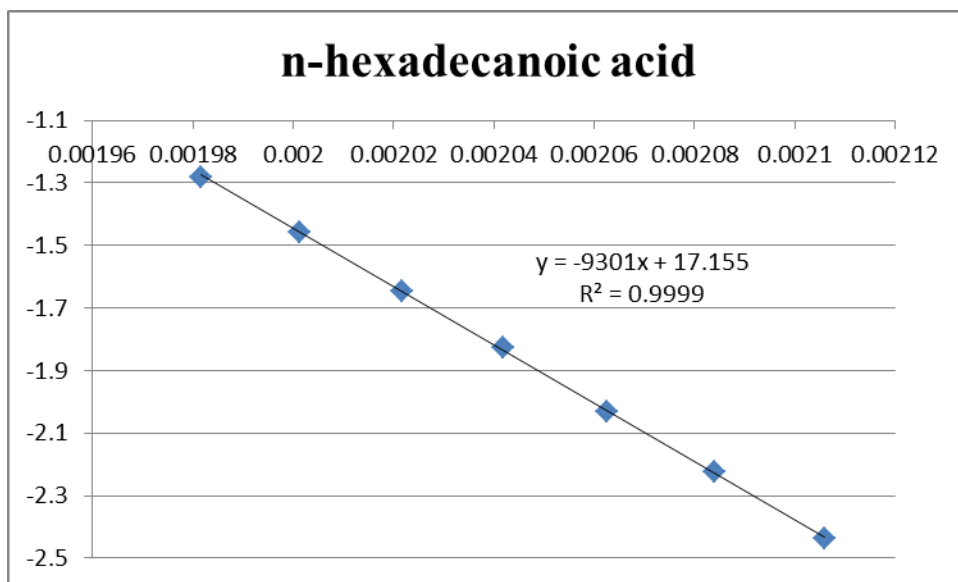
n-heptadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-2.763099162
479.85	0.002084	-2.545023825
484.85	0.002062	-2.345633329
489.75	0.002042	-2.131733815
494.65	0.002022	-1.944539222
499.65	0.002001	-1.752048937
504.65	0.001982	-1.565732279

Slope Coefficient	-9635.36
Intercept Coefficient	17.53242
Standard Error of the Slope	54.48273
Standard Error of the Intercept	0.111314
r^2	0.99984
Standard Error of Regression	0.005964
F-test	31276.5
Degrees of Freedom	5

n-heptadecanoic acid

$y = -9635.4x + 17.532$
$R^2 = 0.9998$
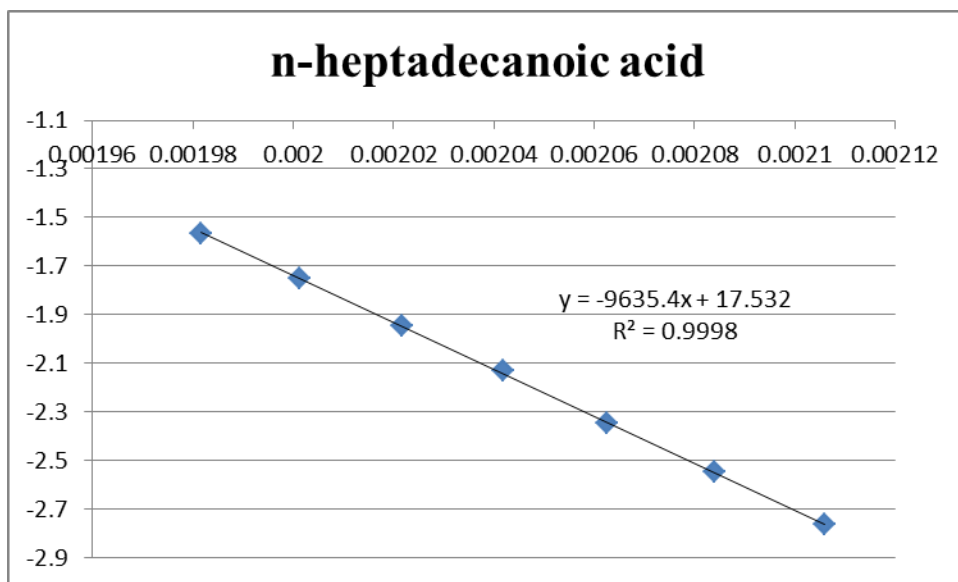
n-octadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-3.086909135
479.85	0.002084	-2.862132023
484.85	0.002062	-2.662181873
489.75	0.002042	-2.432956425
494.65	0.002022	-2.243392744
499.65	0.002001	-2.044071129
504.65	0.001982	-1.848043789

Slope Coefficient	-9967
Intercept Coefficient	17.9053
Standard Error of the Slope	72.06908
Standard Error of the Intercept	0.147245
r^2	0.999739
Standard Error of Regression	0.007888
F-test	19126.3
Degrees of Freedom	5

n-octadecanoic acid

$y = -9967x + 17.905$
$R^2 = 0.9997$
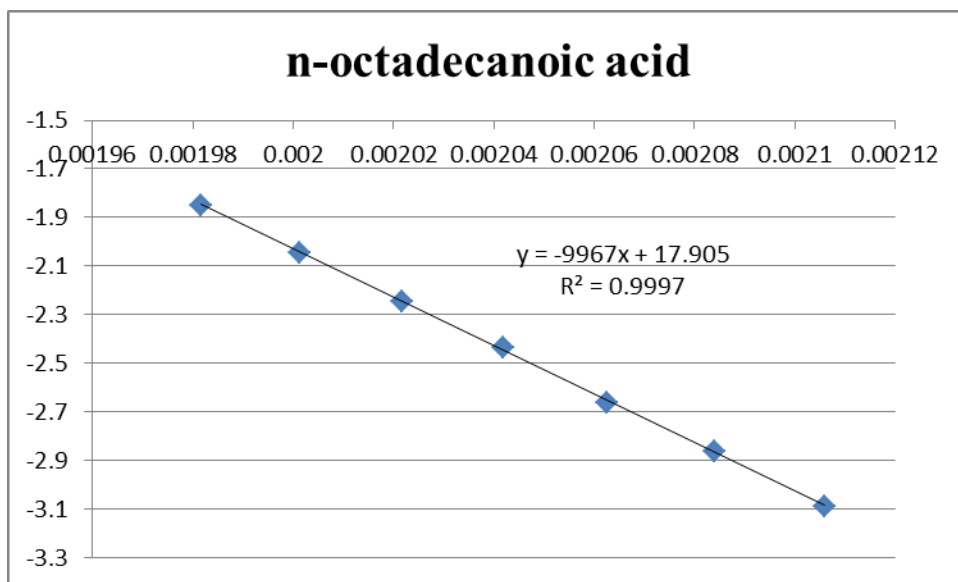
elaidic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-3.180830989
479.85	0.002084	-2.954487955
484.85	0.002062	-2.754219157
489.75	0.002042	-2.526485971
494.65	0.002022	-2.33823134
499.65	0.002001	-2.137531172
504.65	0.001982	-1.940434497

Slope Coefficient	-9966.31
Intercept Coefficient	17.81067
Standard Error of the Slope	69.16214
Standard Error of the Intercept	0.141306
r^2	0.999759
Standard Error of Regression	0.00757
F-test	20764.99
Degrees of Freedom	5

elaidic acid

y = -9966.3x + 17.811
R² = 0.9998
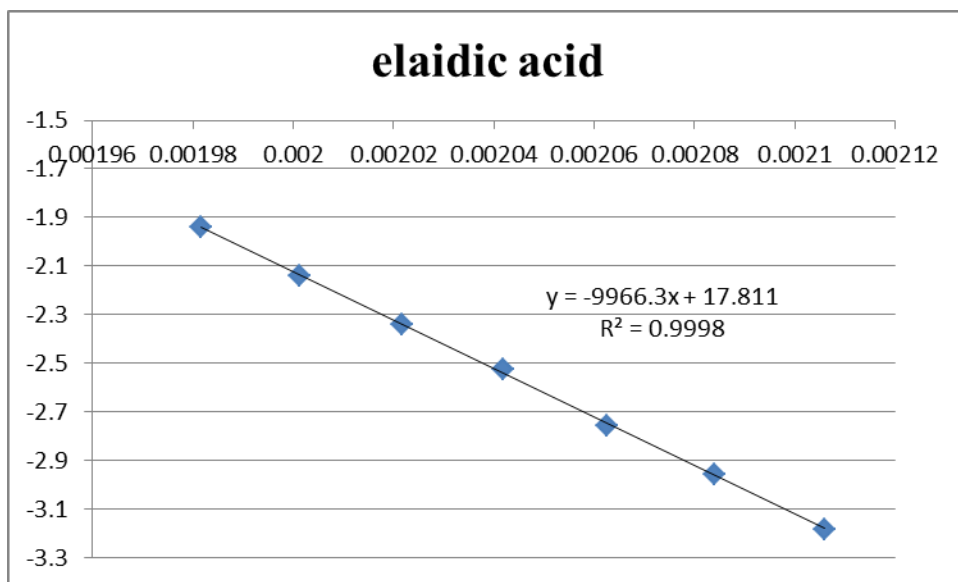
linoleic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-3.3517226
479.85	0.002084	-3.124439734
484.85	0.002062	-2.925498511
489.75	0.002042	-2.693376853
494.65	0.002022	-2.505750103
499.65	0.002001	-2.30423916
504.65	0.001982	-2.104018855

Slope Coefficient	-10021.6
Intercept Coefficient	17.75554
Standard Error of the Slope	77.76869
Standard Error of the Intercept	0.15889
r^2	0.999699
Standard Error of Regression	0.008512
F-test	16606.04
Degrees of Freedom	5

Chart titled "linoleic acid" with trendline equation $y = -10022x + 17.756$ and $R^2 = 0.9997$.
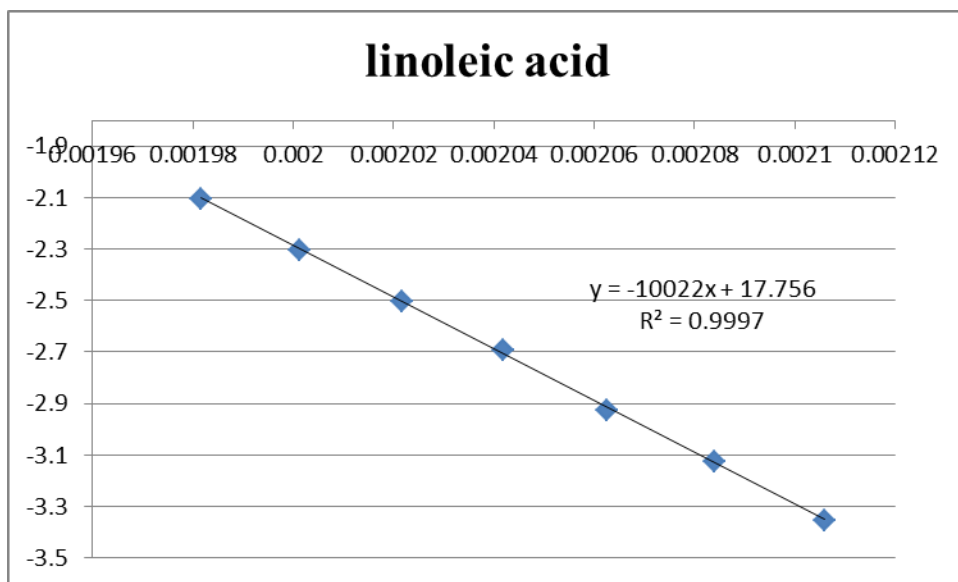
α-lenolenic acid:

T/K	T^{-1}	$\ln(t^{-1})$
474.85	0.002106	-3.552323358
479.85	0.002084	-3.320377834
484.85	0.002062	-3.11392396
489.75	0.002042	-2.881432614
494.65	0.002022	-2.688139104
499.65	0.002001	-2.482446683
504.65	0.001982	-2.280413942

Slope Coefficient	-10219
Intercept Coefficient	17.97158
Standard Error of the Slope	68.34984
Standard Error of the Intercept	0.139647
r^2	0.999776
Standard Error of Regression	0.007481
F-test	22353.31
Degrees of Freedom	5

α-linolenic acid

$y = -10219x + 17.972$
$R^2 = 0.9998$
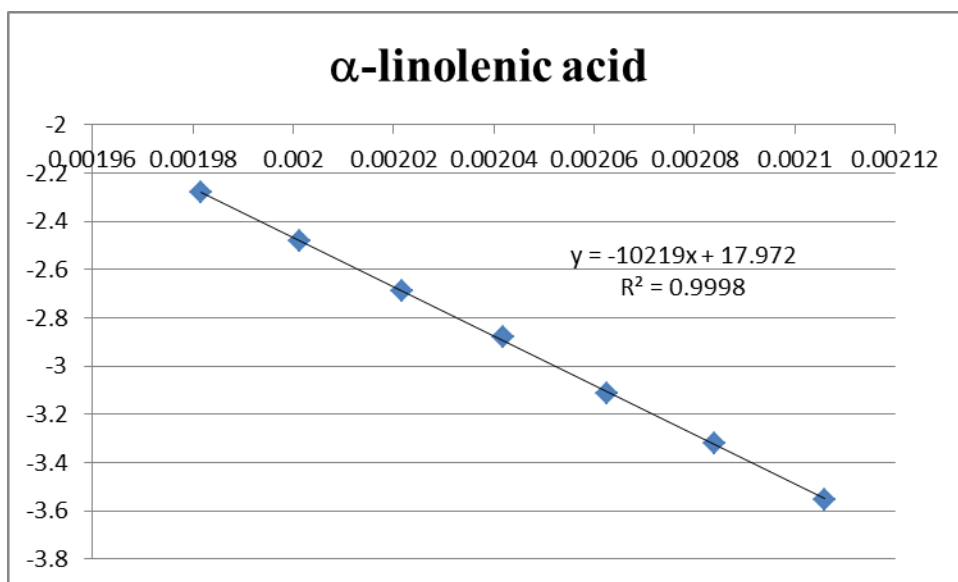
Appendix B-3: Experimental Data for Run 3 for Long-chain Fatty Acids Study

Run 3	484.7	489.6	494.5	499.6	504.6	509.8	514.8
				t/min			
methylene chloride	0.993	0.992	0.969	1.013	0.998	1.023	1.011
n-hexadecanoic acid	8.494	7.156	6.089	5.256	4.544	3.995	3.512
n-heptadecanoic acid	11.206	9.324	7.837	6.666	5.692	4.931	4.281
n-octadecanoic acid	14.937	12.287	10.214	8.556	7.23	6.168	5.294
elaidic acid	16.104	13.225	10.975	9.174	7.731	6.579	5.633
linoleic acid	19.002	15.552	12.855	10.662	8.978	7.572	6.47
n-nonadecanoic acid	19.975	16.254	13.372	11.059	9.258	7.787	6.62
γ-linolenic acid	21.113	17.223	14.193	11.758	9.842	8.291	7.044
α-linolenic acid	22.93	18.654	15.338	12.649	10.578	8.865	7.522
n-eicosanoic acid	26.71	21.531	17.538	14.34	11.878	9.876	8.306
n-henicosanoic acid	35.525	28.359	22.884	18.57	15.197	12.533	10.417
n-docosanoic acid	48.026	38.016	30.414	24.38	19.839	16.144	13.326

Run 3	$\dfrac{\text{slope}}{T/\text{K}}$	intercept	$\dfrac{\Delta_{\text{sln}}^{\text{g}} H_{\text{m}} \text{ (500 K)}}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta_{\text{l}}^{\text{g}} H_{\text{m}} \text{ (298.15)}}{\text{kJ·mol}^{-1}}$ (lit)	$\dfrac{\Delta_{\text{l}}^{\text{g}} H_{\text{m}} \text{ (298.15)}}{\text{kJ·mol}^{-1}}$ (calc)
n-hexadecanoic acid	-9074.2	16.7	75.44	120.7±2.3	121.2 ± 5.6
n-heptadecanoic acid	-9411.7	17.1	78.25	127.3±9.9	126.7 ± 5.7
n-octadecanoic acid	-9760.2	17.5	81.14	133.1±2.0	132.5 ± 5.8
elaidic acid	-10085.8	17.9	83.85	133.0±10.3	133.1 ± 5.9
linoleic acid	-9884.4	17.5	82.17	134.1±10.3	134.5 ± 5.9
n-nonadecanoic acid	-9796.6	17.5	81.44	137.9±2.4	137.9 ± 5.9
γ-linolenic acid	-10054.1	17.7	83.59		135.8 ± 5.9
α-linolenic acid	-10426.8	18.3	86.68	136.9±10.4	137.3 ± 5.9
n-eicosanoic acid	-9963.9	17.6	82.84	143.6±2.5	143.5 ± 6.1
n-henicosanoic acid	-10753.1	18.7	89.4		148.9 ± 6.2
n-docosanoic acid	-11089.5	19	92.19		154.4 ± 6.3
erucic acid	-10219.0	17.972	84.96		154.4 ± 6.3

$$\Delta_{\text{l}}^{\text{g}} H_{\text{m}} (298.15) = (1.99 \pm 0.05) \Delta_{\text{sln}}^{\text{g}} H_{\text{m}} (500 \text{ K}) - (28.8 \pm 4.2) \qquad r^2 = 0.9961$$

n-hexadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.014971715
489.55	0.002043	-1.818631947
494.45	0.002022	-1.632960695
499.55	0.002002	-1.445239246
504.55	0.001982	-1.265802206
509.75	0.001962	-1.089258713
514.75	0.001943	-0.916780514

