Methylene Volume and Phase Transition Kinetics in Medium Chain Monoglycerides and Alkanes

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Introduction

Lipids have many uses, from crystallizing proteins and encapsulating drugs to acting as emulsifiers in food and as surfactants in cosmetics. Moreover, the constituent parts of lipids appear in other compounds, and so understanding their behavior within a lipid might help us to understand their behavior more broadly.

We examined the monoglycerides monomyristin ($C_{17}H_{34}O_4$), monolaurin ($C_{15}H_{30}O_4$), monocaprin ($C_{13}H_{26}O_4$), and monocaprylin ($C_{11}H_{22}O_4$). These lipids are composed of a polar head and a nonpolar carbon chain tail, and they are identical except for the length of that tail. These lipids form various phases at different temperatures and water concentrations.

We focused on the phase transition between two lamellar phases (sheets of lipid bilayers), the L_β and L_α phases. We explored via heat flow and volume data.

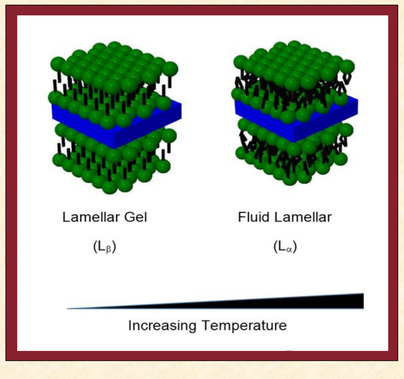

Fig. 2: Select lipid phases, including bilayers L_β and L_α. The lipids in L_β are free to rotate about their axes. The lipids in L_α are also free to move within the plane.

Goals

- Explore the transition behavior of our lipids between lamellar phases
- Explore volume behavior of our lipids and of CH_2 groups

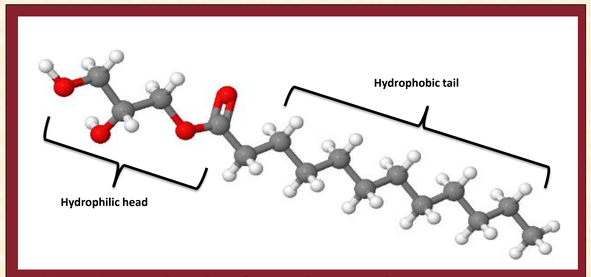

Fig. 1: A molecule of monolaurin, showing oxygen in red, carbon in grey, and hydrogen in white.

Differential Scanning Calorimetry

Data collection:

- Prepared samples of 0.5-2 mg lipid and 8 mg water
- Cycled over temperature range within -40 to 80 °C at various rates
- Took data of heat flow out of sample as a function of temperature

Analysis:[1,2,3]

- Use hysteresis to find transition temperature
- Fit transition width and hysteresis as functions of ramp rate
- Calculate Avrami exponent (dimensionality) using transition temperatures, hysteresis, and widths

