SOLID-LIQUID PHASE EQUILIBRIUM: ALKANE SYSTEMS FOR LOW TEMPERATURE ENERGY STORAGE

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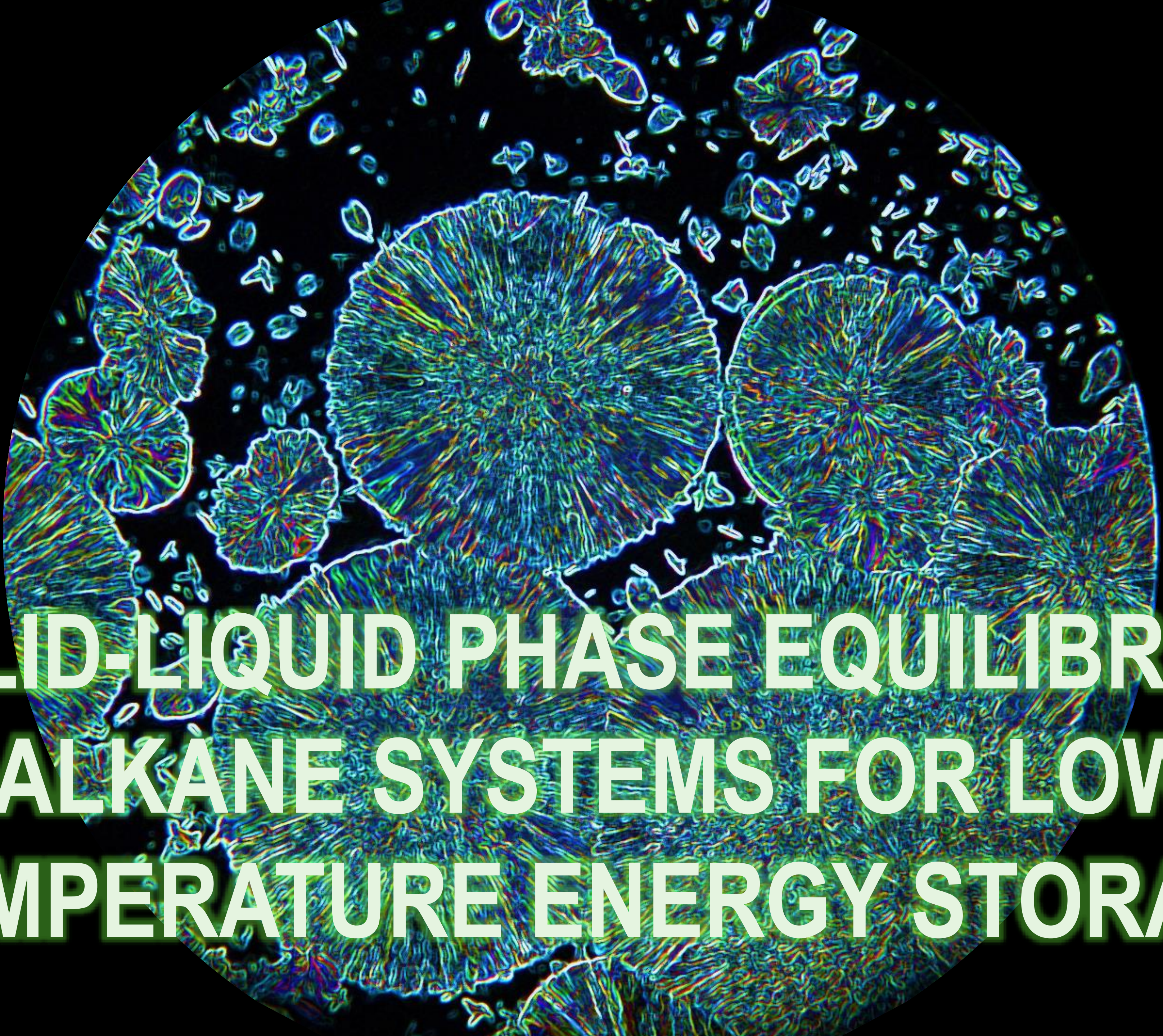

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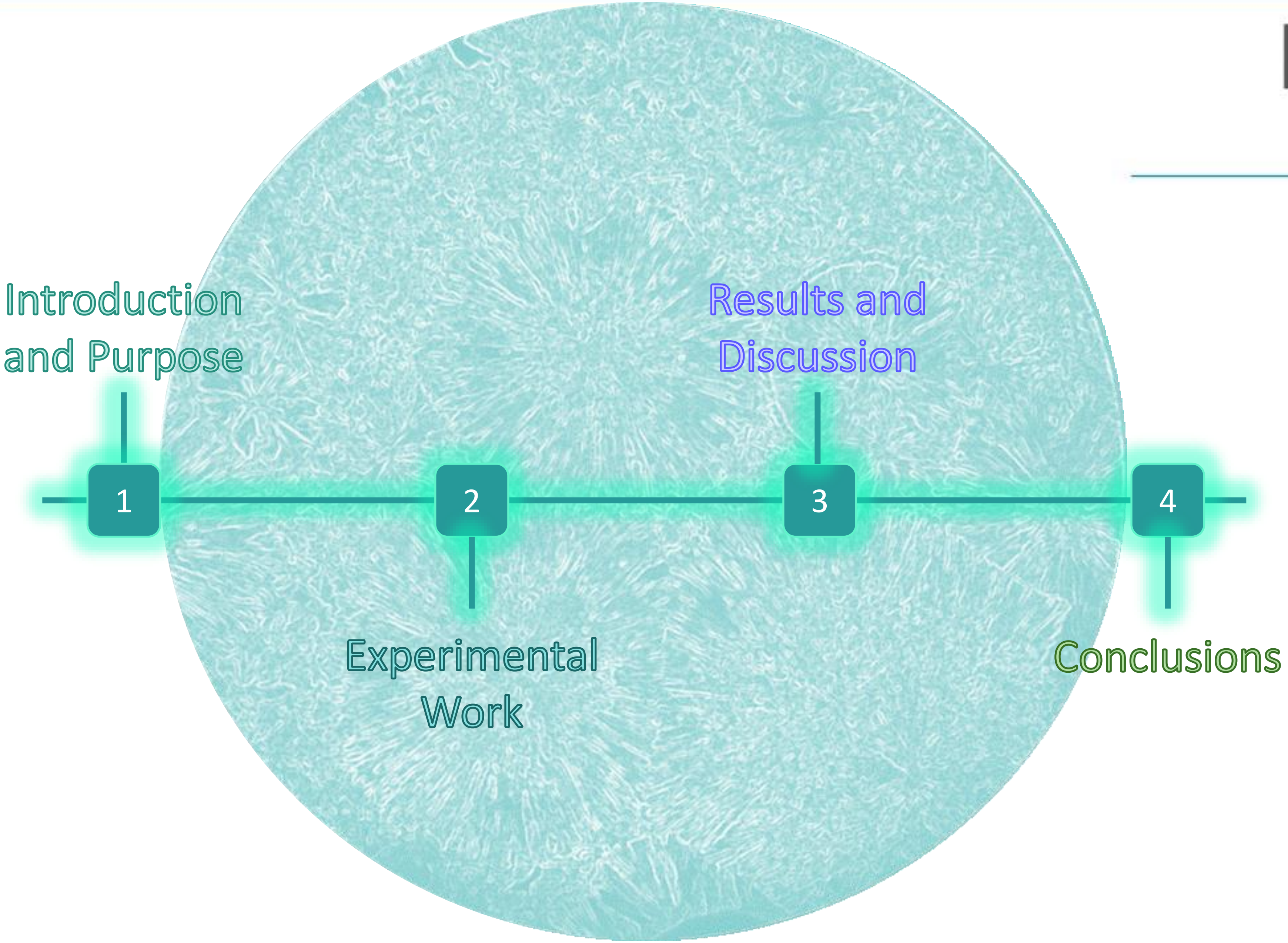
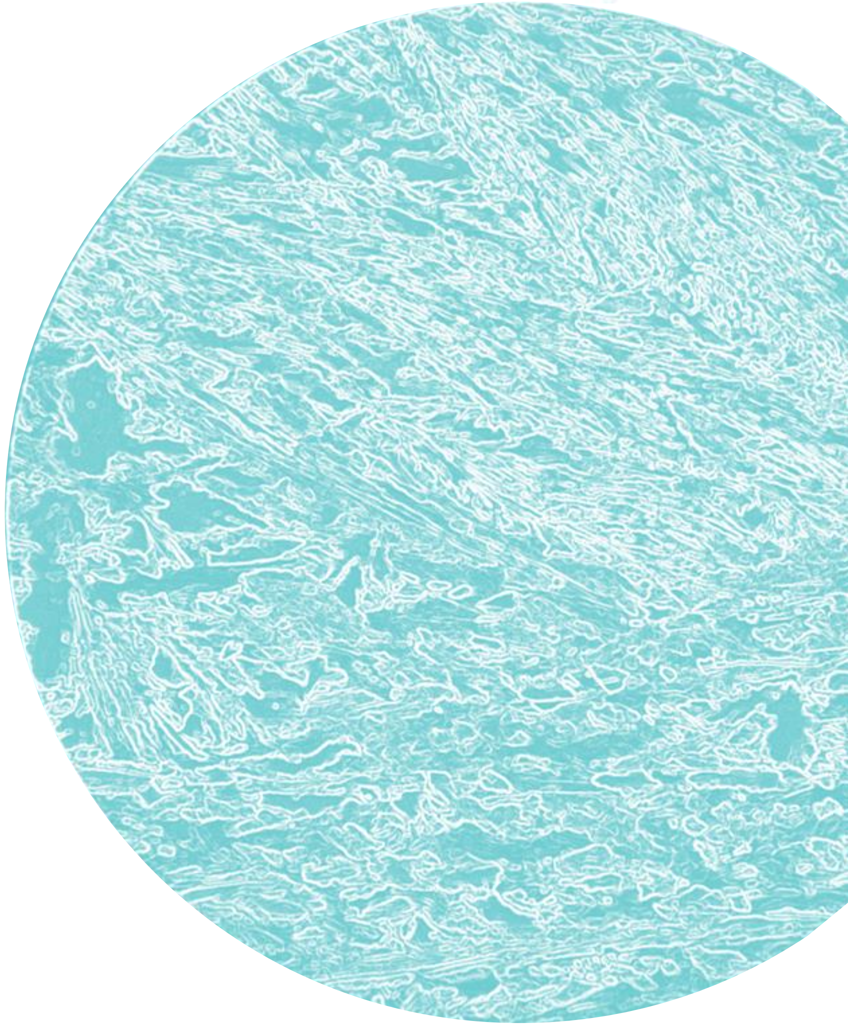

