Thermophysical Properties of *n*-alkane systems for low temperature thermal energy storage

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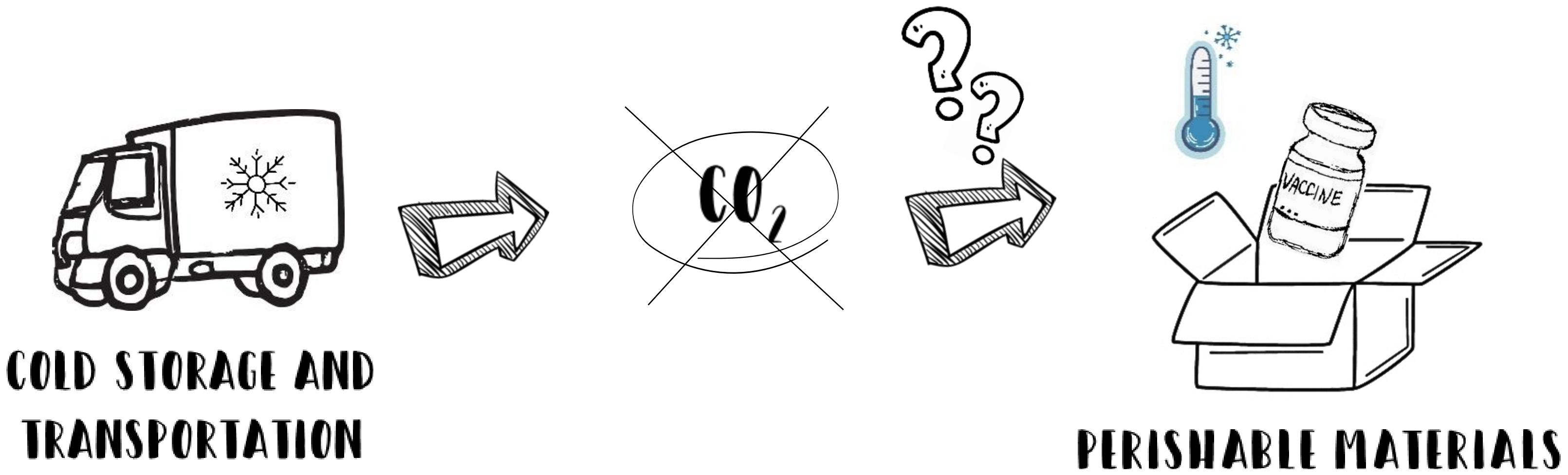
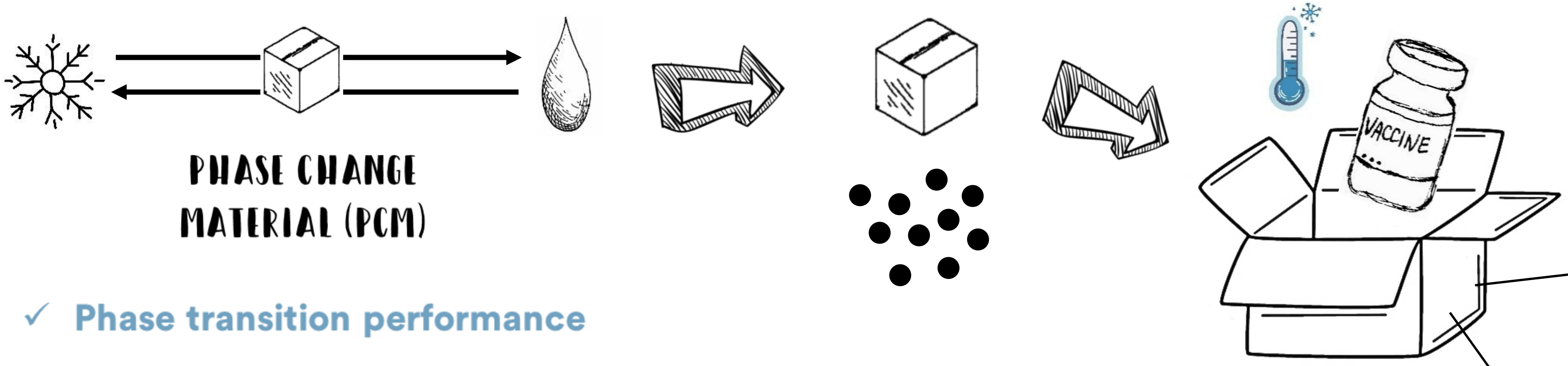
Introduction and Purpose