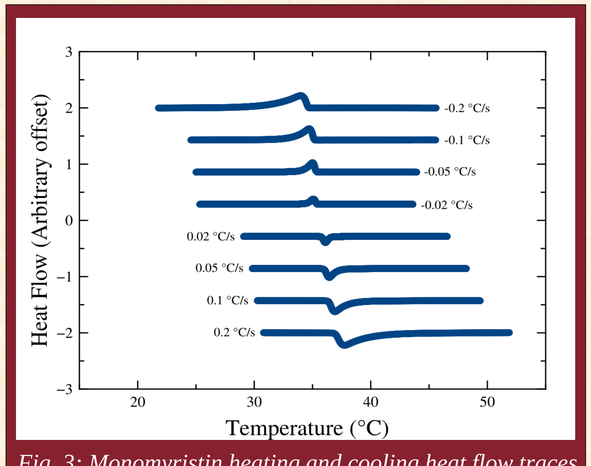

Fig. 3: Monomyristin heating and cooling heat flow traces

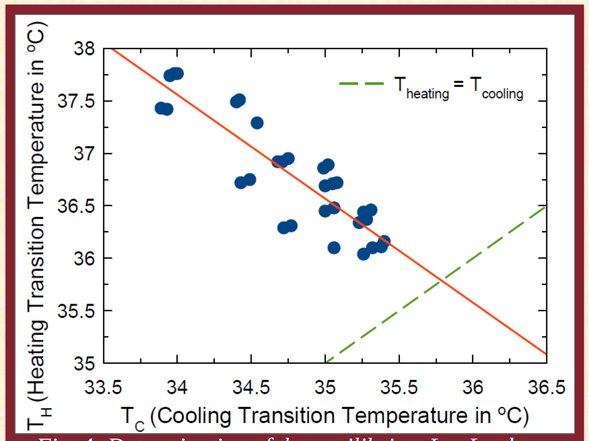

Fig. 4: Determination of the equilibrium L_β - L_α phase transition for monomyristin.

Densitometry

- Fit volume data as a function of temperature for each lipid
- These fits give us y-intercepts (lipid volumes at 0 °C) and slopes (change in lipid volume per °C)
- Plot and fit lipid volumes at 0 °C and change in lipid volume per 0 °C as functions of number of CH_2 groups in the tail
- From these, extract the lipid head group and terminal CH_3 volume at 0 °C and its volume change per °C, as well as the volume of a CH_2 group at 0 °C and its volume change per °C

Lipid Volumes and Fits

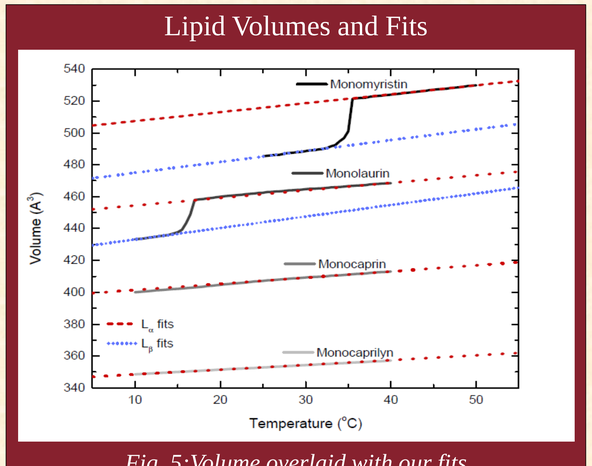

Fig. 5:Volume overlaid with our fits

Results

Lipid	CH_2 groups	L_β - L_α Transition (°C)	n_H	n_C
Monomyristin	12	35.8	1.6	1.5
Monolaurin	10	17.2	1.5	0.9
Monocaprin	8	-7.8	1.3	0.9
Monocaprylin	6	---	---	---
Hexadecane	14	18.6	1.0	---
Tetradecane	12	3.6	1.0	---
Dodecane	10	-5.1	1.0	---
Decane	8	-32.8	1.2	---

Equilibrium transition temperatures seem to go up by 20° C with the addition of two CH_2 groups to the monoglyceride tail.

Parameter	Tail CH_2 groups	Head group and CH_3
Monoglycerides: L_α		
Volume at 0 °C (Å^3)	26.09	188.8
Change in volume (Å^3/ °C)	0.043	0.042
Alkanes		
Volume at 0 °C (Å^3)	26.63	102.1
Change in volume (Å^3/ °C)	0.015	0.280

These parameters allow us to model the volume behavior of these lipids, and compare the volume behavior of CH_2 in these lipids to that in the alkanes.

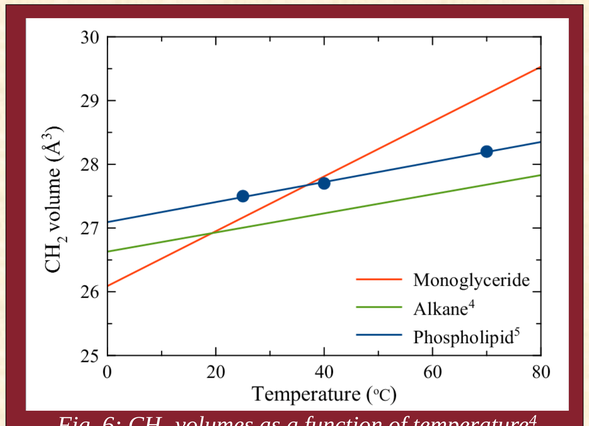

Fig. 6: CH_2 volumes as a function of temperature[4]

References

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