Introduction and Purpose
1
2
Experimental Work
Results and Discussion
3
4
Conclusions

1. INTRODUCTION AND PURPOSE

- Increasing Energy Needs
- Fossil Fuels
- Renewable Energies
- Gap between supply and consumption
- PCMs and Eutectics
- Low Temperature Energy Storage
- Energy Storage as solution

1. INTRODUCTION AND PURPOSE

Characterization of selected systems that can be used for thermal energy storage at low temperatures to understand their behaviour and robustness as PCMs



2. EXPERIMENTAL WORK

Construction of the Solid – Liquid Binary Phase Diagrams

Low Temperature Raman Spectroscopy

Differential Scanning Calorimetry experiments (DSC)

Binary Systems:
n-octane (C_8) + *n*-decane (C_{10})
n-decane (C_{10}) + *n*-dodecane (C_{12})

3. RESULTS AND DISCUSSION

*Preliminary results

DSC RESULTS

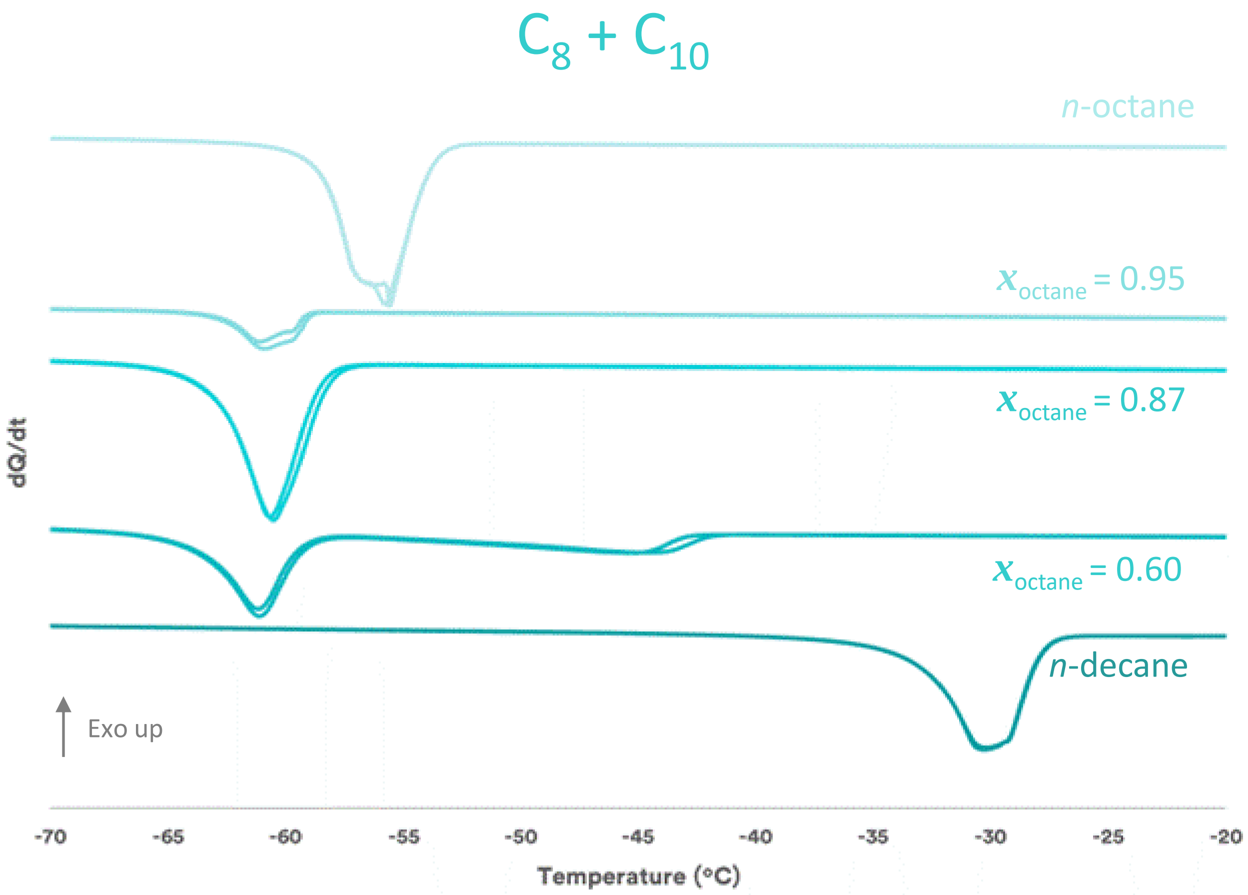


Fig. 1 – DSC heating curves of pure *n*-octane, *n*-decane, and of selected binary mixtures, with octane molar fraction x_{octane}.