Slope Coefficient	-9074.19
Intercept Coefficient	16.71521
Standard Error of the Slope	46.6478
Standard Error of the Intercept	0.093426
r^2	0.999868
Standard Error of Regression	0.004975
F-test	37840.21
Degrees of Freedom	5

n-hexadecanoic acid

$y = -9074.2x + 16.715$
$R^2 = 0.9999$
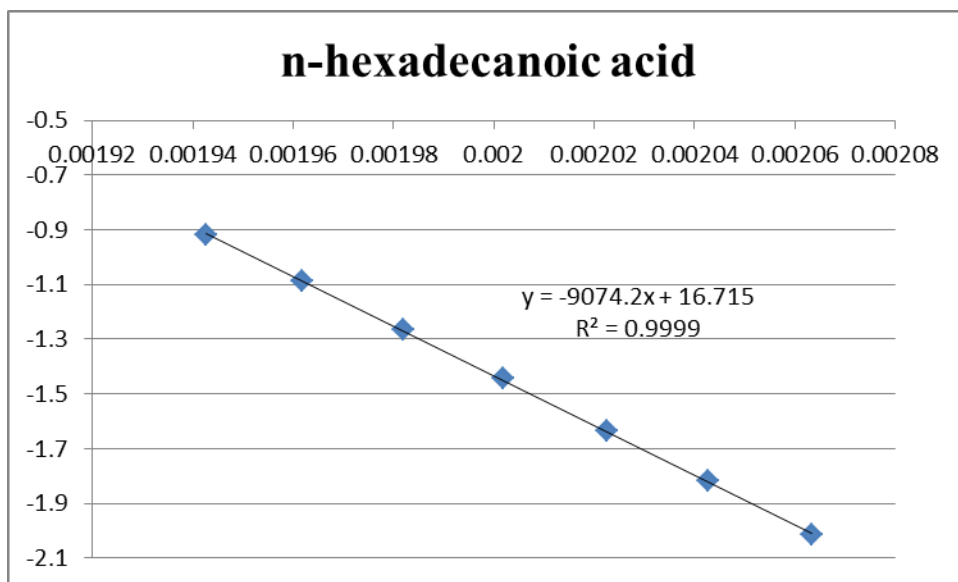
n-heptadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.323593022
489.55	0.002043	-2.120028995
494.45	0.002022	-1.926844698
499.55	0.002002	-1.732192956
504.55	0.001982	-1.5463261
509.75	0.001962	-1.363050349
514.75	0.001943	-1.184779917

Slope Coefficient	-9411.73
Intercept Coefficient	17.1035
Standard Error of the Slope	50.09234
Standard Error of the Intercept	0.100324
r^2	0.999858
Standard Error of Regression	0.005343
F-test	35301.77
Degrees of Freedom	5
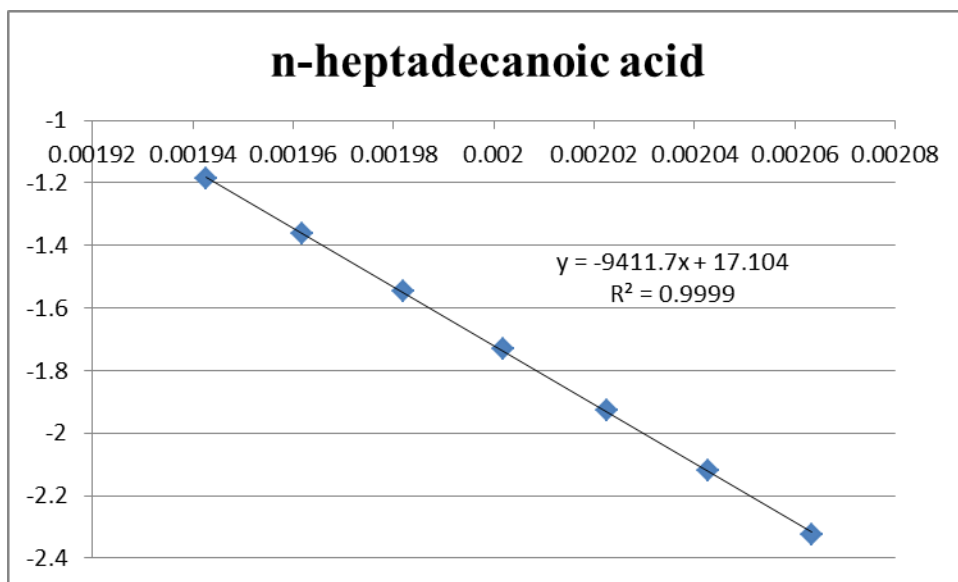
n-octadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.635039084
489.55	0.002043	-2.424323691
494.45	0.002022	-2.224064033
499.55	0.002002	-2.020633554
504.55	0.001982	-1.829779624
509.75	0.001962	-1.638047956
514.75	0.001943	-1.454819457

Slope Coefficient	-9760.21
Intercept Coefficient	17.51131
Standard Error of the Slope	52.50651
Standard Error of the Intercept	0.105159
r^2	0.999855
Standard Error of Regression	0.0056
F-test	34553.52
Degrees of Freedom	5

n-octadecanoic acid

$y = -9760.2x + 17.511$
$R^2 = 0.9999$
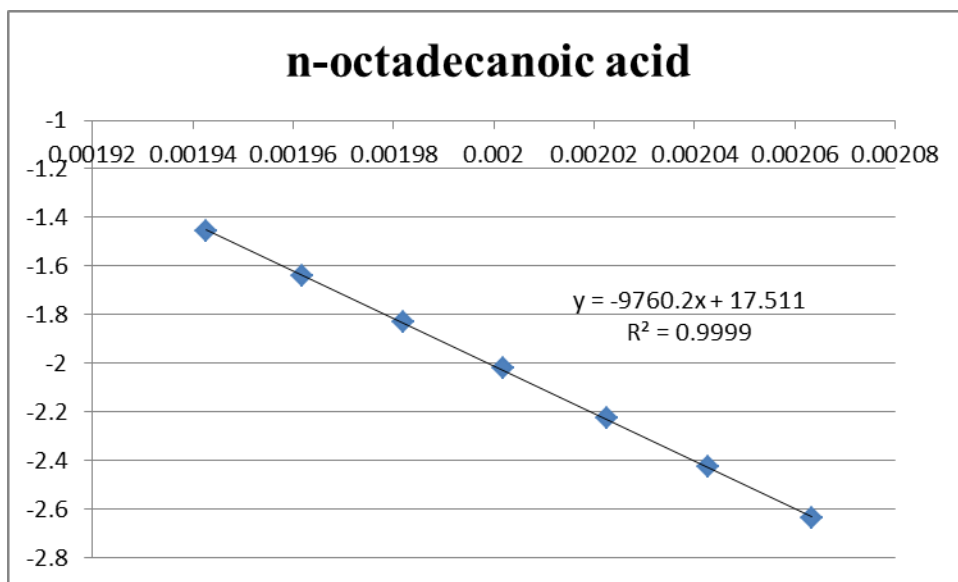
elaidic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.715386433
489.55	0.002043	-2.504150698
494.45	0.002022	-2.303167005
499.55	0.002002	-2.099271396
504.55	0.001982	-1.90711271
509.75	0.001962	-1.714884796
514.75	0.001943	-1.530903383

Slope Coefficient	-9796.58
Intercept Coefficient	17.50583
Standard Error of the Slope	51.41768
Standard Error of the Intercept	0.102979
r^2	0.999862
Standard Error of Regression	0.005484
F-test	36301.49
Degrees of Freedom	5
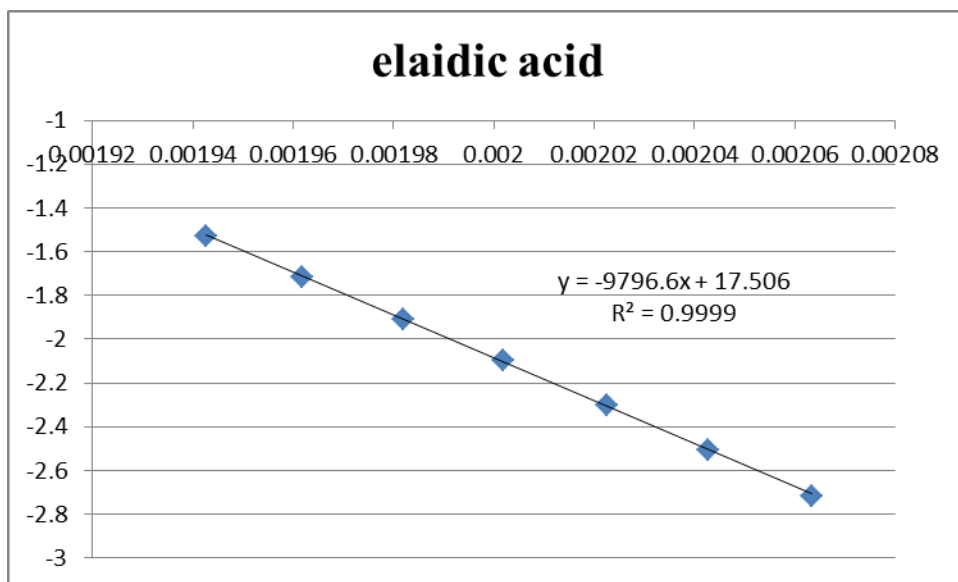
linoleic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.890869942
489.55	0.002043	-2.678290393
494.45	0.002022	-2.475320655
499.55	0.002002	-2.266820214
504.55	0.001982	-2.076937824
509.75	0.001962	-1.879187729
514.75	0.001943	-1.697257345

Slope Coefficient	-9884.36
Intercept Coefficient	17.51162
Standard Error of the Slope	57.11319
Standard Error of the Intercept	0.114386
r^2	0.999833
Standard Error of Regression	0.006091
F-test	29951.9
Degrees of Freedom	5

linoleic acid

$y = -9884.4x + 17.512$
$R^2 = 0.9998$
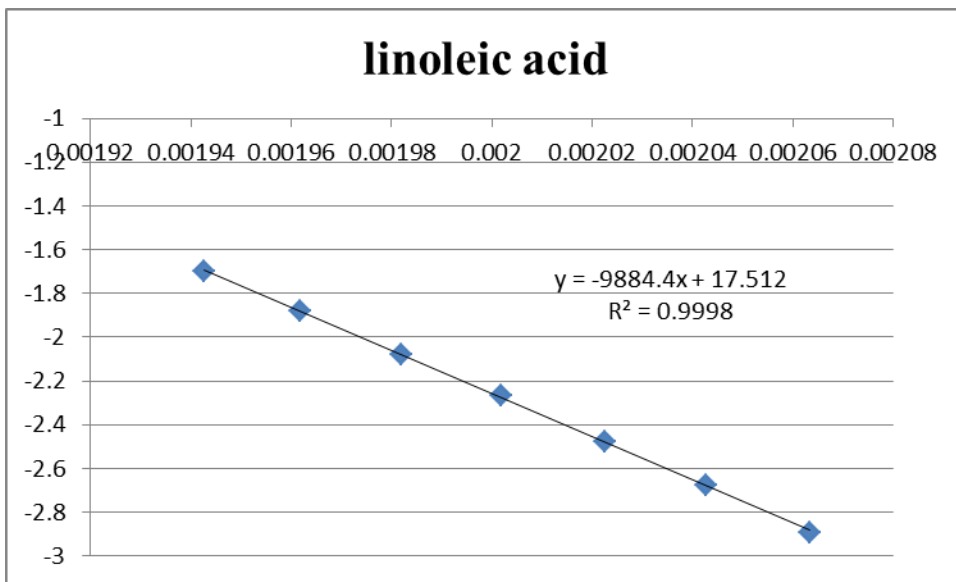
n-nonadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.943450748
489.55	0.002043	-2.725350096
494.45	0.002022	-2.51792288
499.55	0.002002	-2.307156948
504.55	0.001982	-2.111417522
509.75	0.001962	-1.911548206
514.75	0.001943	-1.724452906

Slope Coefficient	-10085.8
Intercept Coefficient	17.87538
Standard Error of the Slope	58.55808
Standard Error of the Intercept	0.11728
r^2	0.999831
Standard Error of Regression	0.006246
F-test	29664.95
Degrees of Freedom	5

n-nonadecanoic acid

$y = -10086x + 17.875$
$R^2 = 0.9998$
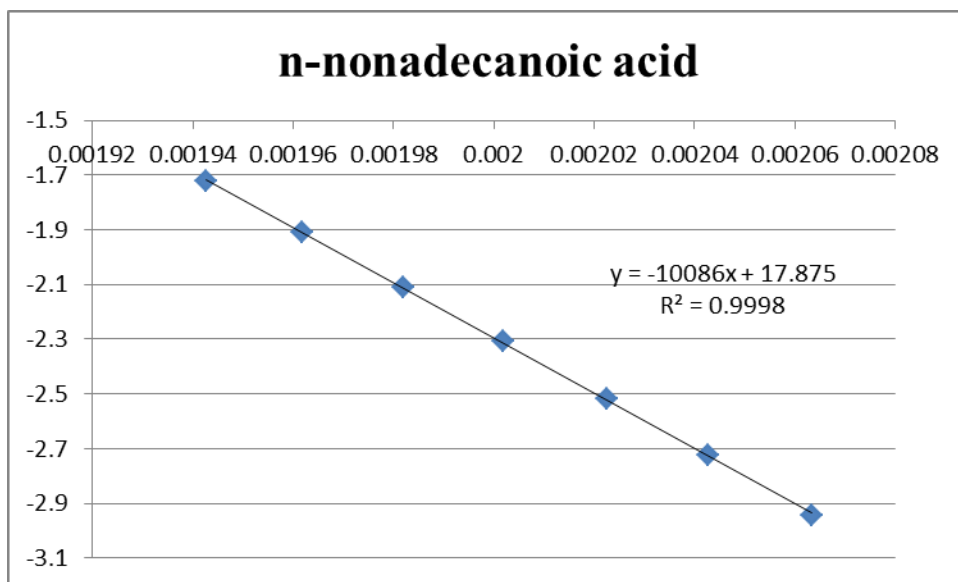
γ-linolenic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.00170345
489.55	0.002043	-2.786904666
494.45	0.002022	-2.581967627
499.55	0.002002	-2.374426596
504.55	0.001982	-2.179811338
509.75	0.001962	-1.983392052
514.75	0.001943	-1.797302568

Slope Coefficient	-9963.86
Intercept Coefficient	17.56498
Standard Error of the Slope	54.07708
Standard Error of the Intercept	0.108305
r^2	0.999853
Standard Error of Regression	0.005768
F-test	33949.14
Degrees of Freedom	5