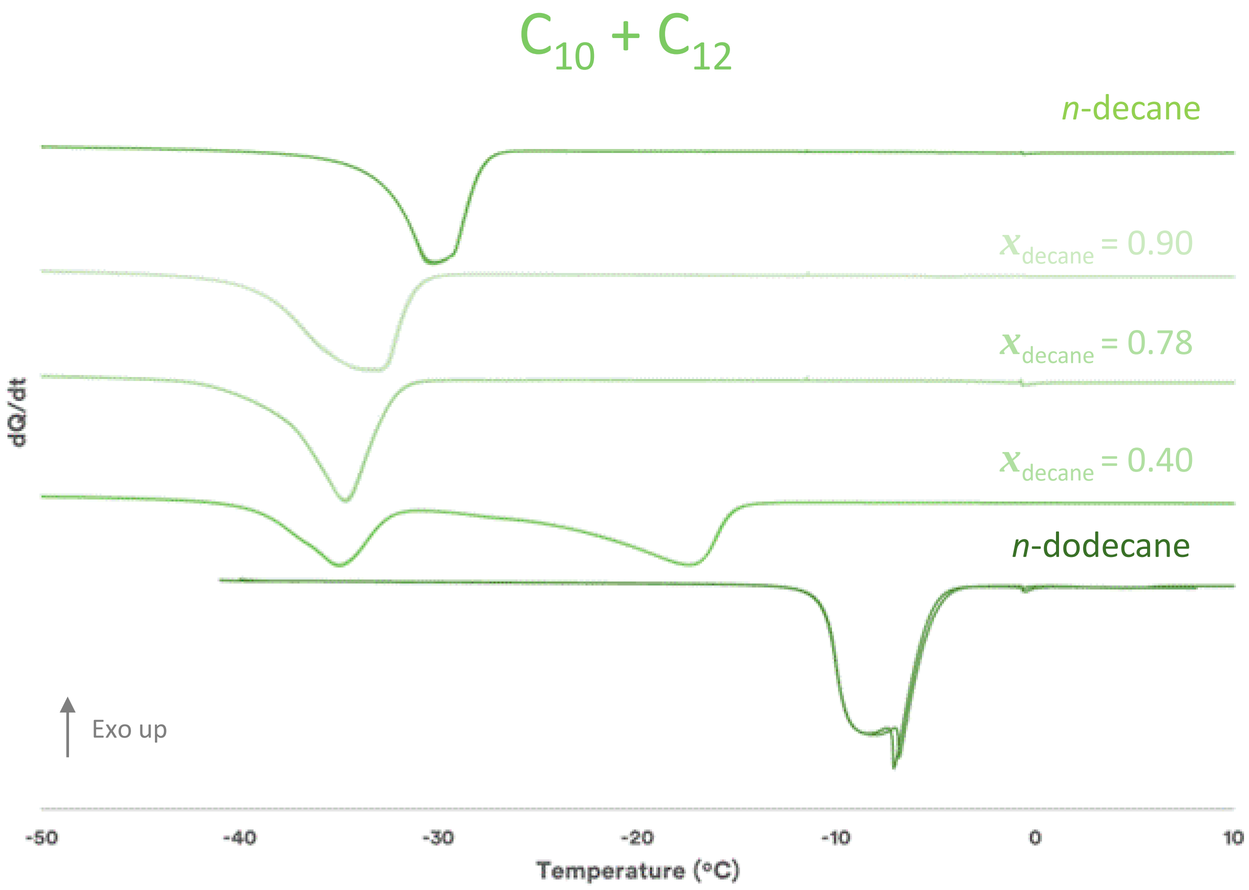


Fig. 2 – DSC heating curves of pure *n*-decane, *n*-dodecane, and of selected binary mixtures, with octane molar fraction x_{decane}.

DSC RESULTS

For pure compounds and eutectic mixtures: only a <u>single peak</u> for the phase transition

For other binary mixtures: <u>two peaks</u> for the phase transition

$C_8 + C_{10}$

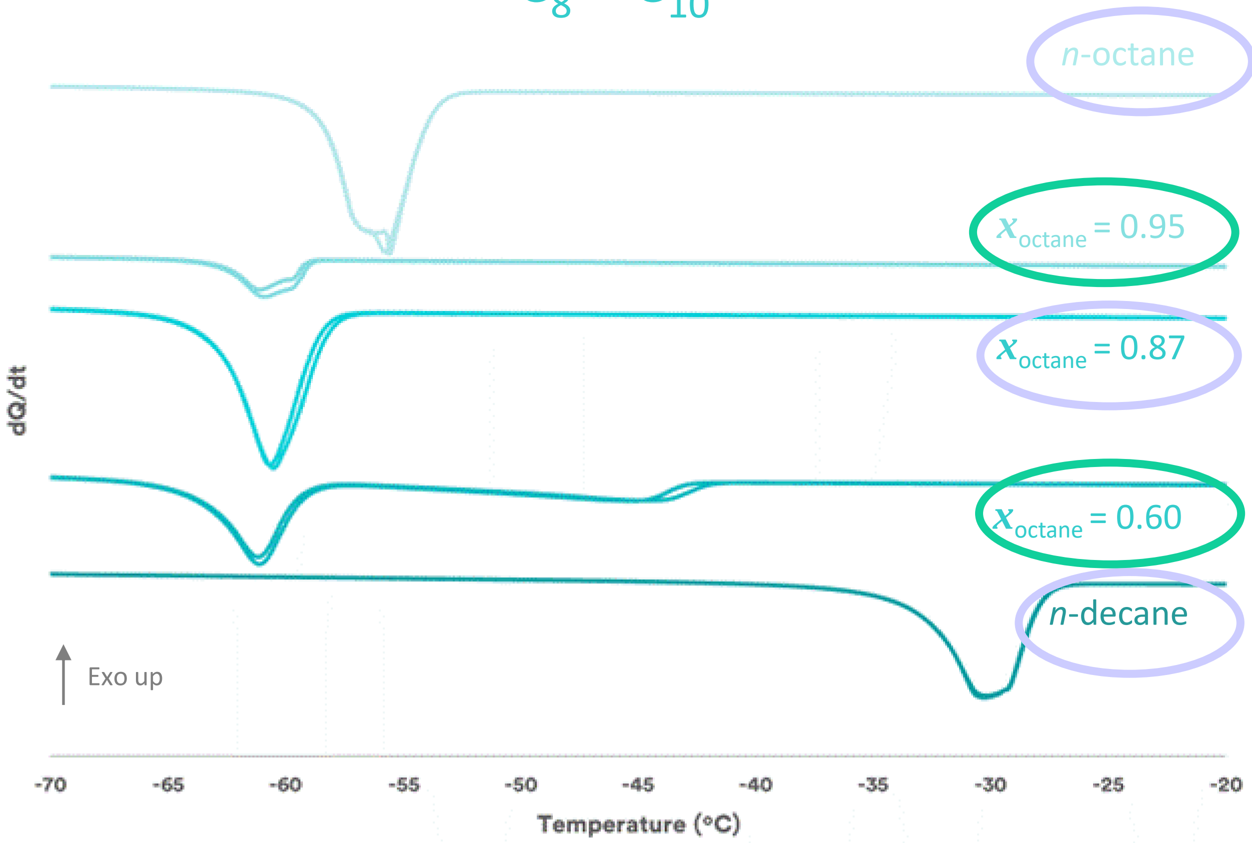


Fig. 1 – DSC heating curves of pure *n*-octane, *n*-decane, and of selected binary mixtures, with octane molar fraction x_{octane}.