γ-linolenic acid

$y = -9963.9x + 17.565$
$R^2 = 0.9999$
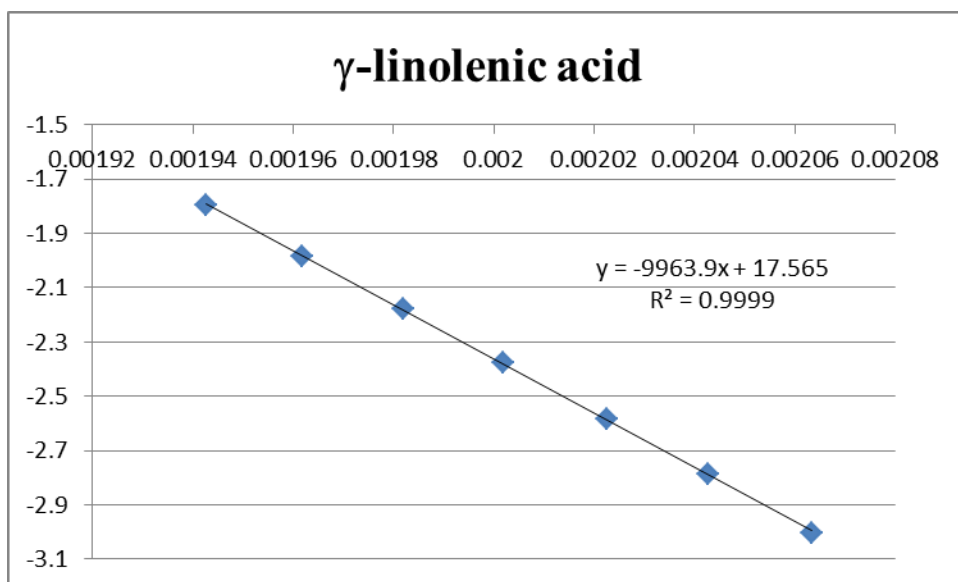
α-linolenic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.088144083
489.55	0.002043	-2.871408517
494.45	0.002022	-2.665006339
499.55	0.002002	-2.45408184
504.55	0.001982	-2.259744634
509.75	0.001962	-2.059406873
514.75	0.001943	-1.873492639

Slope Coefficient	-10054.1
Intercept Coefficient	17.66476
Standard Error of the Slope	56.37395
Standard Error of the Intercept	0.112905
r^2	0.999843
Standard Error of Regression	0.006013
F-test	31807.25
Degrees of Freedom	5

α-linolenic acid

y = -10054x + 17.665
R² = 0.9998
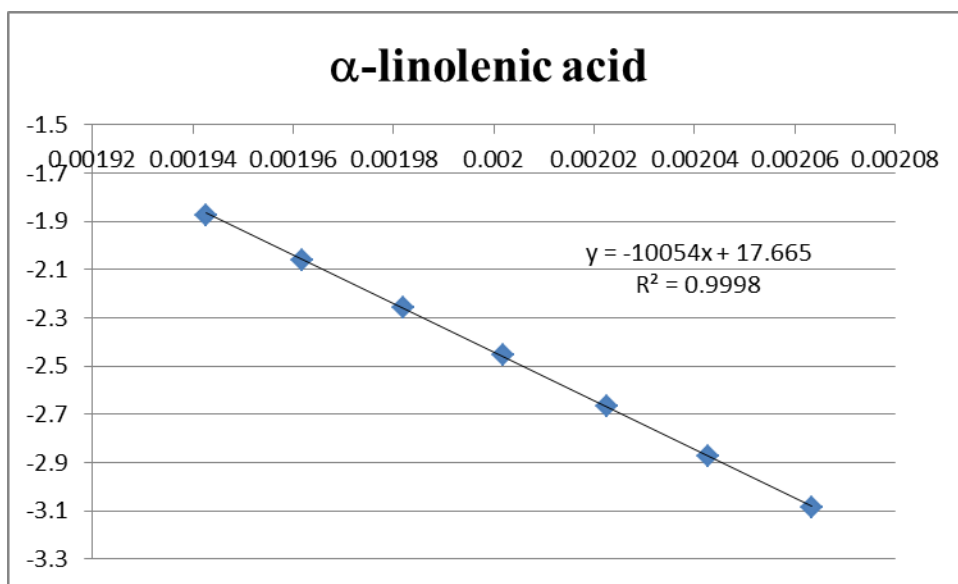
n-eicosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.247144993
489.55	0.002043	-3.022302611
494.45	0.002022	-2.807499855
499.55	0.002002	-2.589796544
504.55	0.001982	-2.386948653
509.75	0.001962	-2.180692292
514.75	0.001943	-1.987219913

Slope Coefficient	-10426.8
Intercept Coefficient	18.27536
Standard Error of the Slope	59.65592
Standard Error of the Intercept	0.119478
r^2	0.999836
Standard Error of Regression	0.006363
F-test	30548.83
Degrees of Freedom	5

n-eicosanoic acid

$y = -10427x + 18.275$
$R^2 = 0.9998$
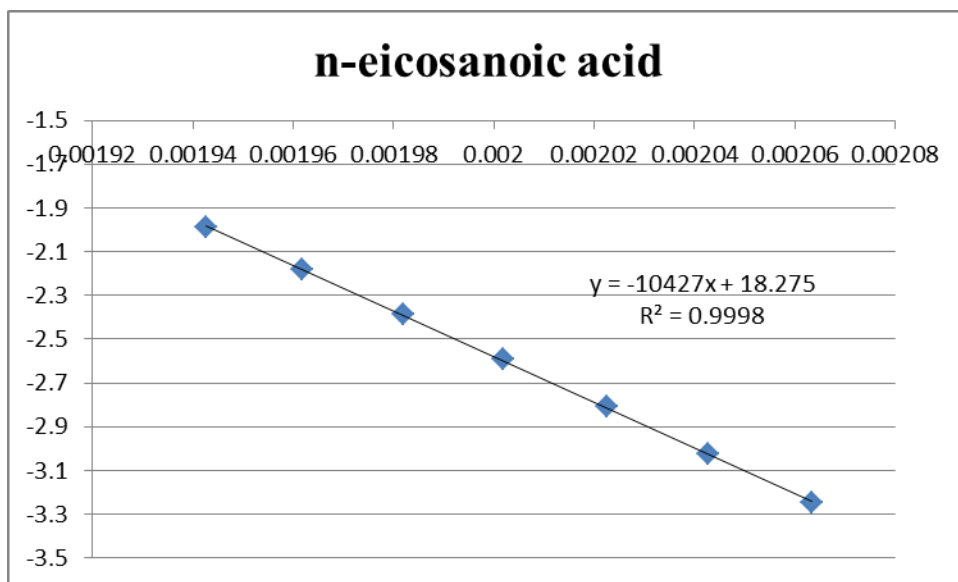
n-heneicosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.541885514
489.55	0.002043	-3.309327932
494.45	0.002022	-3.087132539
499.55	0.002002	-2.865438081
504.55	0.001982	-2.65317261
509.75	0.001962	-2.443217351
514.75	0.001943	-2.241357227

Slope Coefficient	-10753.1
Intercept Coefficient	18.65453
Standard Error of the Slope	61.514
Standard Error of the Intercept	0.1232
r^2	0.999836
Standard Error of Regression	0.006561
F-test	30557.76
Degrees of Freedom	5

n-heneicosanoic acid

$y = -10753x + 18.655$
$R^2 = 0.9998$
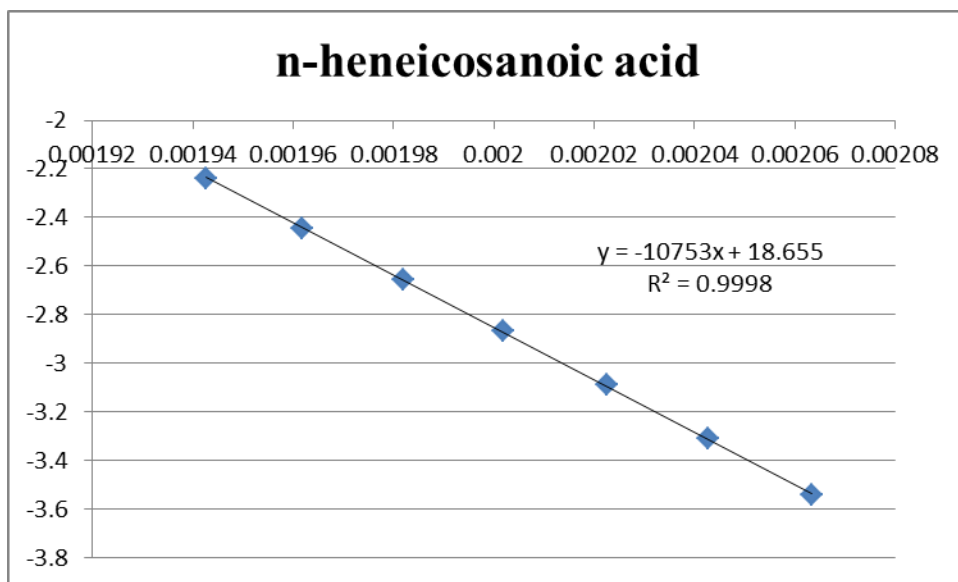
n-docosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.850841337
489.55	0.002043	-3.611568085
494.45	0.002022	-3.382523962
499.55	0.002002	-3.151317577
504.55	0.001982	-2.936055803
509.75	0.001962	-2.716088396
514.75	0.001943	-2.510835266

Slope Coefficient	-11089.5
Intercept Coefficient	19.03974
Standard Error of the Slope	65.13388
Standard Error of the Intercept	0.130449
r^2	0.999828
Standard Error of Regression	0.006947
F-test	28987.22
Degrees of Freedom	5
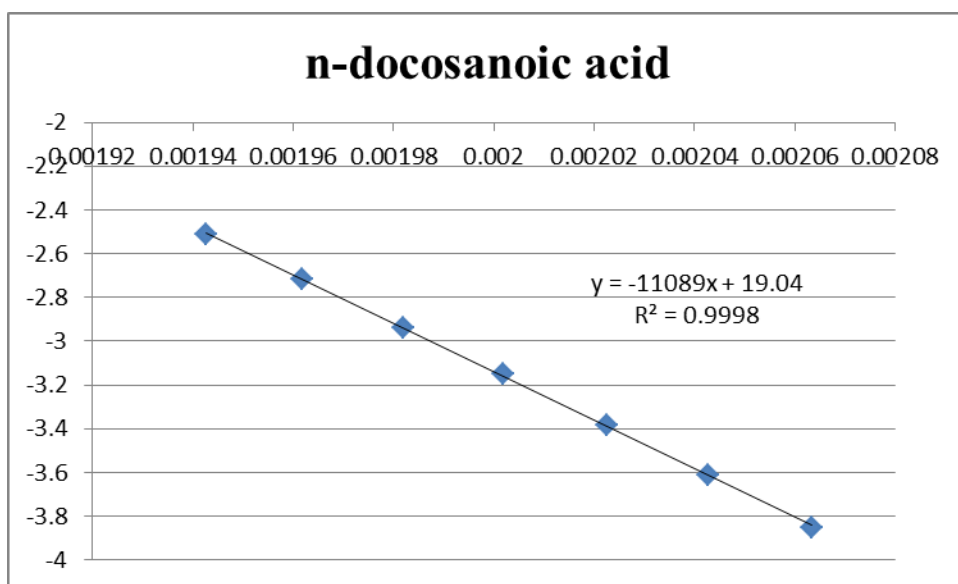
erucic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.928348693
489.55	0.002043	-3.689327035
494.45	0.002022	-3.460485505
499.55	0.002002	-3.228049965
504.55	0.001982	-3.014571514
509.75	0.001962	-2.793201355
514.75	0.001943	-2.589225831

Slope Coefficient	-11086.2
Intercept Coefficient	18.95542
Standard Error of the Slope	67.06253
Standard Error of the Intercept	0.134312
r^2	0.999817
Standard Error of Regression	0.007153
F-test	27327.62
Degrees of Freedom	5

erucic acid

$y = -11086x + 18.955$
$R^2 = 0.9998$
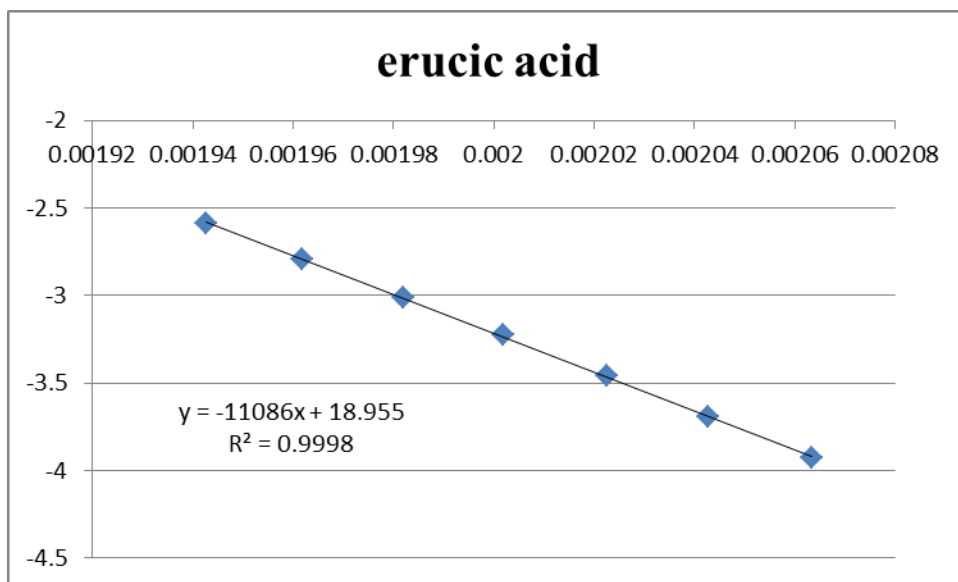
Appendix B-4: Experimental Data for Run 4 for Long-chain
Fatty Acids Study

Run 4	484.8	489.8	494.8	499.8	504.8	509.8	514.9
				t/min			
methylene chloride	0.965	0.995	0.992	0.987	1.019	1.019	1.027
n-hexadecanoic acid	8.479	7.121	6.068	5.208	4.539	3.978	3.523
n-heptadecanoic acid	11.195	9.273	7.804	6.615	5.679	4.912	4.288
n-octadecanoic acid	14.913	12.199	10.186	8.52	7.207	6.157	5.294
elaidic acid	16.07	13.127	10.939	9.132	7.706	6.566	5.63
linoleic acid	18.925	15.383	12.853	10.669	8.933	7.589	6.441
n-nonadecanoic acid	19.927	16.117	13.355	11.045	9.22	7.793	6.603
γ-linolenic acid	21.045	17.072	14.142	11.721	9.796	8.279	7.026
α-linolenic acid	22.837	18.459	15.305	12.636	10.52	8.872	7.487
n-eicosanoic acid	26.645	21.342	17.514	14.339	11.827	9.888	8.28
n-heneicosanoic acid	35.434	28.17	22.775	18.493	15.135	12.506	10.395
n-docosanoic acid	47.844	37.667	30.41	24.436	19.736	16.186	13.268
erucic acid	51.547	40.578	32.853	26.362	21.263	17.437	14.252

Run 4	slope T/K	intercept	$\dfrac{\Delta_{sln}^{g}H_{m}\,(500\ \text{K})}{\text{kJ·mol}^{-1}}$	$\dfrac{\Delta_{l}^{g}H_{m}\,(298.15)}{\text{kJ·mol}^{-1}}$ (lit)	$\dfrac{\Delta_{l}^{g}H_{m}\,(298.15)}{\text{kJ·mol}^{-1}}$ (calc)
n-hexadecanoic	-9125.1	16.816	75.86	120.7±2.0	121.2 ± 7.4
n-heptadecanoic	-9464.5	17.208	78.68	127.3±9.9	126.9 ± 7.5
n-octadecanoic	-9801.2	17.591	81.48	133.1±2.0	132.6 ± 7.7
elaidic acid	-9834.8	17.58	81.76	133.0±10.3	133.2 ± 7.7
linoleic acid	-9909.7	17.56	82.39	134.1±10.3	134.5 ± 7.7
n-nonadecanoic	-9909.7	17.56	82.39	134.1±10.3	134.5 ± 7.7
γ-linolenic acid	-9997.6	17.631	83.12		135.9 ± 7.7
α-linolenic acid	-10082.5	17.72	83.82	136.9±10.4	137.4 ± 7.8
n-eicosanoic acid	-10121.5	17.944	84.15	137.9±2.0	138.0 ± 7.8
n-heneicosanoic	-9997.6	17.631	83.12		135.9 ± 7.7
n-docosanoic acid	-10082.5	17.72	83.82	136.9±10.4	137.4 ± 7.8
erucic acid	-10458.8	18.336	86.95	143.6±2.5	143.8 ± 7.9

$$\Delta_{l}^{g}H_{m}\,(298.15) = (2.04 \pm 0.07)\,\Delta_{sln}^{g}H_{m}\,(500\ \text{K}) - (33.5 \pm 5.4) \qquad r^{2} = 0.9958$$

n-hexadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-2.016655569
489.75	0.002042	-1.817367777
494.75	0.002021	-1.629725503
499.75	0.002001	-1.445291069
504.75	0.001981	-1.273603111
509.75	0.001962	-1.102780425
514.85	0.001942	-0.938963214