$C_{10} + C_{12}$

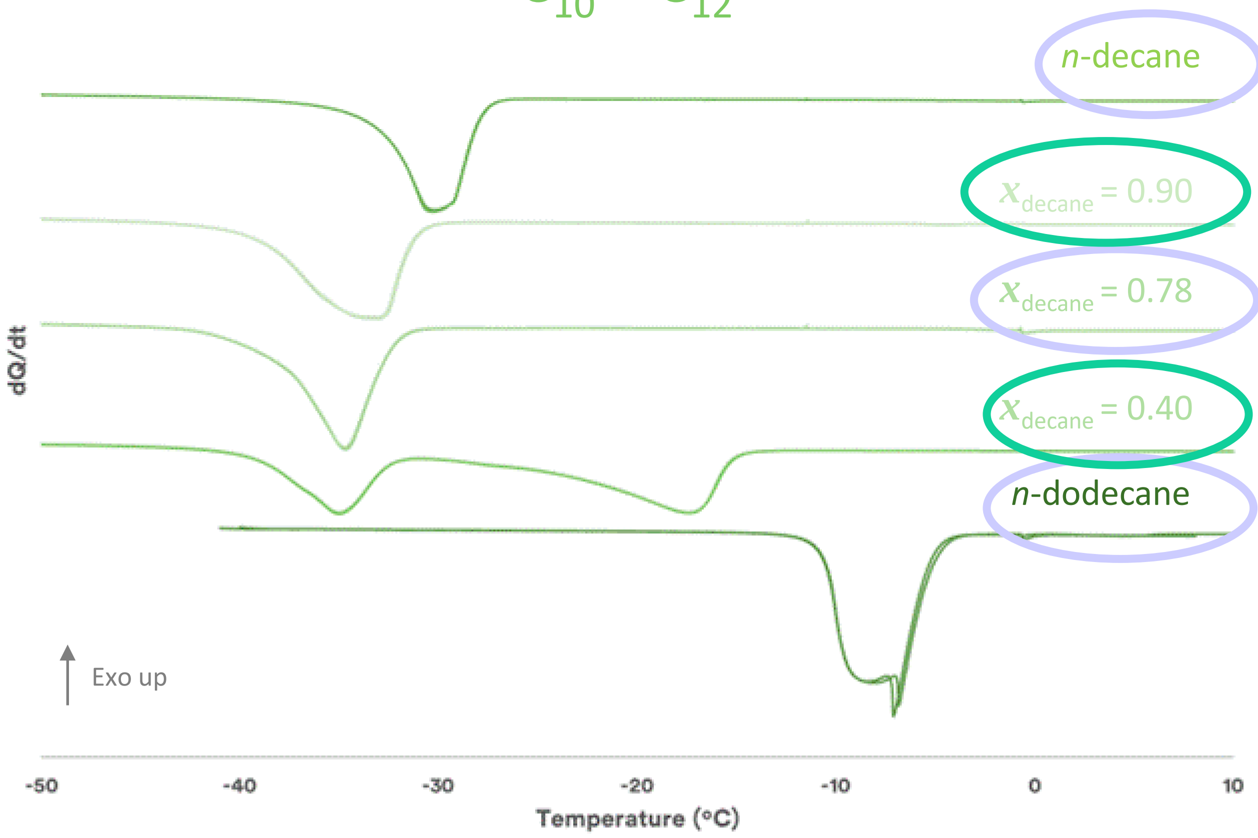


Fig. 2 – DSC heating curves of pure *n*-decane, *n*-dodecane, and of selected binary mixtures, with octane molar fraction x_{decane}.

RAMAN SPECTROSCOPY

C_8 C_{10} C_{12}

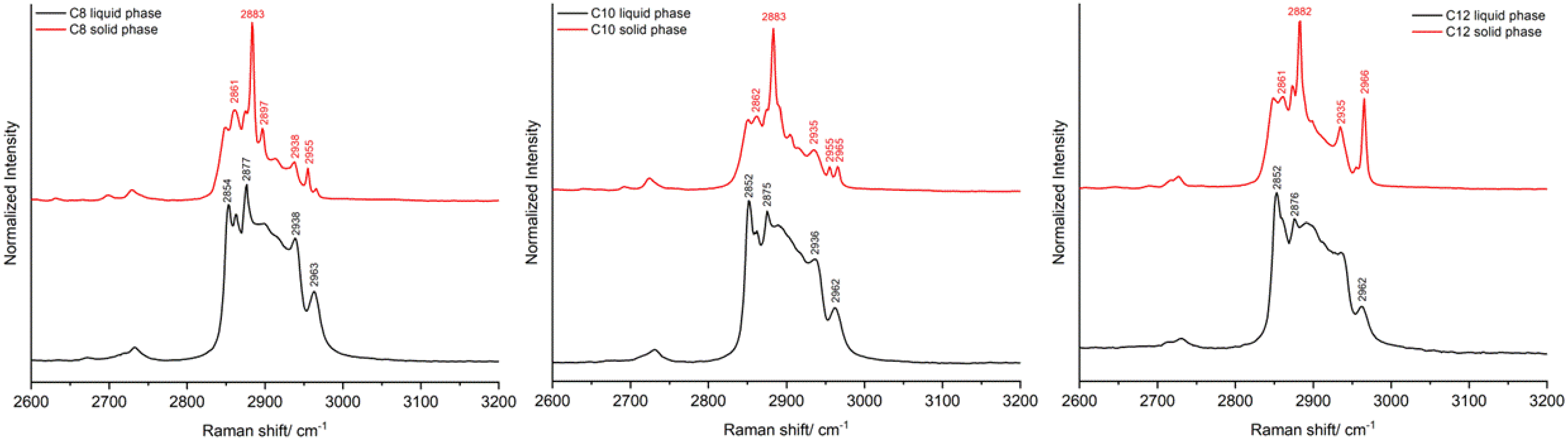


Fig. 3 – Raman spectra of room-temperature liquid phase and cooled solid phase samples of C_8, C_{10} and C_{12}, with marker bands in the 2600-3200 cm^{-1} range.

RAMAN SPECTROSCOPY

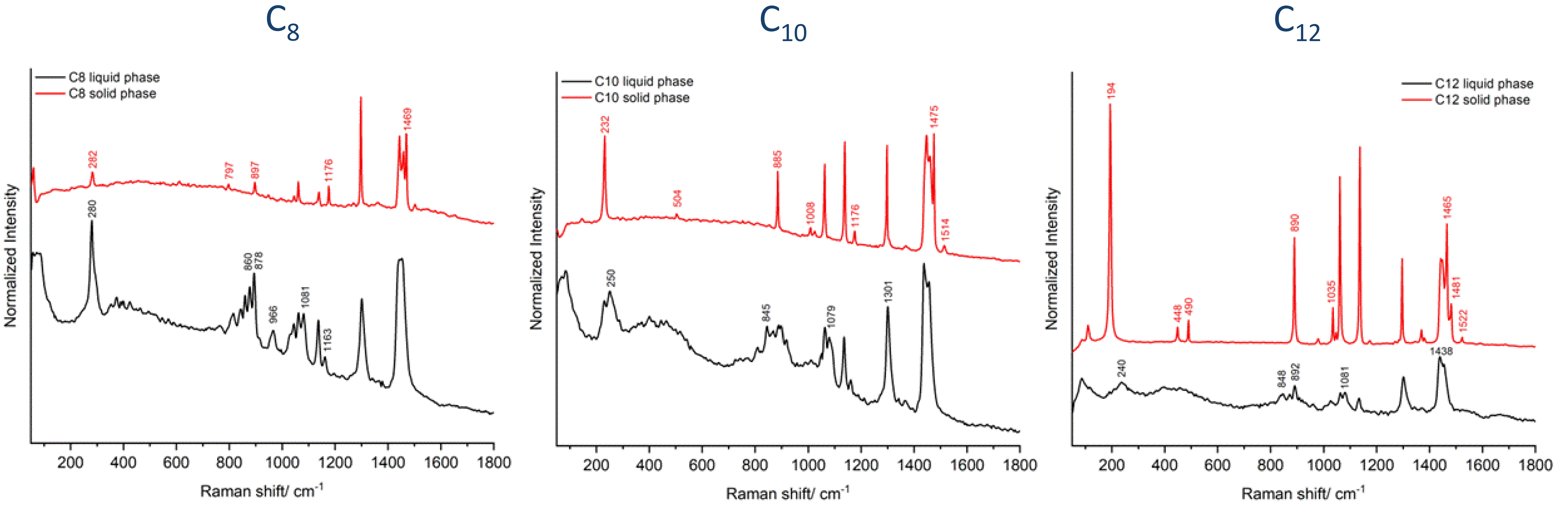


Fig. 4 – Raman spectra of room-temperature liquid phase and cooled solid phase samples of C_8, C_{10} and C_{12}, with marker bands in the 50-1800 cm^{-1} range.

RAMAN SPECTROSCOPY

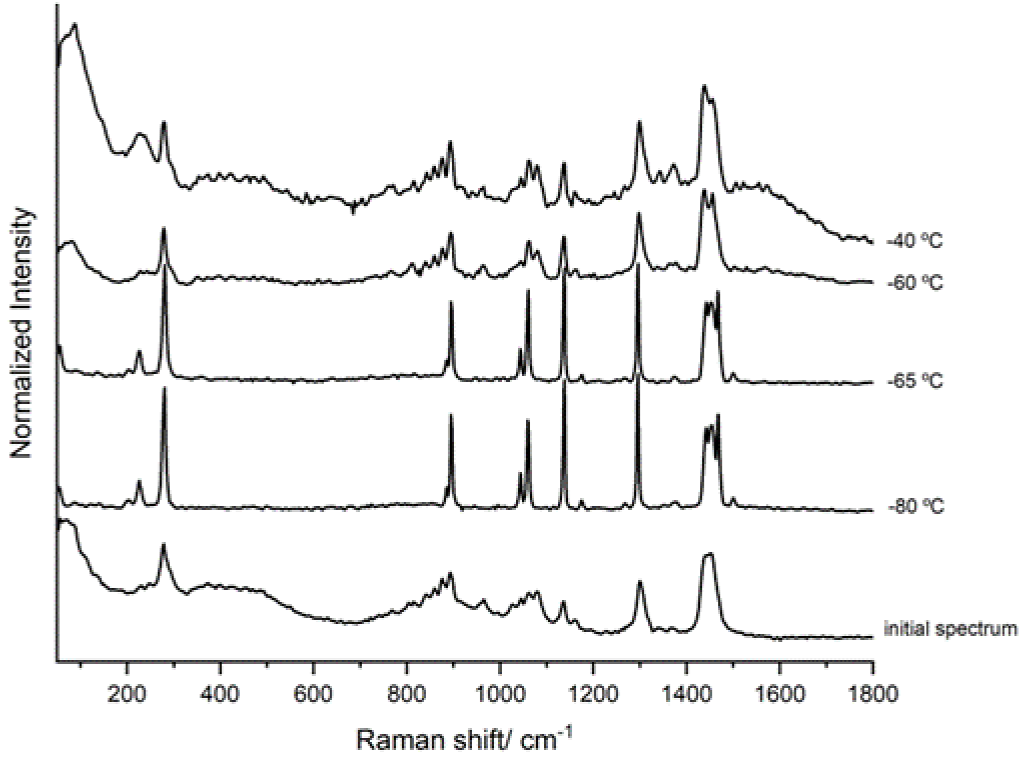


Fig. 5 – Temperature-variation Raman spectra of the 87:13 C_8-C_{10} binary system.

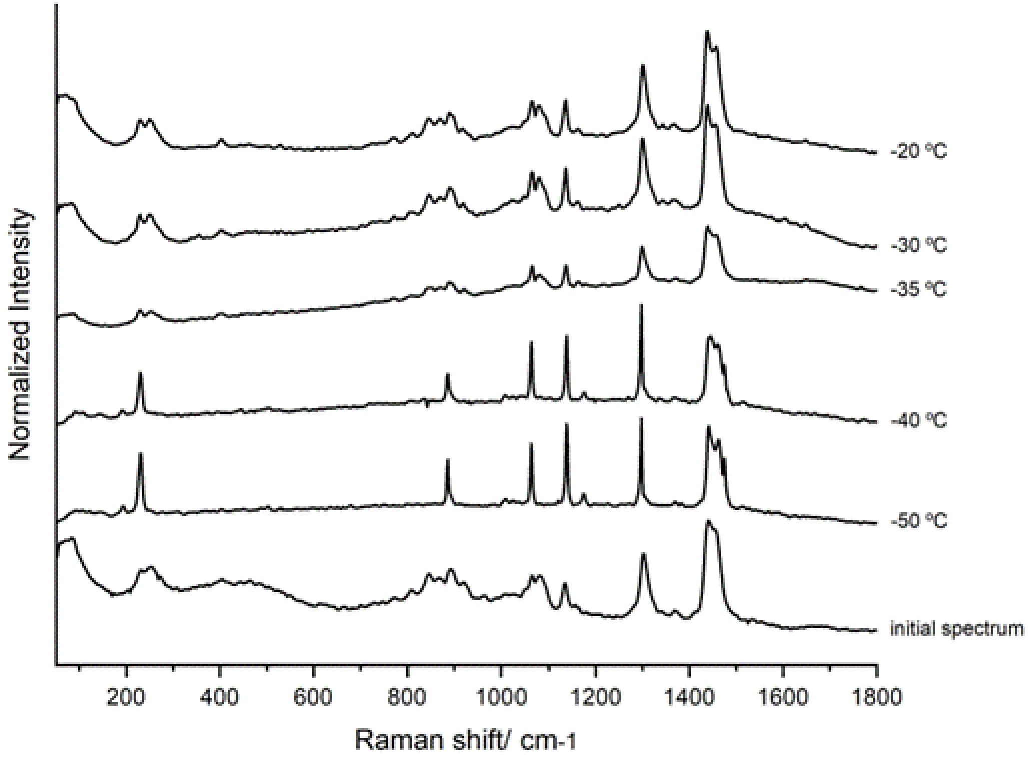
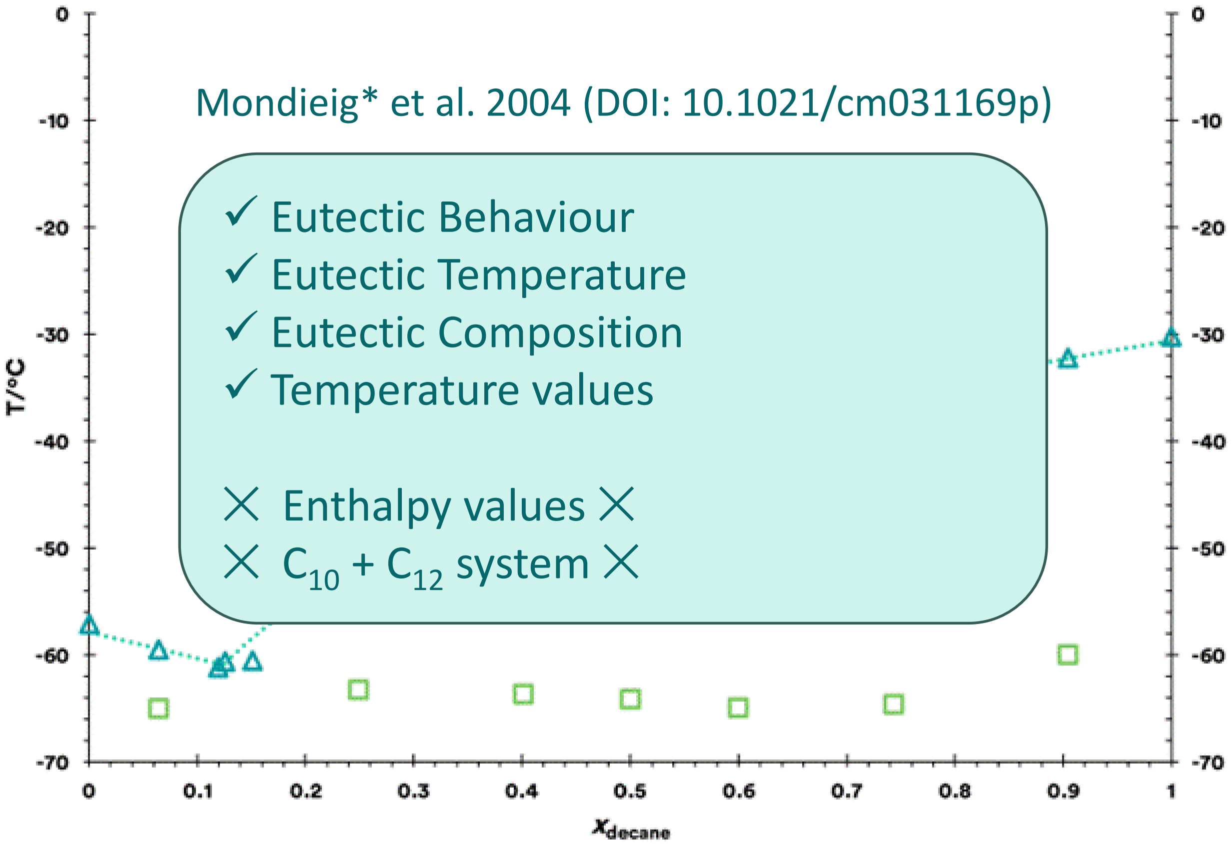


Fig. 6 – Temperature-variation Raman spectra of the 78:22 C_{10}-C_{12} binary system.