Slope Coefficient	-8930.56
Intercept Coefficient	16.41611
Standard Error of the Slope	71.6703
Standard Error of the Intercept	0.143495
r^2	0.999678
Standard Error of Regression	0.007614
F-test	15526.69
Degrees of Freedom	5

n-hexadecanoic acid

$y = -8930.6x + 16.416$
$R^2 = 0.9997$
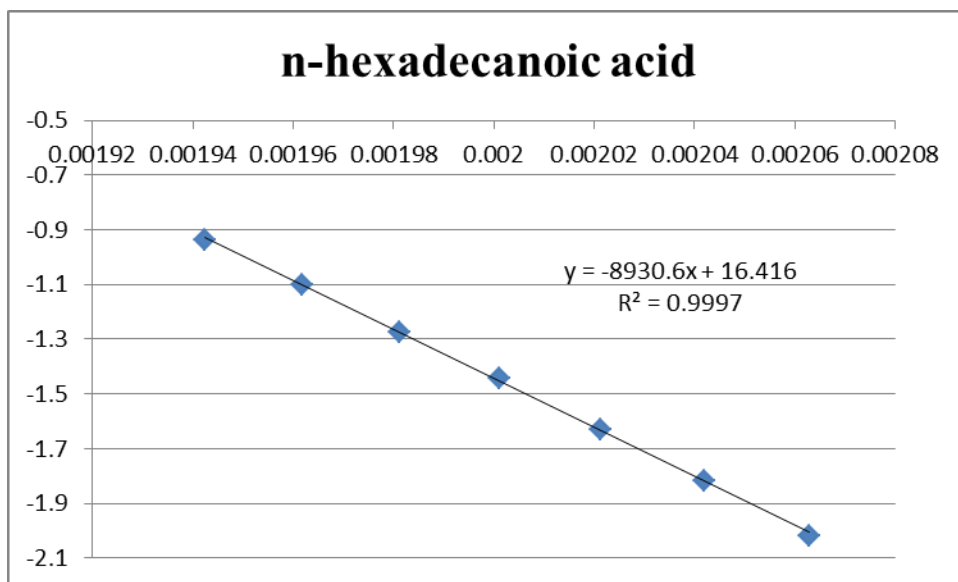
n-heptadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-2.325301573
489.75	0.002042	-2.117205508
494.75	0.002021	-1.922573041
499.75	0.002001	-1.731574317
504.75	0.001981	-1.550513018
509.75	0.001962	-1.372789117
514.85	0.001942	-1.200704

Slope Coefficient	-9315.27
Intercept Coefficient	16.90102
Standard Error of the Slope	67.84559
Standard Error of the Intercept	0.135837
r^2	0.999735
Standard Error of Regression	0.007208
F-test	18851.58
Degrees of Freedom	5

n-heptadecanoic acid

$y = -9315.3x + 16.901$
$R^2 = 0.9997$
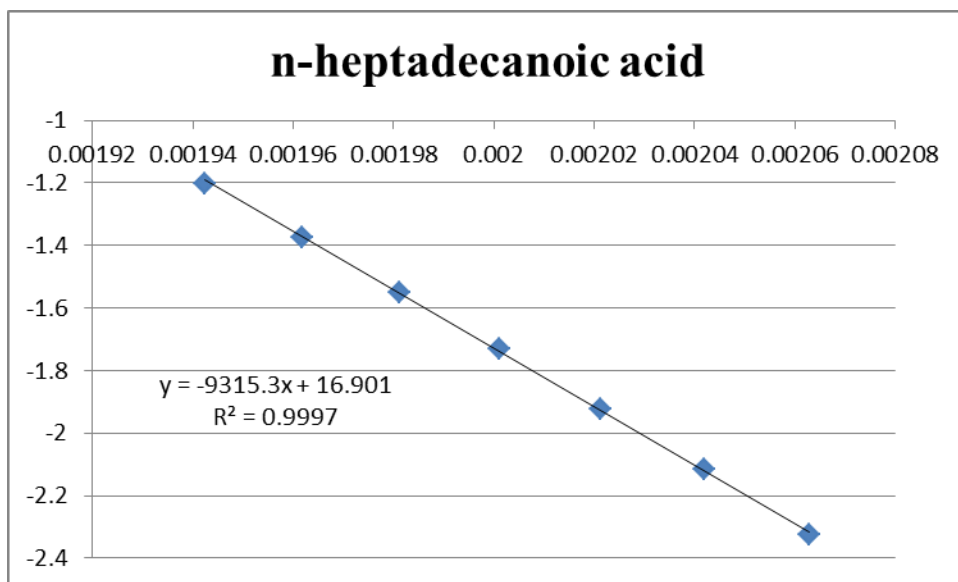
n-octadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-2.63530643
489.75	0.002042	-2.418907278
494.75	0.002021	-2.22140565
499.75	0.002001	-2.022134865
504.75	0.001981	-1.831220551
509.75	0.001962	-1.647004006
514.85	0.001942	-1.465326805

Slope Coefficient	-9687.01
Intercept Coefficient	17.35648
Standard Error of the Slope	55.48951
Standard Error of the Intercept	0.111098
r^2	0.999836
Standard Error of Regression	0.005895
F-test	30475.98
Degrees of Freedom	5

n-octadecanoic acid

$y = -9687x + 17.356$
$R^2 = 0.9998$
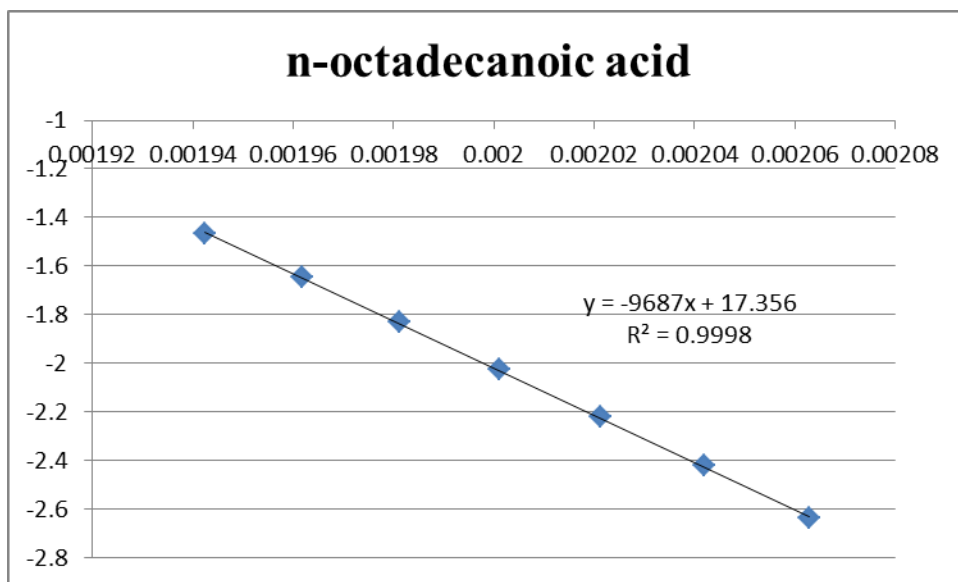
elaidic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-2.71500373
489.75	0.002042	-2.498304839
494.75	0.002021	-2.299892461
499.75	0.002001	-2.100062349
504.75	0.001981	-1.908221138
509.75	0.001962	-1.722953839
514.85	0.001942	-1.539966016

Slope Coefficient	-9728.81
Intercept Coefficient	17.36257
Standard Error of the Slope	52.16119
Standard Error of the Intercept	0.104435
r^2	0.999856
Standard Error of Regression	0.005541
F-test	34787.58
Degrees of Freedom	5

elaidic acid

$y = -9728.8x + 17.363$
$R^2 = 0.9999$
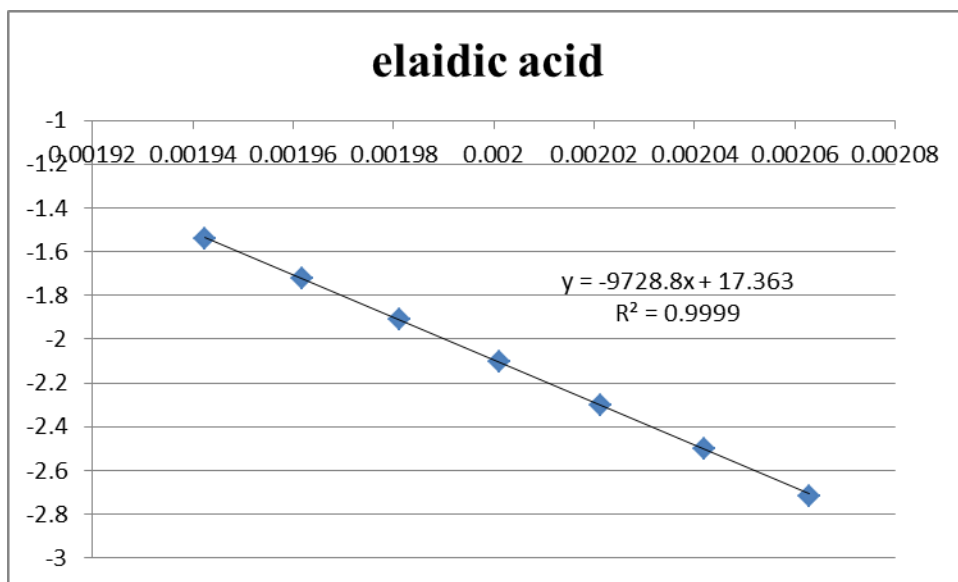
linoleic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-2.888132605
489.75	0.002042	-2.668470277
494.75	0.002021	-2.475493243
499.75	0.002001	-2.27254448
504.75	0.001981	-2.075401218
509.75	0.001962	-1.890668788
514.85	0.001942	-1.700349395

Slope Coefficient	-9819.73
Intercept Coefficient	17.37506
Standard Error of the Slope	46.14722
Standard Error of the Intercept	0.092394
r^2	0.99989
Standard Error of Regression	0.004903
F-test	45280.19
Degrees of Freedom	5

linoleic acid

$y = -9819.7x + 17.375$
$R^2 = 0.9999$
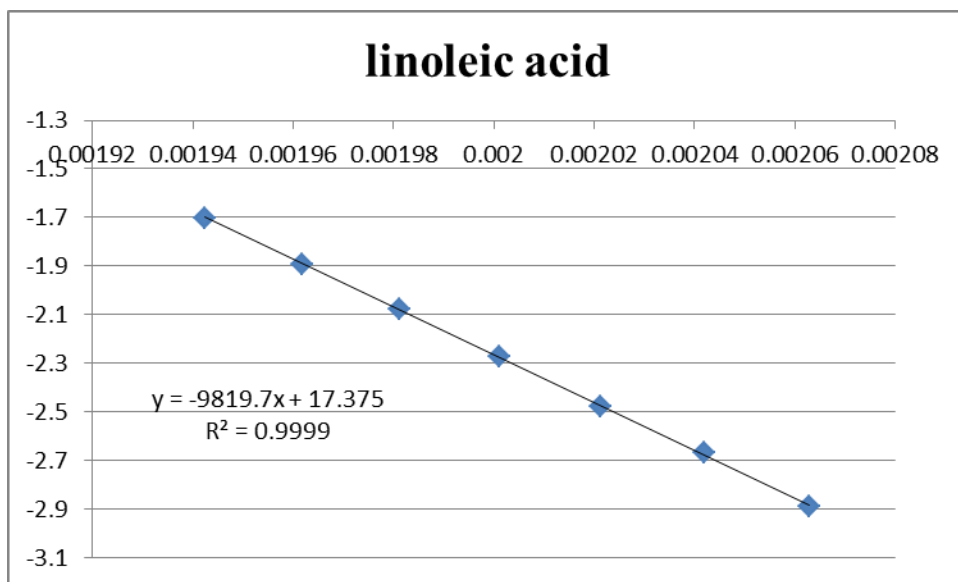
n-nonadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-2.942433485
489.75	0.002042	-2.718135629
494.75	0.002021	-2.516853214
499.75	0.002001	-2.310485577
504.75	0.001981	-2.110725127
509.75	0.001962	-1.920934905
514.85	0.001942	-1.729534247

Slope Coefficient	-10034.1
Intercept Coefficient	17.76435
Standard Error of the Slope	49.15061
Standard Error of the Intercept	0.098407
r^2	0.99988
Standard Error of Regression	0.005222
F-test	41676.85
Degrees of Freedom	5

n-nonadecanoic acid

$y = -10034x + 17.764$
$R^2 = 0.9999$
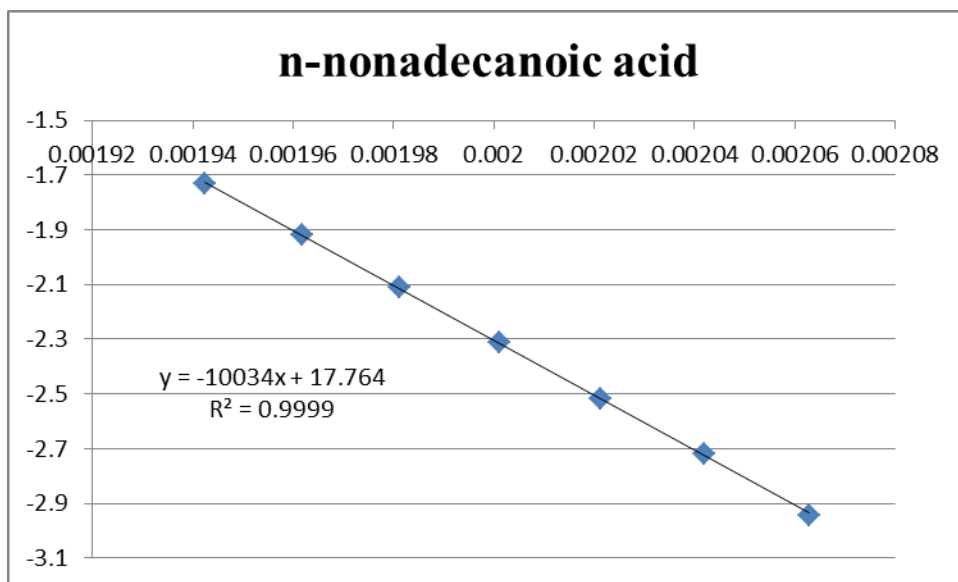
γ-linolenic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-2.999727173
489.75	0.002042	-2.779220983
494.75	0.002021	-2.57844218
499.75	0.002001	-2.375421466
504.75	0.001981	-2.178200873
509.75	0.001962	-1.98975809
514.85	0.001942	-1.801783704

Slope Coefficient	-9916.25
Intercept Coefficient	17.46376
Standard Error of the Slope	46.73613
Standard Error of the Intercept	0.093573
r^2	0.999889
Standard Error of Regression	0.004965
F-test	45018.35
Degrees of Freedom	5

γ-linolenic acid

$y = -9916.3x + 17.464$
$R^2 = 0.9999$
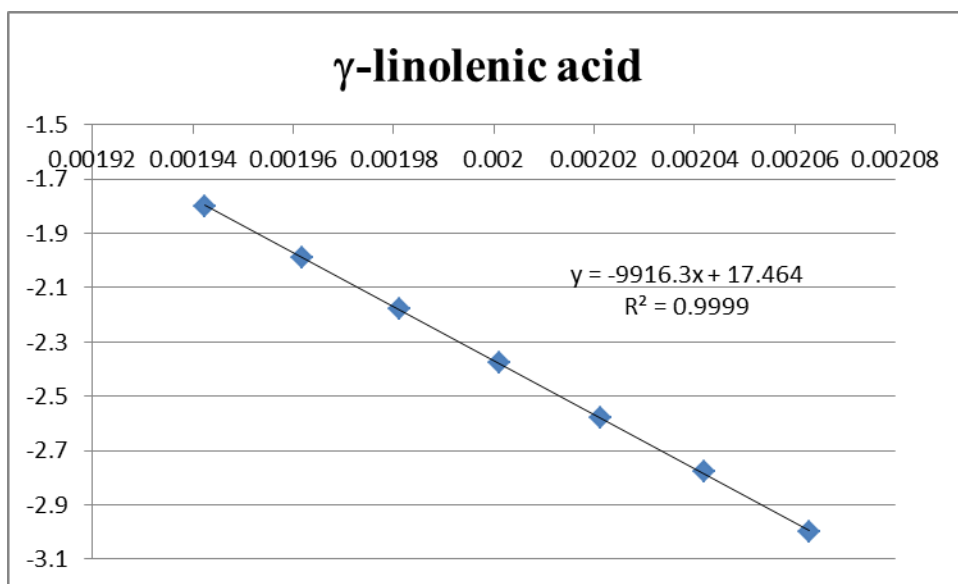
α-linolenic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-3.085183578
489.75	0.002042	-2.861827117
494.75	0.002021	-2.663045243
499.75	0.002001	-2.457073727
504.75	0.001981	-2.257034136
509.75	0.001962	-2.067729417
514.85	0.001942	-1.875192485