BINARY PHASE DIAGRAM

$C_8 + C_{10}$

Mondieig* et al. 2004 (DOI: 10.1021/cm031169p)



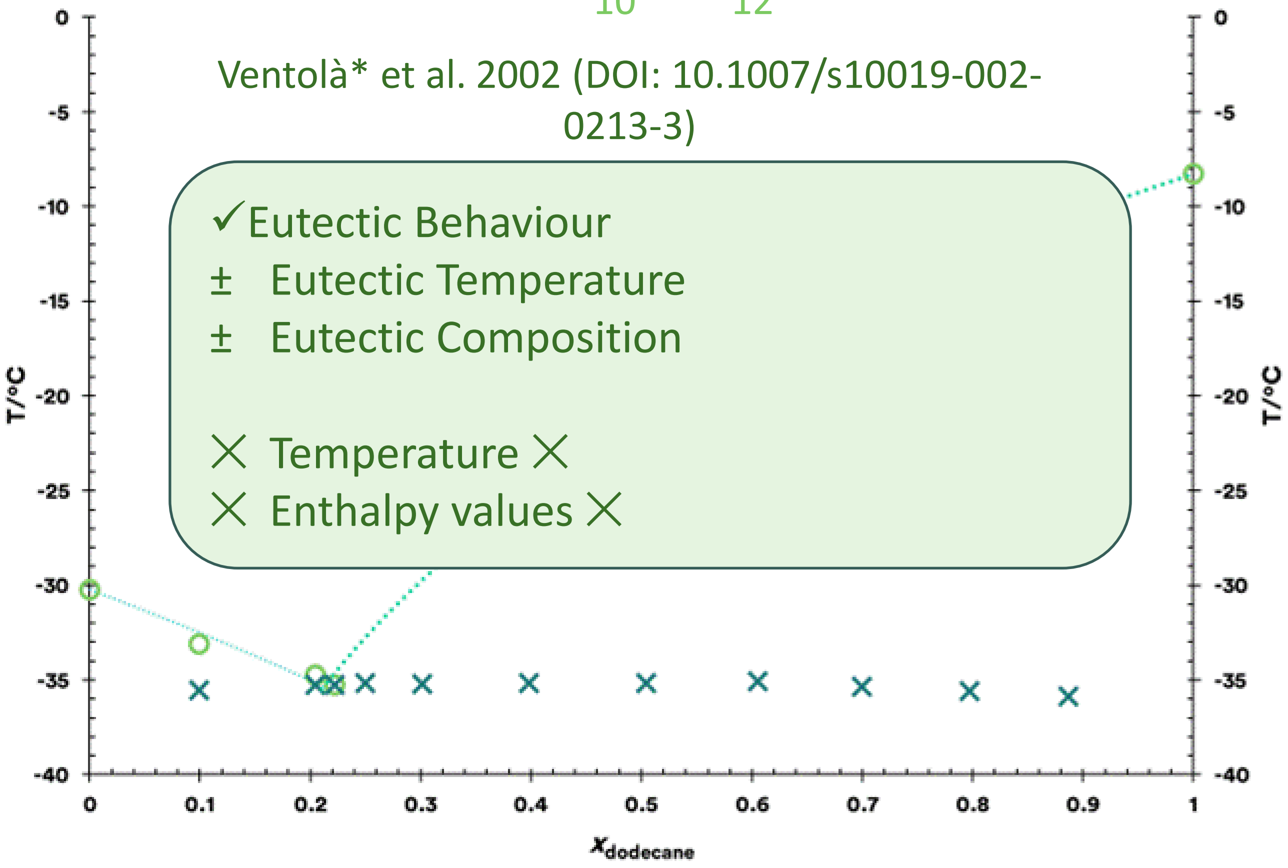
- ✓ Eutectic Behaviour
- ✓ Eutectic Temperature
- ✓ Eutectic Composition
- ✓ Temperature values

- ✕ Enthalpy values ✕
- ✕ $C_{10} + C_{12}$ system ✕

Fig. 7 – Binary solid-liquid phase diagram of *n*-octane and *n*-decane.

$C_{10} + C_{12}$

Ventolà* et al. 2002 (DOI: 10.1007/s10019-002-0213-3)



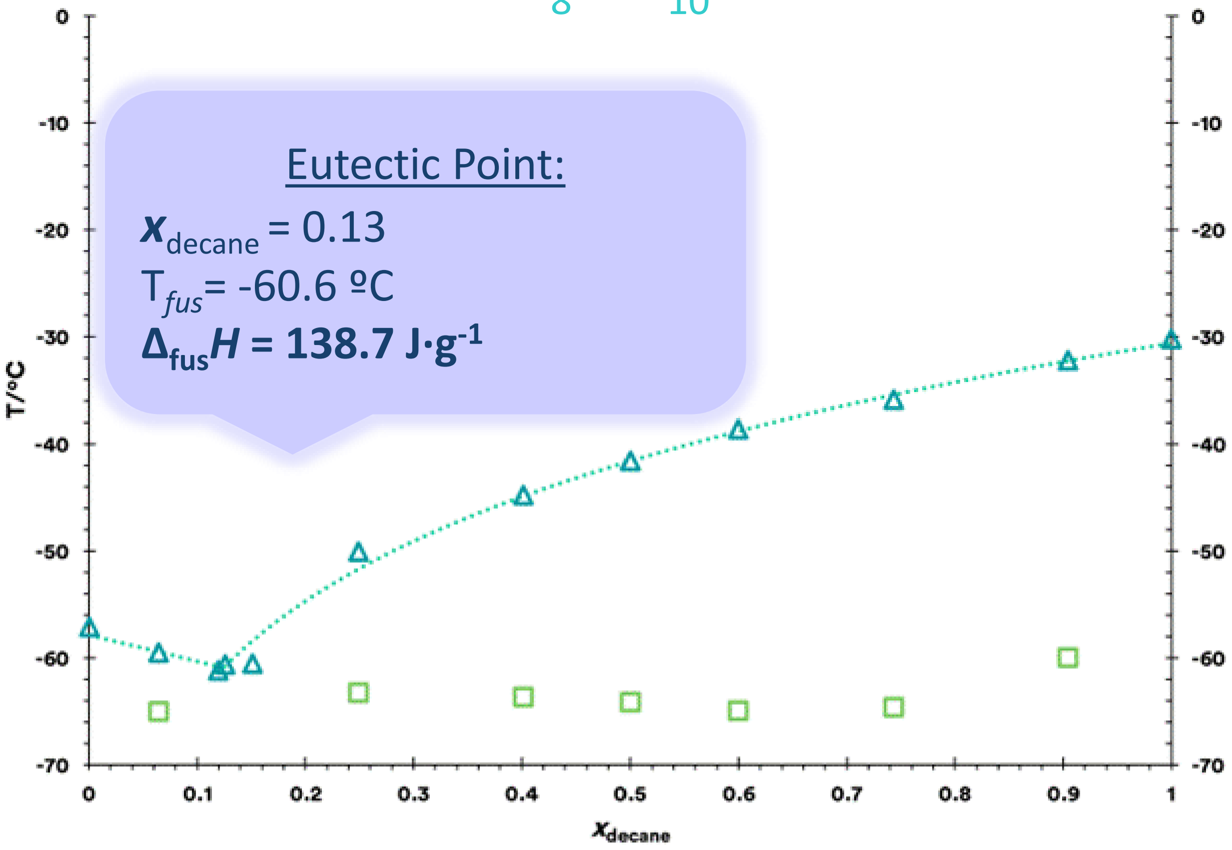
- ✓ Eutectic Behaviour
- ± Eutectic Temperature
- ± Eutectic Composition

- ✕ Temperature ✕
- ✕ Enthalpy values ✕

Fig. 8 – Binary solid-liquid phase diagram of *n*-decane and *n*-dodecane.

BINARY PHASE DIAGRAM

$C_8 + C_{10}$



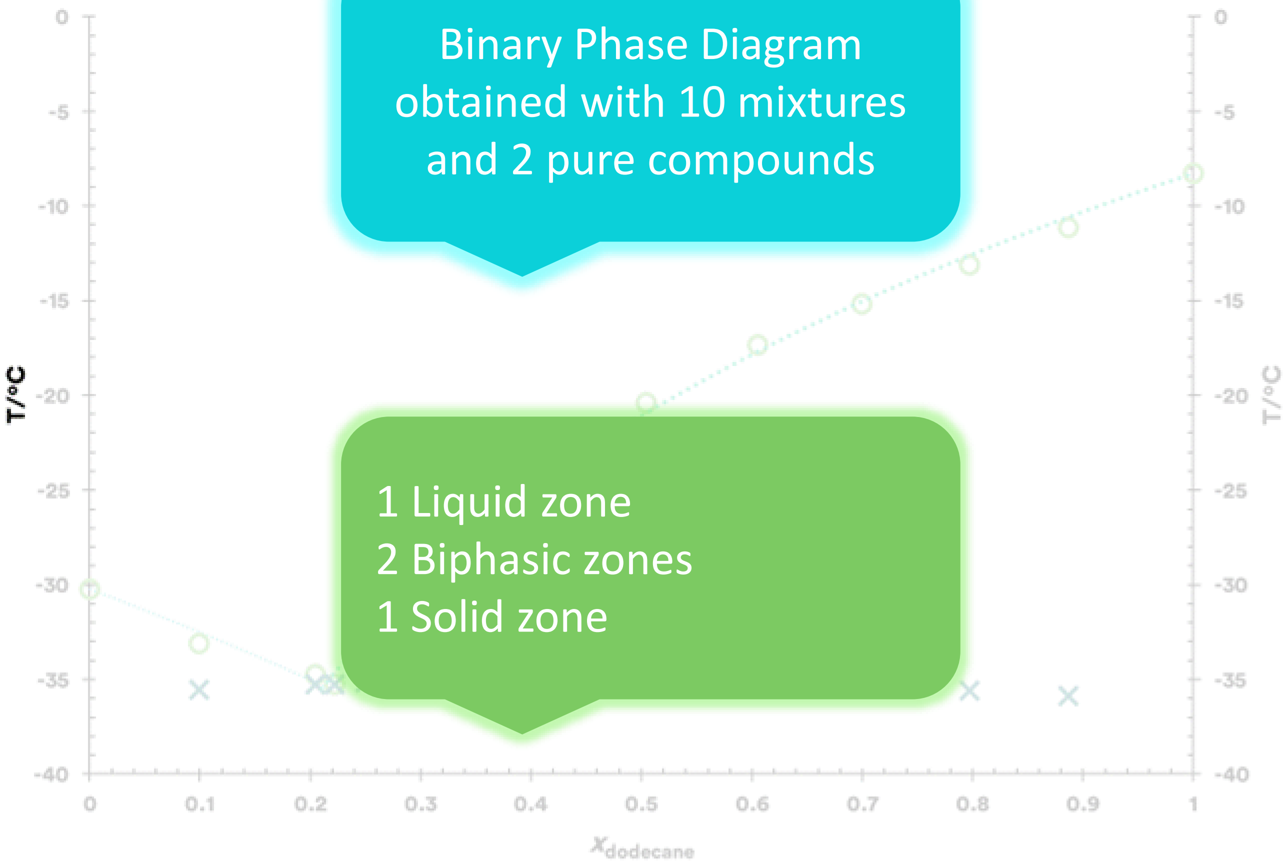
Eutectic Point:

$x_{decane} = 0.13$

$T_{fus} = -60.6$ ºC

$\Delta_{fus}H = 138.7\ J\cdot g^{-1}$

Fig. 7 – Binary solid-liquid phase diagram of *n*-octane and *n*-decane.



Binary Phase Diagram obtained with 10 mixtures and 2 pure compounds

1 Liquid zone
2 Biphasic zones
1 Solid zone

Fig. 8 – Binary solid-liquid phase diagram of *n*-decane and *n*-dodecane.

BINARY PHASE DIAGRAM

Binary Phase Diagram obtained with 10 mixtures and 2 pure compounds

1 Liquid zone
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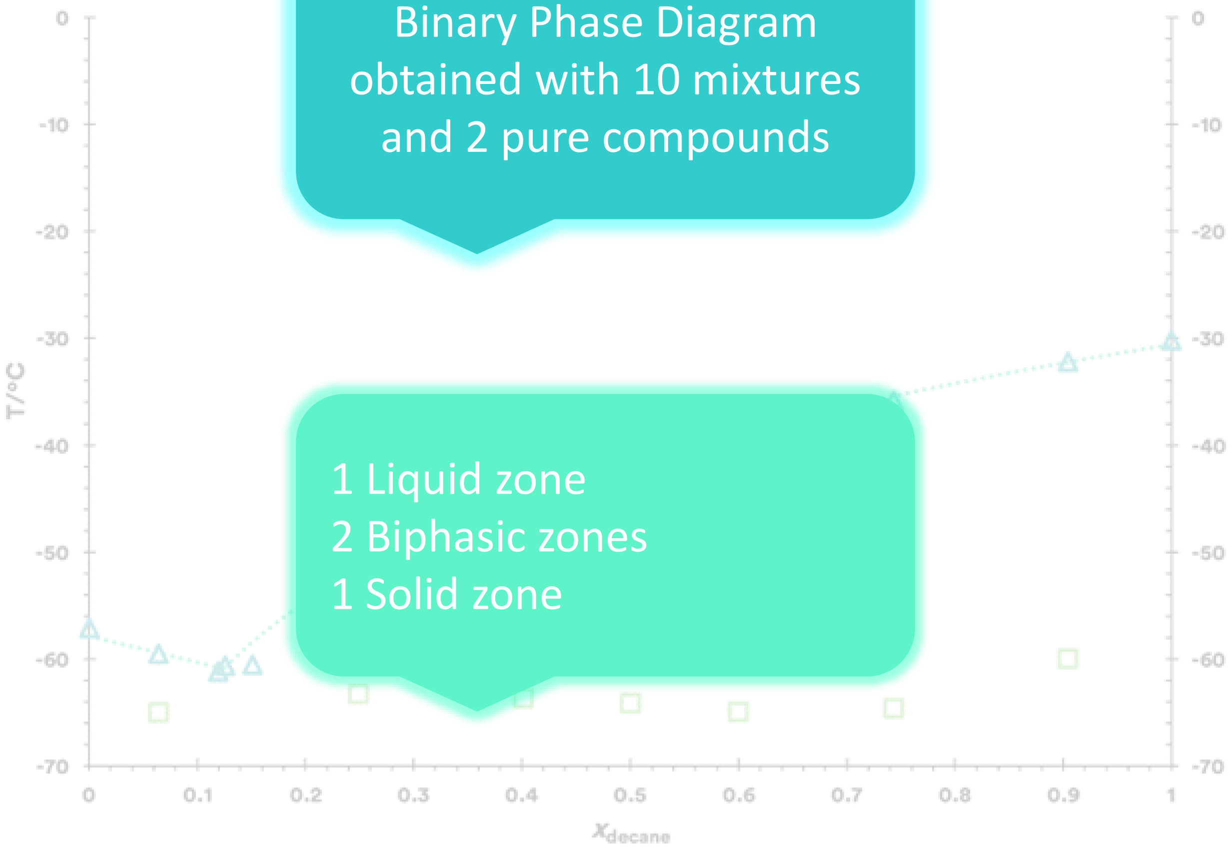

Fig. 7 – Binary solid-liquid phase diagram of *n*-octane and *n*-decane.