Slope Coefficient	-10006.9
Intercept Coefficient	17.56466
Standard Error of the Slope	44.77821
Standard Error of the Intercept	0.089653
r^2	0.9999
Standard Error of Regression	0.004757
F-test	49942.44
Degrees of Freedom	5

α-linolenic acid

$y = -10007x + 17.565$
$R^2 = 0.9999$
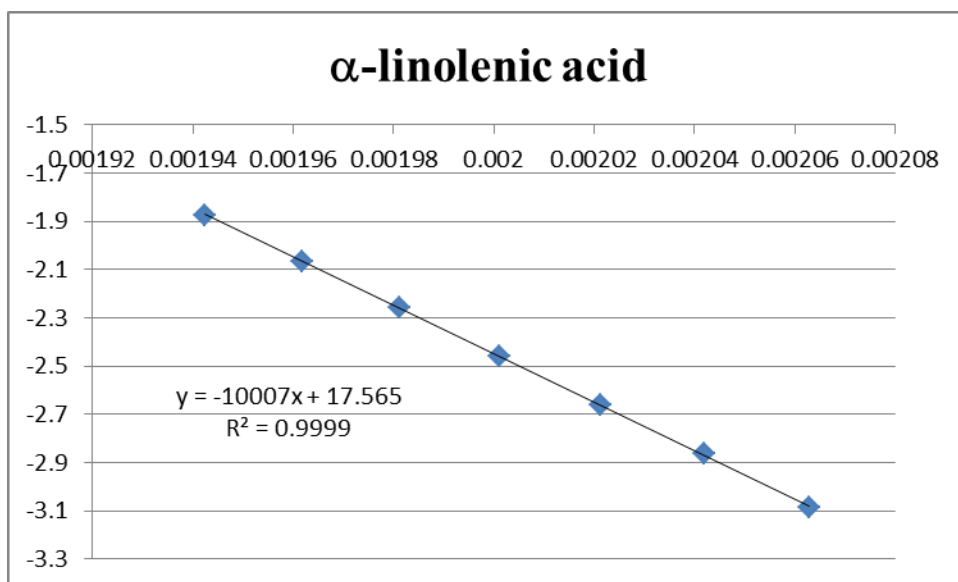
n-eicosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-3.24570041
489.75	0.002042	-3.014400801
494.75	0.002021	-2.806273953
499.75	0.002001	-2.593271111
504.75	0.001981	-2.38523632
509.75	0.001962	-2.188578883
514.85	0.001942	-1.989845711

Slope Coefficient	-10391.5
Intercept Coefficient	18.19786
Standard Error of the Slope	46.17868
Standard Error of the Intercept	0.092457
r^2	0.999901
Standard Error of Regression	0.004906
F-test	50637.75
Degrees of Freedom	5

n-eicosanoic acid

$y = -10392x + 18.198$
$R^2 = 0.9999$
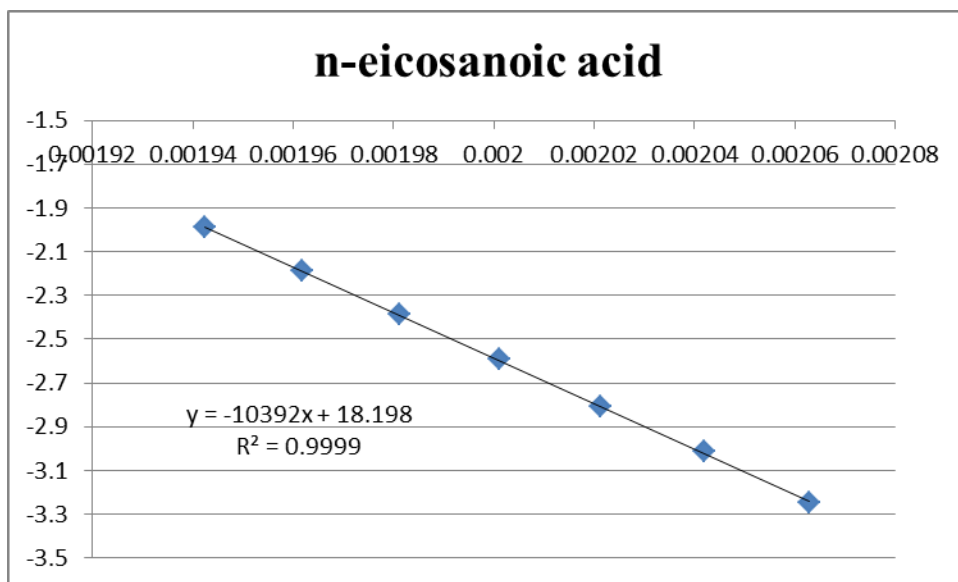
n-heneicosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-3.540058614
489.75	0.002042	-3.303367709
494.75	0.002021	-3.082363951
499.75	0.002001	-2.863781678
504.75	0.001981	-2.651118087
509.75	0.001962	-2.445854023
514.85	0.001942	-2.243857363

Slope Coefficient	-10738.2
Intercept Coefficient	18.61943
Standard Error of the Slope	49.99759
Standard Error of the Intercept	0.100103
r^2	0.999892
Standard Error of Regression	0.005312
F-test	46128.15
Degrees of Freedom	5

n-heneicosanoic acid

y = -10738x + 18.619
R² = 0.9999
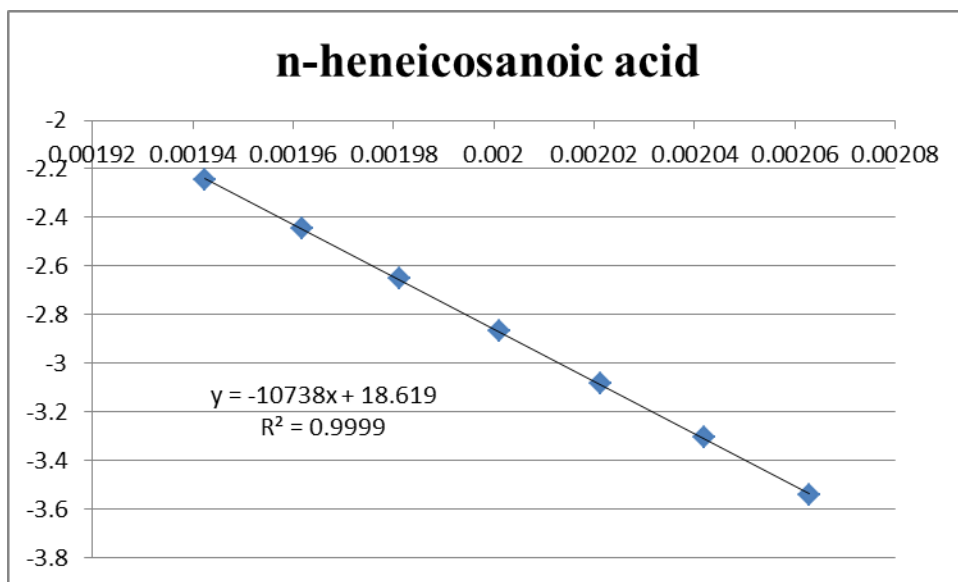
n-docosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-3.847568194
489.75	0.002042	-3.602813433
494.75	0.002021	-3.38250612
499.75	0.002001	-3.155761122
504.75	0.001981	-2.93228379
509.75	0.001962	-2.722661354
514.85	0.001942	-2.509788033

Slope Coefficient	-11073.7
Intercept Coefficient	19.00192
Standard Error of the Slope	43.0603
Standard Error of the Intercept	0.086213
r^2	0.999924
Standard Error of Regression	0.004575
F-test	66134.59
Degrees of Freedom	5

y = -11074x + 19.002
R² = 0.9999
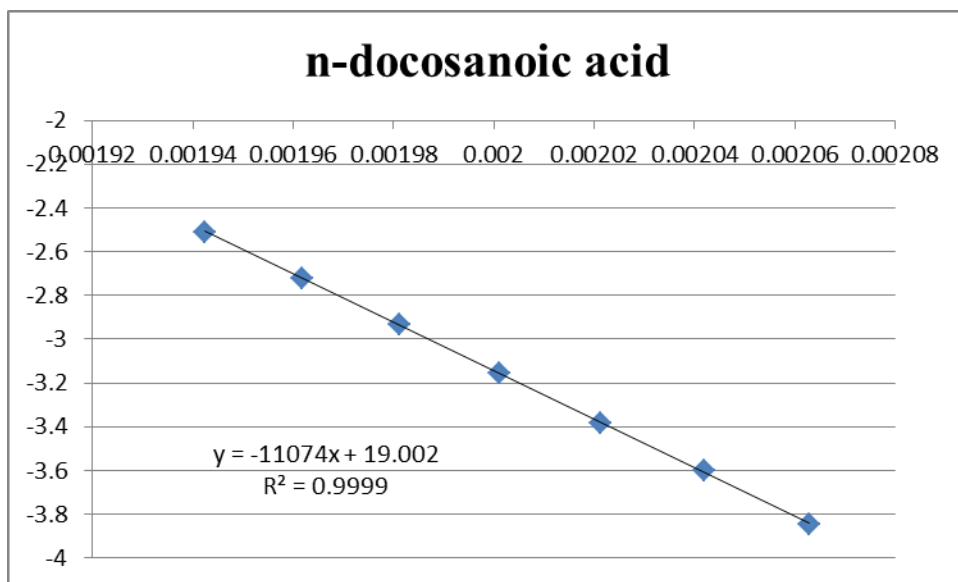
erucic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.75	0.002063	-3.923594263
489.75	0.002042	-3.679153437
494.75	0.002021	-3.462215982
499.75	0.002001	-3.234604546
504.75	0.001981	-3.010477584
509.75	0.001962	-2.801642679
514.85	0.001942	-2.586770637

Slope Coefficient	-11061.5
Intercept Coefficient	18.89968
Standard Error of the Slope	44.82531
Standard Error of the Intercept	0.089747
r^2	0.999918
Standard Error of Regression	0.004762
F-test	60894.83
Degrees of Freedom	5

erucic acid

$y = -11061x + 18.9$
$R^2 = 0.9999$
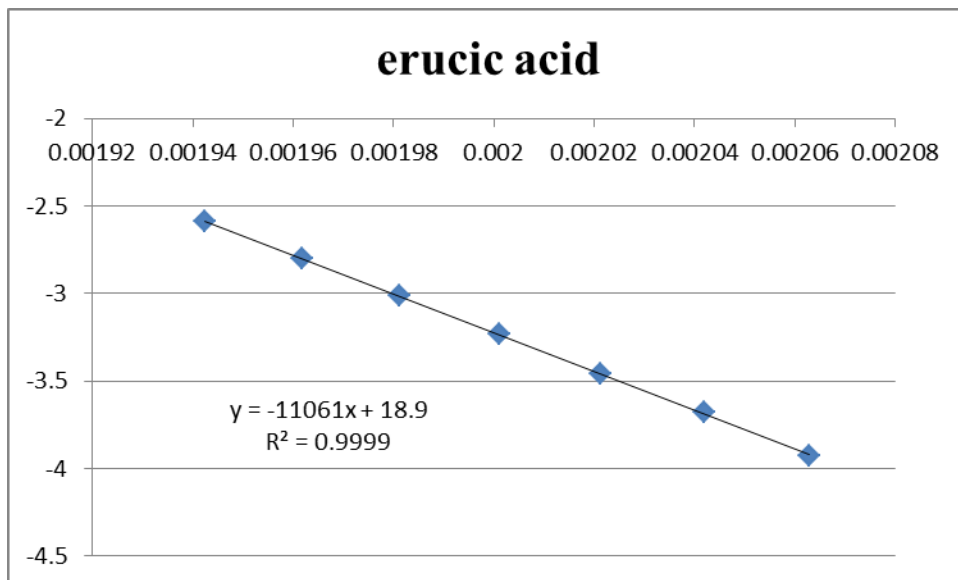
Appendix C

Appendix C-1: Experimental Data for Run 1 for More Long-chain
Fatty Acids Study

Run 1	486.0	491.0	495.9	500.9	505.8	510.9	516.0
				t/min			
methylene chloride	0.235	0.261	0.257	0.250	0.260	0.271	0.271
n-hexadecanoic acid	2.299	1.965	1.652	1.412	1.226	1.082	0.959
petroselininc acid	4.336	3.591	2.965	2.474	2.093	1.789	1.539
linoleic acid	5.128	4.224	3.455	2.873	2.397	2.048	1.751
n-eicosanoic acid	7.252	5.860	4.734	3.880	3.196	2.683	2.257
gondoic acid	7.920	6.393	5.154	4.225	3.463	2.910	2.445
erucic acid	14.207	11.258	8.931	7.185	5.785	4.763	3.927
n-tetracosanoic acid	25.075	19.346	14.947	11.819	9.125	7.506	6.025
nervonic acid	27.320	21.162	16.291	12.902	9.889	8.184	6.568
cervonic acid	27.910	21.843	17.094	13.588	10.738	8.750	7.096
n-hexacosanoic acid	42.445	32.574	25.094	19.571	15.227	12.162	9.700

Run 1	slope T/K	intercept	$\Delta_{sln}^{g} H_m$ (500 K) kJ·mol^{-1}	$\Delta_{l}^{g} H_m$ (298.15) kJ·mol^{-1} (lit)	$\Delta_{l}^{g} H_m$ (298.15) kJ·mol^{-1} (calc)
n-hexadecanoic acid	-9239.19	18.293	76.81	120.7	120.7 ± 2.3
petroselinic acid	-9842.61	18.848	81.83		130.9 ± 2.4
linoleic acid	-10043.8	19.086	83.50	134.1	134.3 ± 2.4
n-eicosanoic acid	-10578.9	19.829	87.95	143.6	143.4 ± 2.5
gondoic acid	-10589.8	19.760	88.04		143.6 ± 2.3
erucic acid	-11245.4	20.512	93.49	154.5	154.7 ± 2.4
n-tetracosanoic acid	-12266.8	22.042	101.98		172.0 ± 2.6
nervonic acid	-12260.4	21.941	101.93		171.9 ± 2.6
cervonic acid	-11745.5	20.857	97.65		163.2 ± 2.6
n-hexacosanoic acid	-12570.9	22.134	104.51		177.1 ± 2.7

$\Delta_{l}^{g} H_m$ (298.15 K)/kJ·mol^{-1} = (2.04 ± 0.02) $\Delta_{sln}^{g} H_m$ (500 K) - (36.0 ± 1.6); $r^2 = 0.9998$

n-hexadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-0.7244867
490.95	0.002037	-0.5330287
495.85	0.002017	-0.3333157
500.85	0.001997	-0.1505804
505.75	0.001977	0.0340172
510.85	0.001958	0.20890136
515.95	0.001938	0.37397975

Slope Coefficient	-9239.19
Intercept Coefficient	18.29264
Standard Error of the Slope	80.59503
Standard Error of the Intercept	0.161003
r^2	0.99962
Standard Error of Regression	0.008486
F-test	13141.69
Degrees of Freedom	5

n-hexadecanoic acid

$y = -9239.2x + 18.293$
$R^2 = 0.9996$
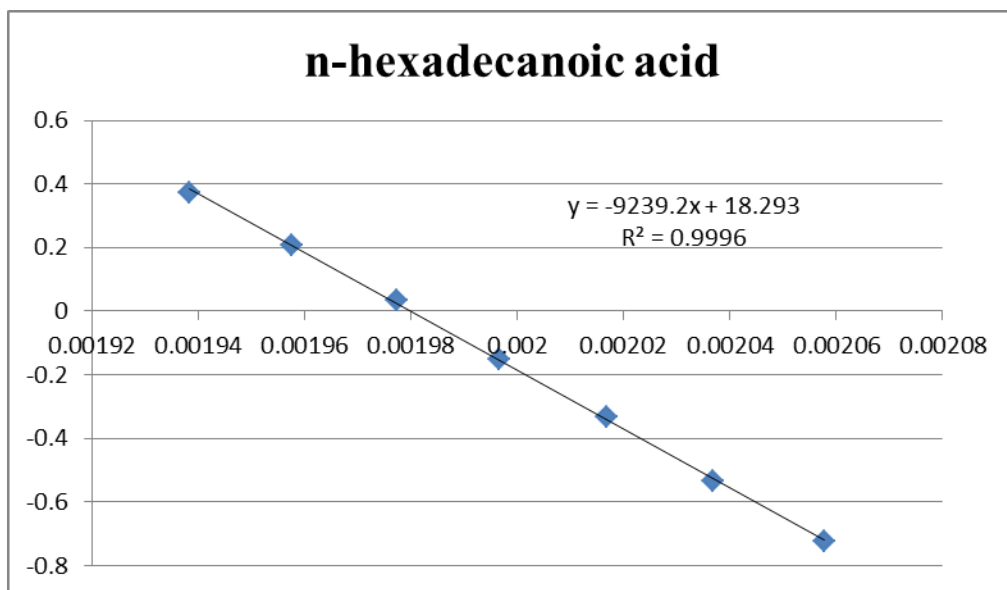
petroselinic acid:

T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-1.4112176
490.95	0.002037	-1.2030776
495.85	0.002017	-0.9963698
500.85	0.001997	-0.7993516
505.75	0.001977	-0.6060952
510.85	0.001958	-0.4172987
515.95	0.001938	-0.2375539

Slope Coefficient	-9842.61
Intercept Coefficient	18.84836
Standard Error of the Slope	62.79703
Standard Error of the Intercept	0.125448
r^2	0.999797
Standard Error of Regression	0.006612
F-test	24566.46
Degrees of Freedom	5

petroselinic acid

$y = -9842.6x + 18.848$
$R^2 = 0.9998$
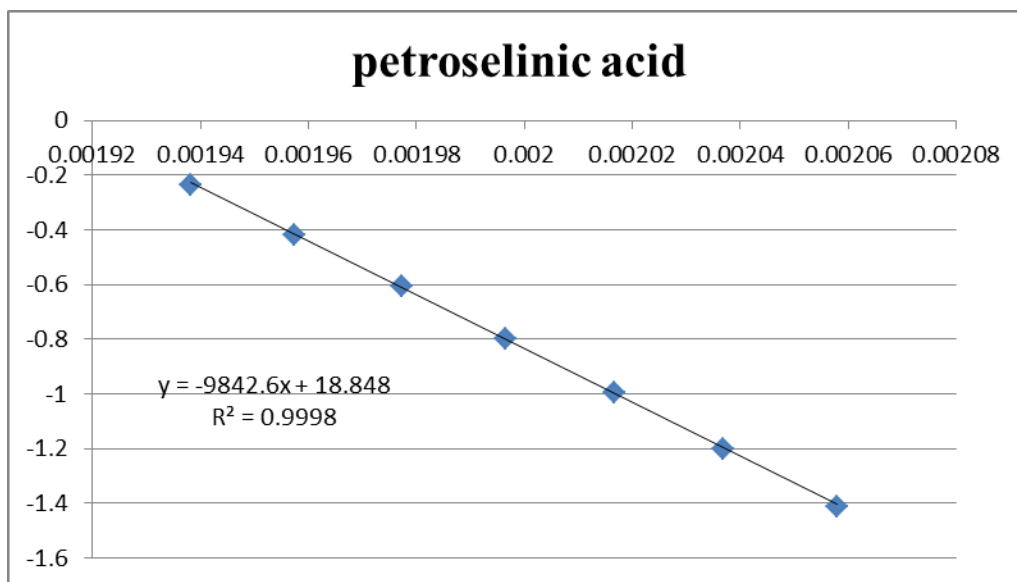
linoleic acid:

T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-1.587884
490.95	0.002037	-1.376946
495.85	0.002017	-1.1626557
500.85	0.001997	-0.9644778
505.75	0.001977	-0.7594193
510.85	0.001958	-0.5751603
515.95	0.001938	-0.3918757

Slope Coefficient	-10043.8
Intercept Coefficient	19.08636
Standard Error of the Slope	88.25315
Standard Error of the Intercept	0.176302
r^2	0.999614
Standard Error of Regression	0.009293
F-test	12952.08
Degrees of Freedom	5

linoleic acid

$y = -10044x + 19.086$
$R^2 = 0.9996$
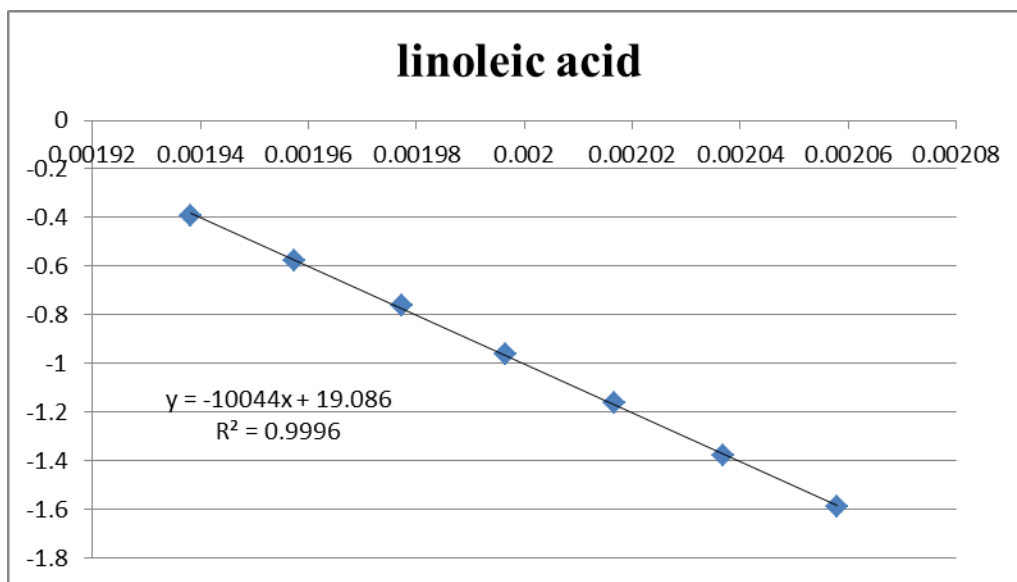
n-eicosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-1.9482974
490.95	0.002037	-1.7226065
495.85	0.002017	-1.4990284
500.85	0.001997	-1.2892256
505.75	0.001977	-1.0770088
510.85	0.001958	-0.8803139
515.95	0.001938	-0.6862395

Slope Coefficient	-10578.9
Intercept Coefficient	19.82859
Standard Error of the Slope	84.31948
Standard Error of the Intercept	0.168443
r^2	0.999682
Standard Error of Regression	0.008878
F-test	15740.6
Degrees of Freedom	5

n-eicosanoic acid

$y = -10579x + 19.829$
$R^2 = 0.9997$

gondoic acid:
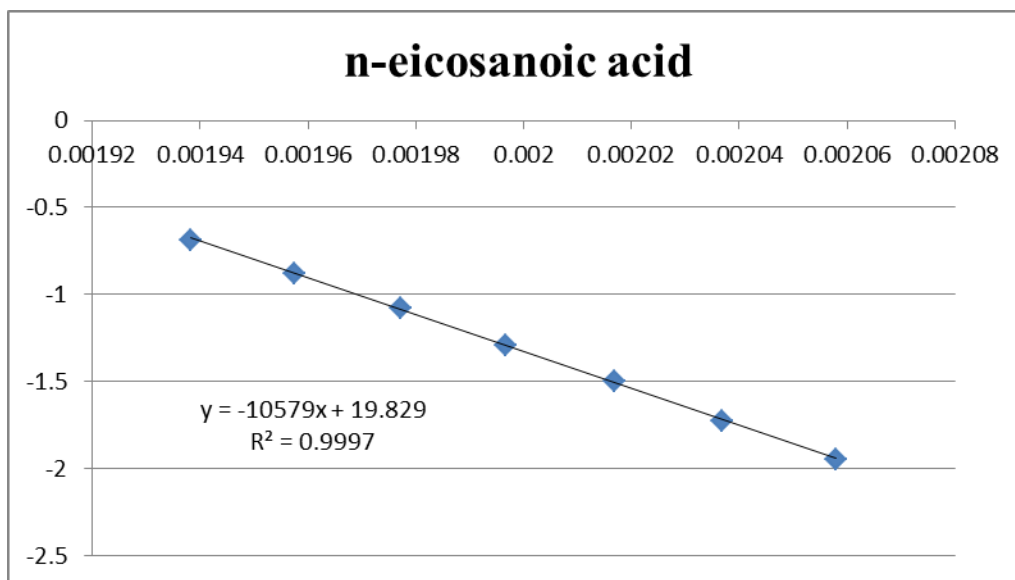
T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-2.0393006
490.95	0.002037	-1.8135176
495.85	0.002017	-1.5887524
500.85	0.001997	-1.3800964
505.75	0.001977	-1.1642702
510.85	0.001958	-0.970376
515.95	0.001938	-0.7766121

Slope Coefficient	-10589.8
Intercept Coefficient	19.76039
Standard Error of the Slope	94.31951
Standard Error of the Intercept	0.18842
r^2	0.999604
Standard Error of Regression	0.009931
F-test	12605.81
Degrees of Freedom	5

gondoic acid

$y = -10590x + 19.76$
$R^2 = 0.9996$
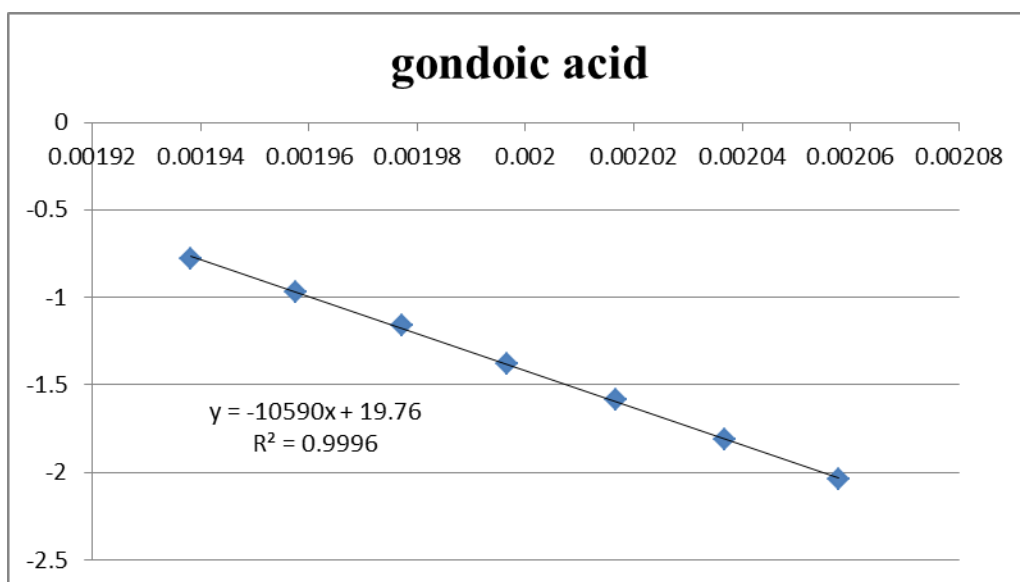
erucic acid:

T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-2.6370615
490.95	0.002037	-2.3976658
495.85	0.002017	-2.1603366
500.85	0.001997	-1.9365713
505.75	0.001977	-1.709243
510.85	0.001958	-1.5022756
515.95	0.001938	-1.2963258

Slope Coefficient	-11245.4
Intercept Coefficient	20.51184
Standard Error of the Slope	95.01137
Standard Error of the Intercept	0.189802
r^2	0.999643
Standard Error of Regression	0.010004
F-test	14008.82
Degrees of Freedom	5

erucic acid

$y = -11245x + 20.512$
$R^2 = 0.9996$
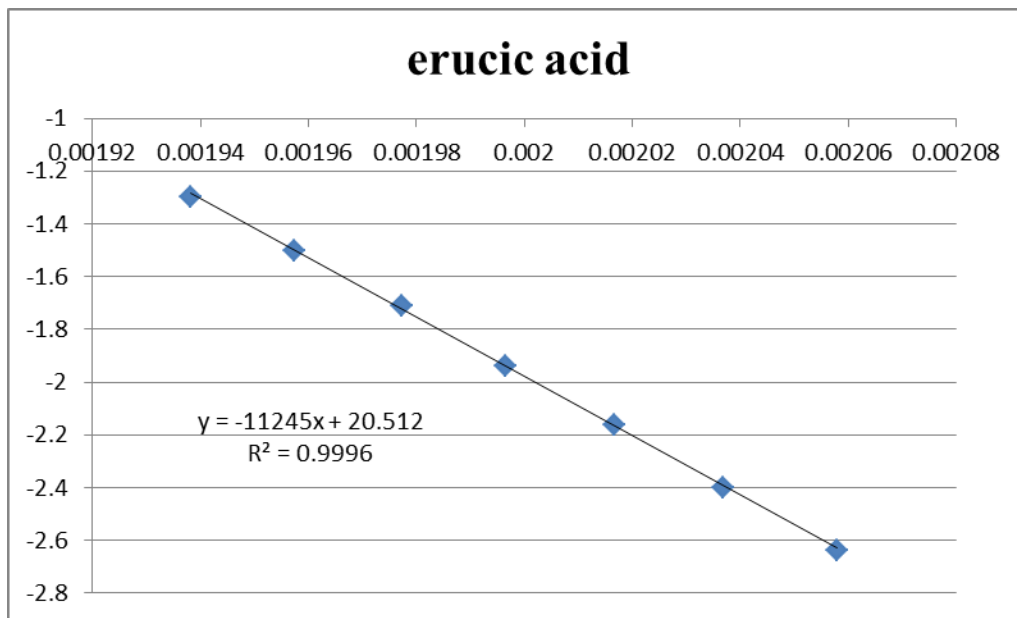
n-tetracosanoic acid:

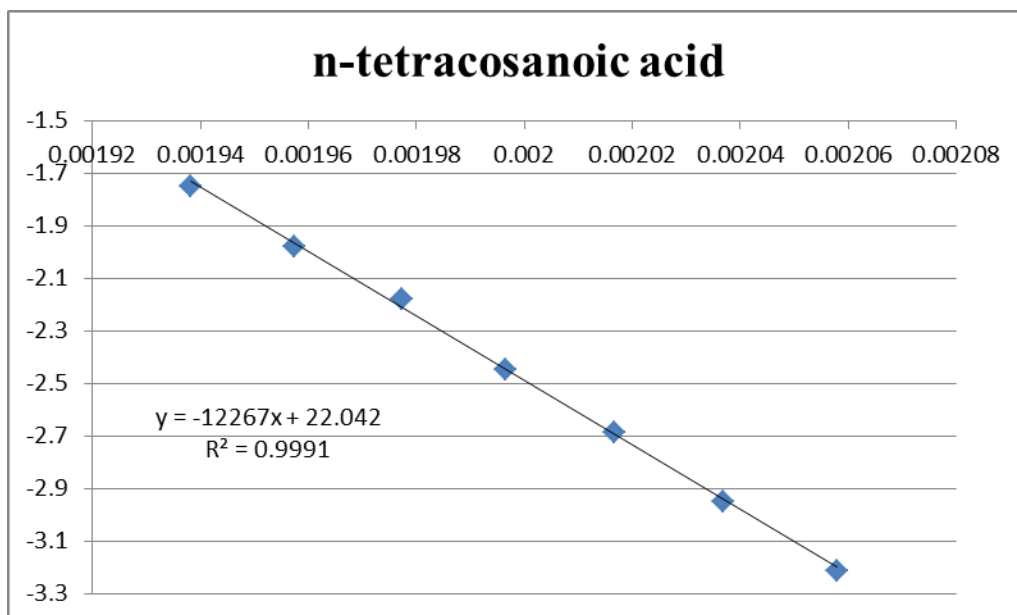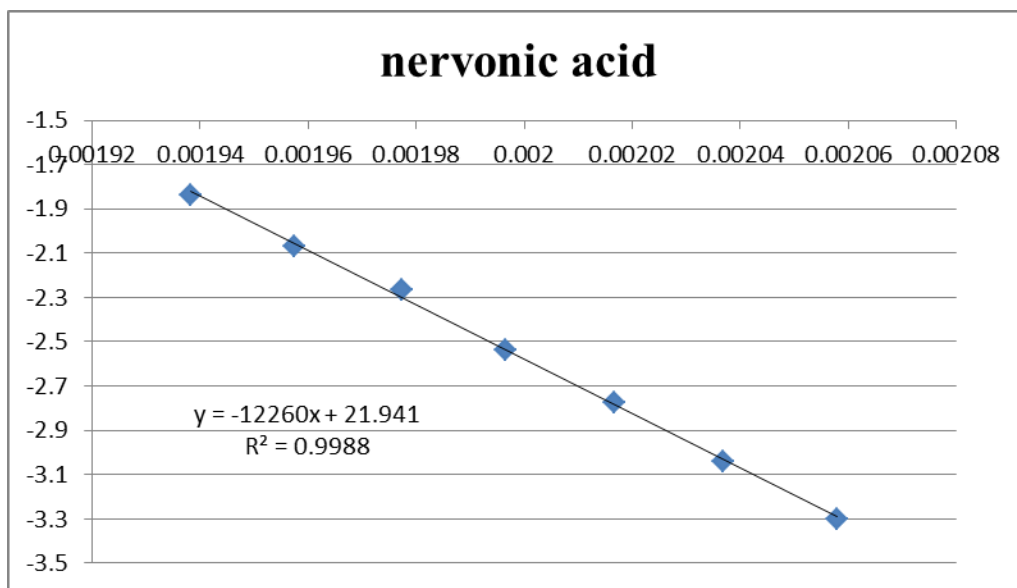| T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-3.2124519
490.95	0.002037	-2.9488887
495.85	0.002017	-2.687198
500.85	0.001997	-2.448366
505.75	0.001977	-2.1821625
510.85	0.001958	-1.9789709
515.95	0.001938	-1.7498255