$C_{10} + C_{12}$

Eutectic Point:

$x_{dodecane} = 0.22$

$T_{fus} = -35.3$ ºC

$\Delta_{fus}H = 136.6\ J \cdot g^{-1}$

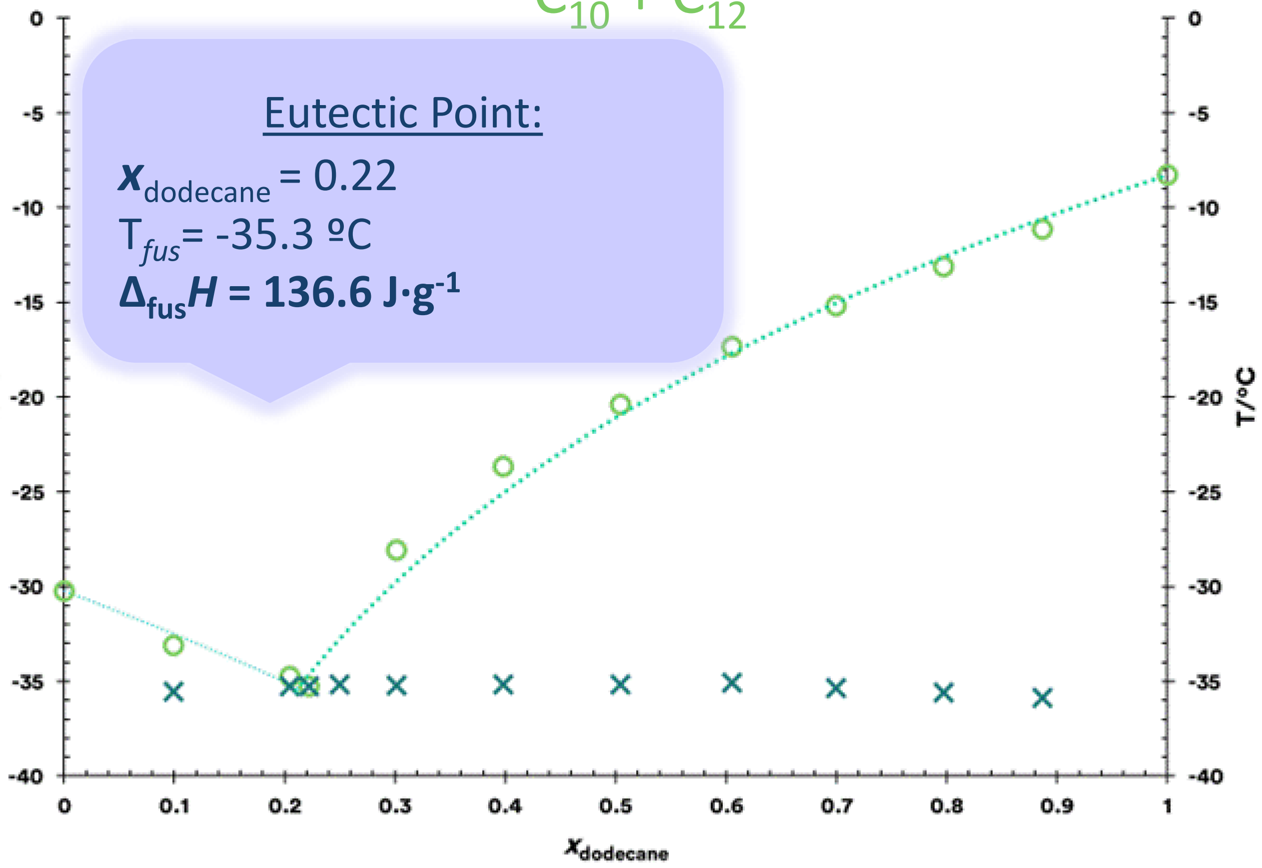

Fig. 8 – Binary solid-liquid phase diagram of *n*-decane and *n*-dodecane.

BINARY PHASE DIAGRAM - FITTING

Freezing-point depression curve[1]

$$\ln\left(\frac{1}{x}\right) = \frac{L_{Mi}}{R}\left(\frac{1}{T} - \frac{1}{T_{Mi}}\right)$$

$$\ln\left(\frac{1}{x}\right) = a + b \cdot \frac{1}{T}$$

Fitting Parameters

$$a = -\frac{L_{Mi}}{R} \cdot \frac{1}{T_{Mi}} \quad ; \quad b = \frac{L_{Mi}}{R}$$

Binary Phase Diagram $C_8 + C_{10}$

Table 1 – Comparison of the experimental results with the fitting results for the pure compounds*n*-octane and *n*-decane.

n-octanec			*n*-decane		
L_{Mi}/kJ·mol^{-1}	$\Delta_{fus}H$/kJ·mol^{-1}	Dev./ kJ·mol^{-1}	L_{Mi}/kJ·mol^{-1}	$\Delta_{fus}H$/kJ·mol^{-1}	Dev./ kJ·mol^{-1}
16.7	21.4	4.7	29.5	24.1	5.4
T_{Mi}/ºC	T_{fus}/ºC	Dev./ºC	T_{Mi}/ºC	T_{fus}/ºC	Dev./ºC
-57.9	-57.1	0.8	-30.6	-30.2	0.4
Eutectic Point					
x_{decane} (exp.)	x_{decane} (fit)	T_{exp}/ºC	T_{fit}/ºC	Dev./ºC	
0.126	0.126	-60.6	-60.9	0.3	

Maximum absolute deviation for all data: ±2.2 ºC

[1]K. Denbigh, Principles of Chemical Equilibrium, 2nd Ed. London, United Kingdom: Cambridge University Press, 1966.

BINARY PHASE DIAGRAM - FITTING

Freezing-point depression curve[1]

$$\ln\left(\frac{1}{x}\right) = \frac{L_{Mi}}{R}\left(\frac{1}{T} - \frac{1}{T_{Mi}}\right)$$

$$\ln\left(\frac{1}{x}\right) = a + b \cdot \frac{1}{T}$$

Fitting Parameters

$$a = -\frac{L_{Mi}}{R} \cdot \frac{1}{T_{Mi}} \quad ; \quad b = \frac{L_{Mi}}{R}$$

Binary Phase Diagram $C_{10} + C_{12}$

Table 2 – Comparison of the experimental results with the fitting results for the pure compoundsn-decane and *n*-dodecane.

n-decane			*n*-dodecane		
L_{Mi}/kJ·mol^{-1}	$\Delta_{fus}H$/kJ·mol^{-1}	Dev./ kJ·mol^{-1}	L_{Mi}/kJ·mol^{-1}	$\Delta_{fus}H$/kJ·mol^{-1}	Dev./ kJ·mol^{-1}
22.4	24.1	1.7	30.0	34.3	4.3
T_{Mi}/ºC	T_{fus}/ºC	Dev./ºC	T_{Mi}/ºC	T_{fus}/ºC	Dev./ºC
-30.4	-30.2	0.2	-8.4	-8.3	0.1
Eutectic Point					
$x_{dodecane}$ (exp.)	$x_{dodecane}$ (fit.)	T_{exp}/ºC	T_{fit}/ºC	Dev./ºC	
0.221	0.193	-35.3	-35.2	0.1	

Maximum absolute deviation for all data: ±0.9 ºC

[1]K. Denbigh, Principles of Chemical Equilibrium, 2nd Ed. London, United Kingdom: Cambridge University Press, 1966.

4. CONCLUSIONS

Two studied systems of *n*-alkanes:

- *n*-octane C_8 + ***n***-decane C_{10}
- *n*-decane C_{10} + *n*-dodecane C_{12}

Experimental Techniques:

- DSC
- Raman Sprectroscopy

Solid-liquid binary phase digrams:

- Eutectic Systems
- Fitting of the liquidus line

Potencial PCMs for low Temp. ES:

- C_8/C_{10}: T_{fus}= -60.6 ºC; $\boldsymbol{\Delta_{fus}H = 138.7\ J\cdot g^{-1}}$
- C_{10}/C_{12}: T_{fus}= -35.3 ºC; $\boldsymbol{\Delta_{fus}H = 136.6\ J\cdot g^{-1}}$

ACKNOWLEDGMENTS

This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, Projects UIDB/00100/2020, UIDP/00100/2020, UIDB/00313/2020 and UIDP/00313/2020 and IMS - LA/P/0056/2020.

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TÉCNICO LISBOA

IMS

CQE Química Estrutural

IST-ID Associação do Instituto Superior Técnico para a Investigação e Desenvolvimento

fct Fundação para a Ciência e a Tecnologia