Slope Coefficient	-12266.8
Intercept Coefficient	22.04201
Standard Error of the Slope	166.4035
Standard Error of the Intercept	0.332421
r^2	0.999081
Standard Error of Regression	0.017522
F-test	5434.22
Degrees of Freedom	5

n-tetracosanoic acid

$y = -12267x + 22.042$
$R^2 = 0.9991$

nervonic acid:

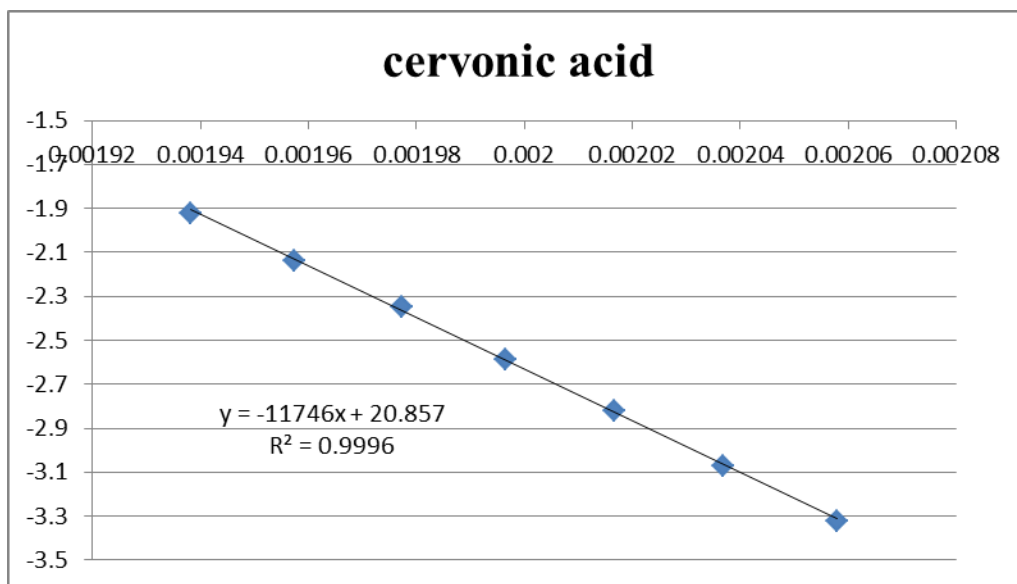| T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-3.2989781
490.95	0.002037	-3.0397973
495.85	0.002017	-2.7747629
500.85	0.001997	-2.5378067
505.75	0.001977	-2.2647875
510.85	0.001958	-2.0685585
515.95	0.001938	-1.8400479

Slope Coefficient	-12260.4
Intercept Coefficient	21.9412
Standard Error of the Slope	190.5011
Standard Error of the Intercept	0.38056
r^2	0.998794
Standard Error of Regression	0.020059
F-test	4142.068
Degrees of Freedom	5

nervonic acid

$y = -12260x + 21.941$
$R^2 = 0.9988$

cervonic acid:

| T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-3.3205162
490.95	0.002037	-3.0718708
495.85	0.002017	-2.823588
500.85	0.001997	-2.5906372
505.75	0.001977	-2.3492914
510.85	0.001958	-2.1376116
515.95	0.001938	-1.9205489

Slope Coefficient	-11745.5
Intercept Coefficient	20.85715
Standard Error of the Slope	105.6311
Standard Error of the Intercept	0.211017
r^2	0.999596
Standard Error of Regression	0.011122
F-test	12364.07
Degrees of Freedom	5

cervonic acid

$y = -11746x + 20.857$
$R^2 = 0.9996$

n-hexacosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
485.95	0.002058	-3.7426464
490.95	0.002037	-3.4754806
495.85	0.002017	-3.2123358
500.85	0.001997	-2.9612007
505.75	0.001977	-2.705825
510.85	0.001958	-2.475808
515.95	0.001938	-2.2437603

Slope Coefficient	-12570.9
Intercept Coefficient	22.13374
Standard Error of the Slope	101.2996
Standard Error of the Intercept	0.202364
r^2	0.999675
Standard Error of Regression	0.010666
F-test	15399.81
Degrees of Freedom	5

n-hexacosanoic acid

$y = -12571x + 22.134$
$R^2 = 0.9997$
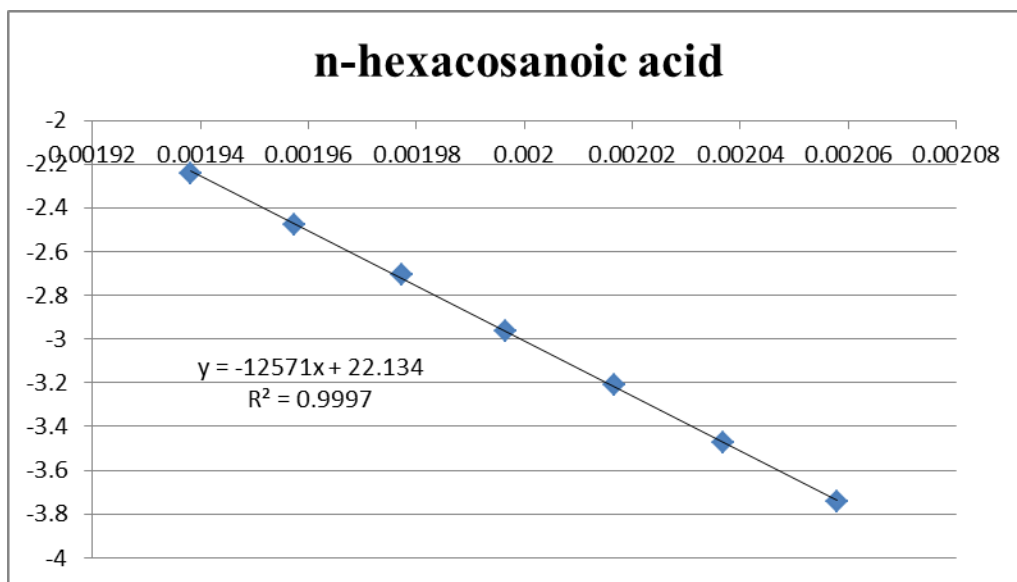
Appendix C-2: Experimental Data for Run 2 for More Long-chain
Fatty Acids Study

Run 2	484.7	489.6	494.5	499.3	504.1	508.9	513.6
				t/min			
methylene chloride	0.259	0.253	0.261	0.258	0.260	0.254	0.260
n-hexadecanoic acid	2.313	1.932	1.656	1.414	1.223	1.063	0.955
petroselininc acid	4.333	3.549	2.949	2.461	2.077	1.765	1.539
linoleic acid	5.123	4.176	3.446	2.863	2.400	2.022	1.764
n-eicosanoic acid	7.232	5.822	4.713	3.865	3.190	2.652	2.277
gondoic acid	7.908	6.359	5.135	4.213	3.468	2.878	2.478
erucic acid	14.173	11.214	8.869	7.156	5.782	4.717	3.989
n-tetracosanoic acid	25.062	19.526	14.898	11.872	9.372	7.449	6.308
nervonic acid	27.247	21.306	16.239	12.952	10.189	8.076	6.877
cervonic acid	27.759	21.725	16.942	13.502	10.751	8.653	7.240
n-hexacosanoic acid	42.443	32.583	24.943	19.503	15.248	12.092	9.907

Run 2	slope T/K	intercept	$\Delta_{sln}^{g} H_{m}$ (500 K) kJ·mol^{-1}	$\Delta_{l}^{g} H_{m}$ (298.15) kJ·mol^{-1} (lit)	$\Delta_{l}^{g} H_{m}$ (298.15) kJ·mol^{-1} (calc)
n-hexadecanoic acid	-9380.49	18.641	77.99	120.7	120.8 ± 1.7
petroselinic acid	-10019.6	19.275	83.30		131.4 ± 1.8
linoleic acid	-10179	19.427	84.62	134.1	134.0 ± 1.9
n-eicosanoic acid	-10753	20.251	89.40	143.6	143.5 ± 1.9
gondoic acid	-10747.8	20.148	89.35		143.4 ± 1.8
erucic acid	-11431.7	20.961	95.04	154.5	154.7 ± 1.9
n-tetracosanoic acid	-12332.9	22.245	102.53		169.6 ± 2.0
nervonic acid	-12323.8	22.140	102.46		169.5 ± 2.0
cervonic acid	-11917	21.281	99.07		162.7 ± 2.0
n-hexacosanoic acid	-12803.1	22.682	106.44		177.4 ± 2.0

$\Delta_{l}^{g} H_{m}$ (298.15 K)/kJ·mol^{-1} = (1.99 ± 0.01) $\Delta_{sln}^{g} H_{m}$ (500 K) - (34.3 ± 1.0); r^2 = 0.9999

n-hexadecanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-0.7196843
489.55	0.002043	-0.5184428
494.45	0.002022	-0.3327559
499.25	0.002003	-0.1442615
504.05	0.001984	0.03804544
508.85	0.001965	0.21149531
513.55	0.001947	0.36375468

Slope Coefficient	-9380.49
Intercept Coefficient	18.64092
Standard Error of the Slope	70.57478
Standard Error of the Intercept	0.141457
r^2	0.999717
Standard Error of Regression	0.007228
F-test	17666.57
Degrees of Freedom	5

n-hexadecanoic acid

y = -9380.5x + 18.641
R² = 0.9997
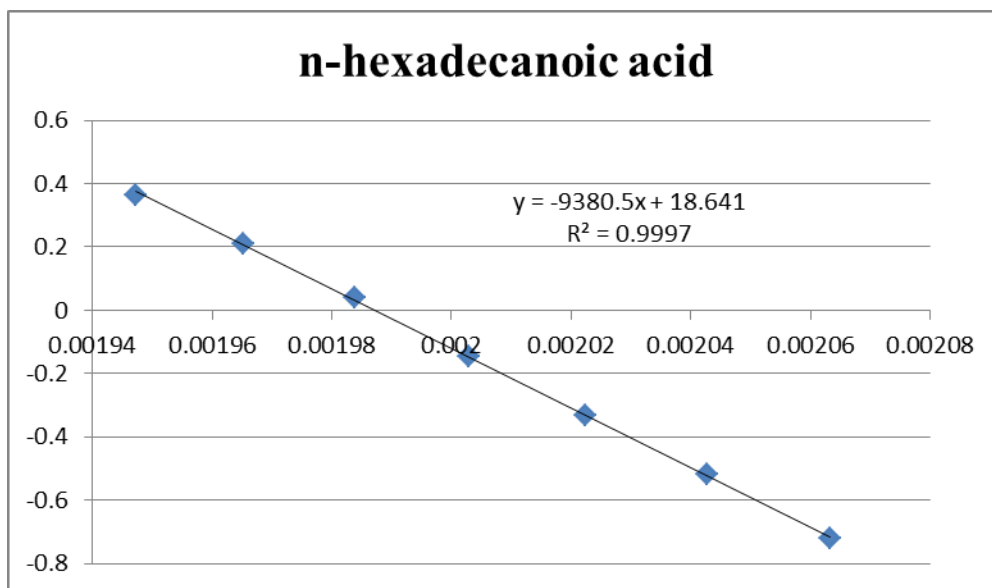
petroselinic acid:

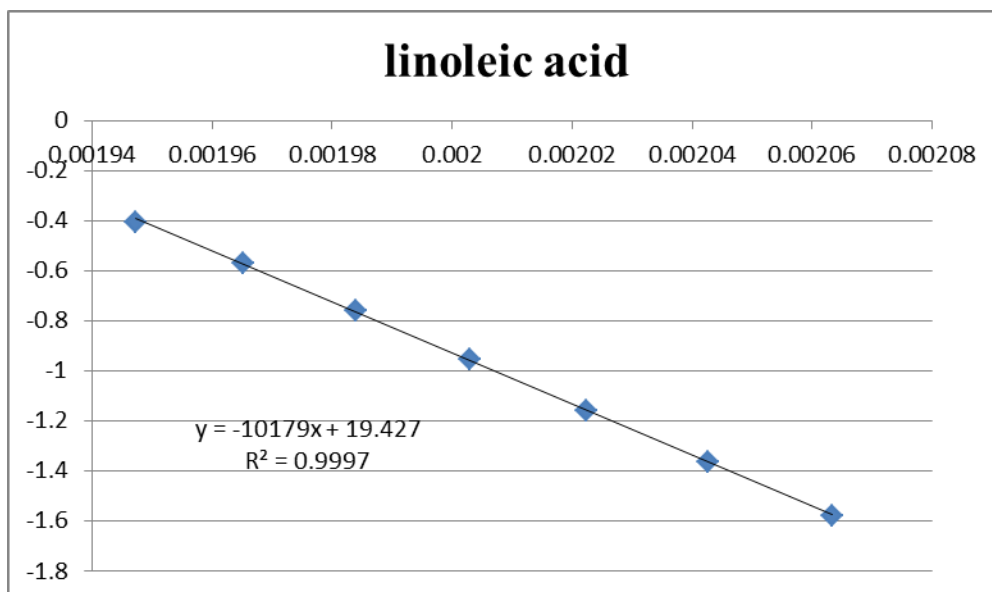| T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-1.4046558
489.55	0.002043	-1.1928699
494.45	0.002022	-0.9885222
499.25	0.002003	-0.7896122
504.05	0.001984	-0.5970419
508.85	0.001965	-0.4127415
513.55	0.001947	-0.2461824

Slope Coefficient	-10019.6
Intercept Coefficient	19.27452
Standard Error of the Slope	64.22895
Standard Error of the Intercept	0.128738
r^2	0.999795
Standard Error of Regression	0.006578
F-test	24335.31
Degrees of Freedom	5

petroselinic acid

$y = -10020x + 19.275$
$R^2 = 0.9998$
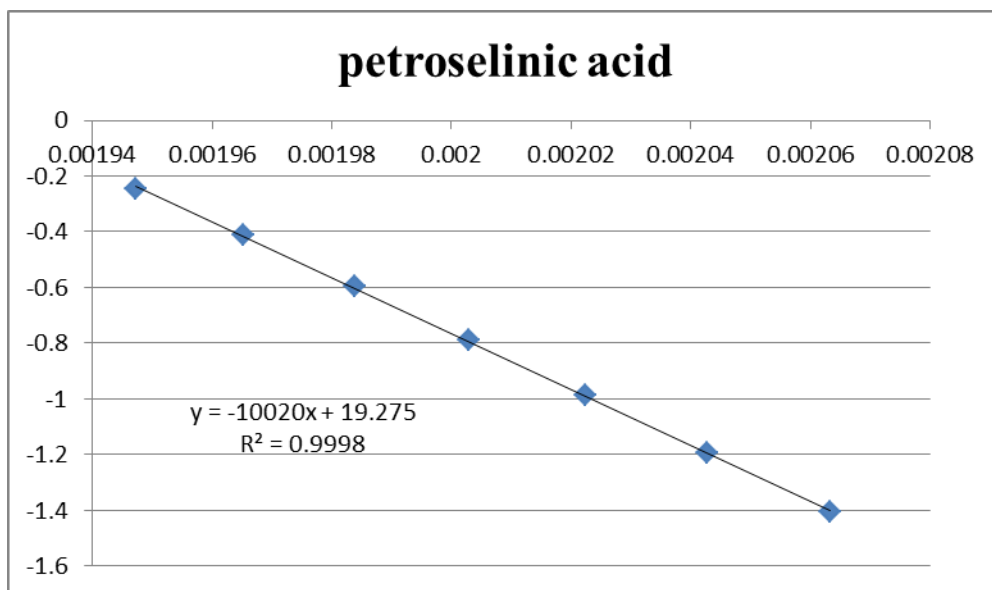
linoleic acid:

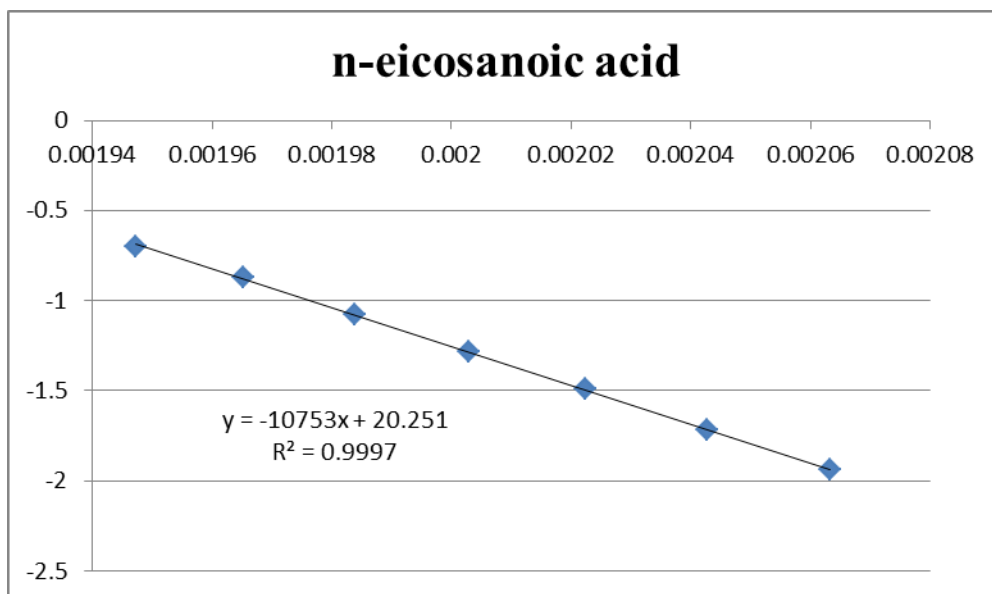| T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-1.5819364
489.55	0.002043	-1.366801
494.45	0.002022	-1.1582629
499.25	0.002003	-0.9571653
504.05	0.001984	-0.7605989
508.85	0.001965	-0.5698843
513.55	0.001947	-0.408027

Slope Coefficient	-10179
Intercept Coefficient	19.42671
Standard Error of the Slope	82.49459
Standard Error of the Intercept	0.165348
r^2	0.999672
Standard Error of Regression	0.008449
F-test	15225.07
Degrees of Freedom	5

linoleic acid

$y = -10179x + 19.427$
$R^2 = 0.9997$

n-eicosanoic acid:

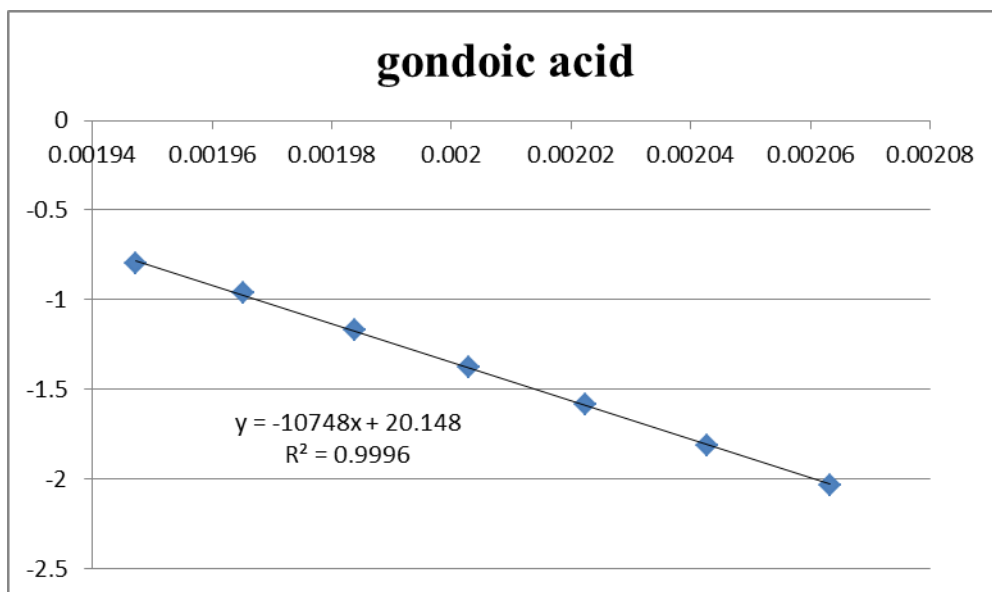| T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-1.9419905
489.55	0.002043	-1.7172987
494.45	0.002022	-1.4933167
499.25	0.002003	-1.2828796
504.05	0.001984	-1.0749786
508.85	0.001965	-0.8748529
513.55	0.001947	-0.7016799

Slope Coefficient	-10753
Intercept Coefficient	20.25069
Standard Error of the Slope	83.03528
Standard Error of the Intercept	0.166432
r^2	0.999702
Standard Error of Regression	0.008505
F-test	16770.07
Degrees of Freedom	5

n-eicosanoic acid

$y = -10753x + 20.251$
$R^2 = 0.9997$

gondoic acid:

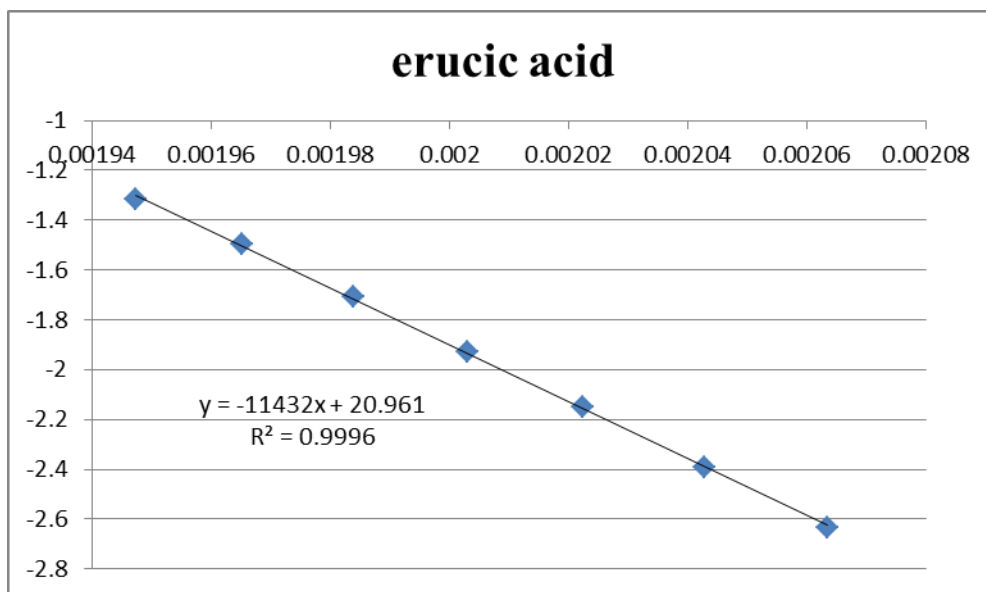| T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.0345207
489.55	0.002043	-1.8093631
494.45	0.002022	-1.5838902
499.25	0.002003	-1.374803
504.05	0.001984	-1.1654511
508.85	0.001965	-0.9646673
513.55	0.001947	-0.7968081

Slope Coefficient	-10747.8
Intercept Coefficient	20.14849
Standard Error of the Slope	100.9414
Standard Error of the Intercept	0.202322
r^2	0.999559
Standard Error of Regression	0.010339
F-test	11337.1
Degrees of Freedom	5

gondoic acid

$y = -10748x + 20.148$
$R^2 = 0.9996$

erucic acid:

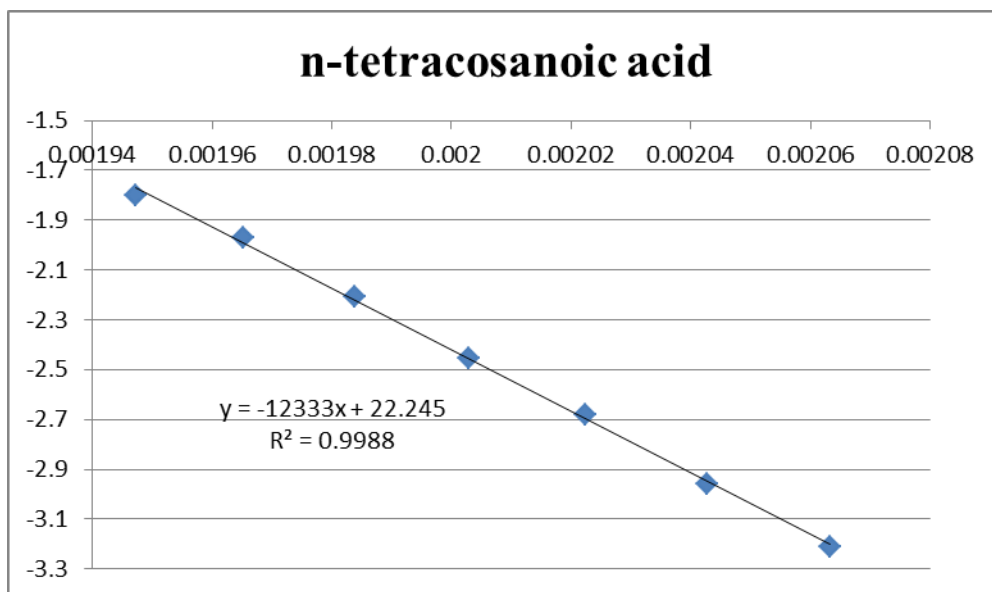| T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-2.6329162
489.55	0.002043	-2.394313
494.45	0.002022	-2.1526446
499.25	0.002003	-1.931211
504.05	0.001984	-1.7086697
508.85	0.001965	-1.495899
513.55	0.001947	-1.3160763

Slope Coefficient	-11431.7
Intercept Coefficient	20.96144
Standard Error of the Slope	106.1191
Standard Error of the Intercept	0.2127
r^2	0.999569
Standard Error of Regression	0.010869
F-test	11604.64
Degrees of Freedom	5

erucic acid

$y = -11432x + 20.961$
$R^2 = 0.9996$

n-tetracosanoic acid:

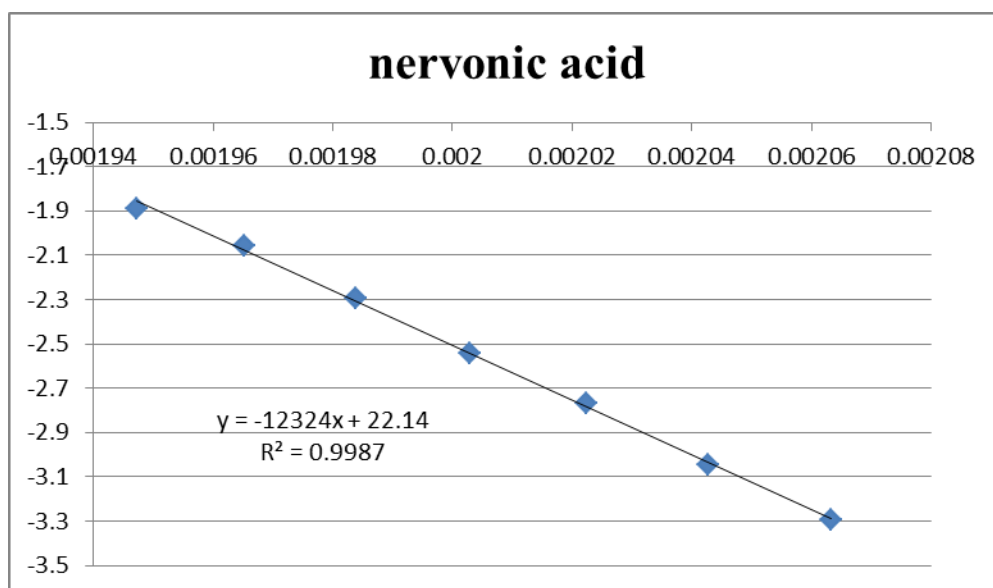| T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.2109791
489.55	0.002043	-2.9587139
494.45	0.002022	-2.6835411
499.25	0.002003	-2.4521672
504.05	0.001984	-2.2095959
508.85	0.001965	-1.9733968
513.55	0.001947	-1.7998039

Slope Coefficient	-12332.9
Intercept Coefficient	22.24524
Standard Error of the Slope	187.2335
Standard Error of the Intercept	0.375282
r^2	0.998849
Standard Error of Regression	0.019177
F-test	4338.766
Degrees of Freedom	5

n-tetracosanoic acid

$y = -12333x + 22.245$
$R^2 = 0.9988$

nervonic acid:

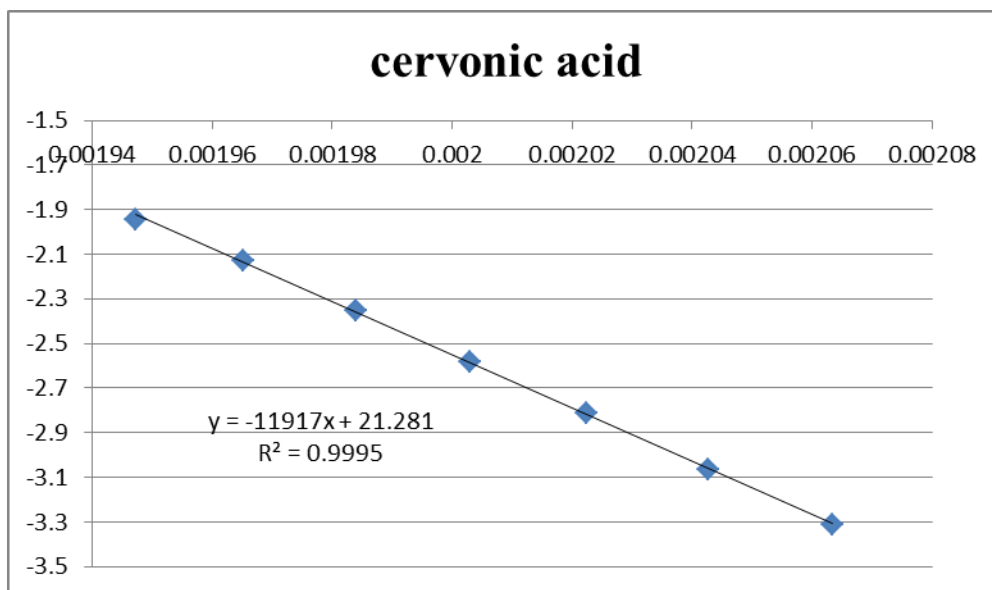| T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.2954029
489.55	0.002043	-3.0470265
494.45	0.002022	-2.7712022
499.25	0.002003	-2.5410831
504.05	0.001984	-2.2954443
508.85	0.001965	-2.0569524
513.55	0.001947	-1.8896337

Slope Coefficient	-12323.8
Intercept Coefficient	22.14001
Standard Error of the Slope	202
Standard Error of the Intercept	0.40488
r^2	0.998658
Standard Error of Regression	0.020689
F-test	3722.095
Degrees of Freedom	5

nervonic acid

$y = -12324x + 22.14$
$R^2 = 0.9987$

cervonic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.3141876
489.55	0.002043	-3.0667321
494.45	0.002022	-2.8142467
499.25	0.002003	-2.5835458
504.05	0.001984	-2.3504737
508.85	0.001965	-2.1281845
513.55	0.001947	-1.9430996

Slope Coefficient	-11917
Intercept Coefficient	21.28137
Standard Error of the Slope	116.9544
Standard Error of the Intercept	0.234418
r^2	0.999519
Standard Error of Regression	0.011979
F-test	10382.47
Degrees of Freedom	5

cervonic acid

$y = -11917x + 21.281$
$R^2 = 0.9995$

n-hexacosanoic acid:

T/K	T^{-1}	$\ln(t^{-1})$
484.65	0.002063	-3.7420476
489.55	0.002043	-3.4760081
494.45	0.002022	-3.2060434
499.25	0.002003	-2.9572458
504.05	0.001984	-2.7072113
508.85	0.001965	-2.4713632
513.55	0.001947	-2.2666579

Slope Coefficient	-12803.1
Intercept Coefficient	22.68197
Standard Error of the Slope	110.7847
Standard Error of the Intercept	0.222052
r^2	0.999626
Standard Error of Regression	0.011347
F-test	13355.86
Degrees of Freedom	5

n-hexacosanoic acid

$y = -12803x + 22.682$
$R^2 = 0.9996$