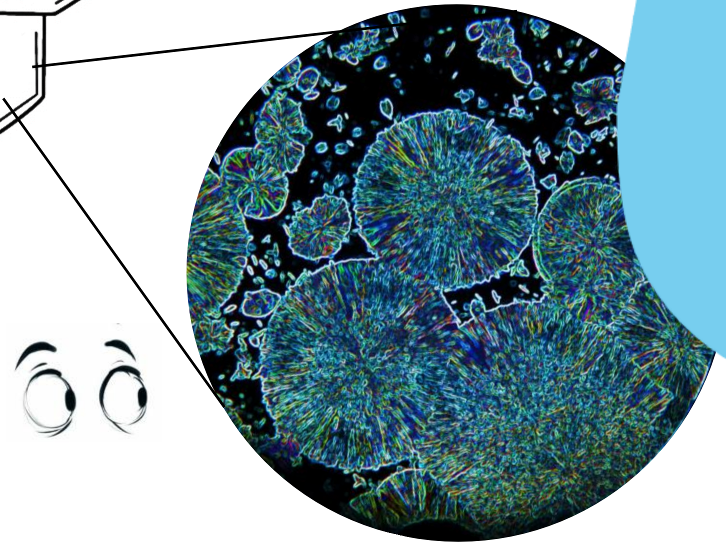


01 Introduction and Purpose

THERMAL ENERGY STORAGE



- ✓ Phase transition performance
- ✓ High energy storage densities
- ✓ Chemical stability



01 Introduction and Purpose

N-ALKANES

ODD AND EVEN LINEAR N-ALKANES

BINARY SYSTEMS

$C_9 + C_{11}$

$C_8 + C_{10}$

$C_{10} + C_{12}$

$C_9 + C_{10}$

- Widely studied for several properties
- Candidates PCMs
- Particular phase transition performance
- Wide range of T (inc. low T)
- Lack of available data for low T
- Sub-industrial products (circular economy)

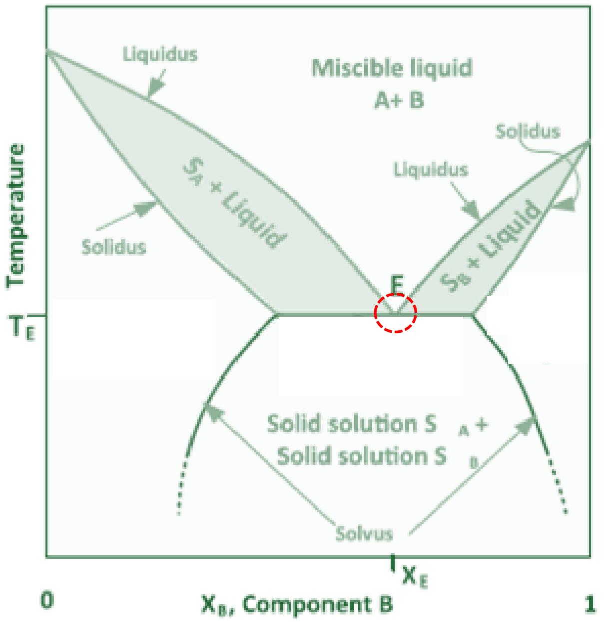
Understand the diferences on phase equilibrium behaviour between odd and even *n*-alkanes

Introduction and Purpose

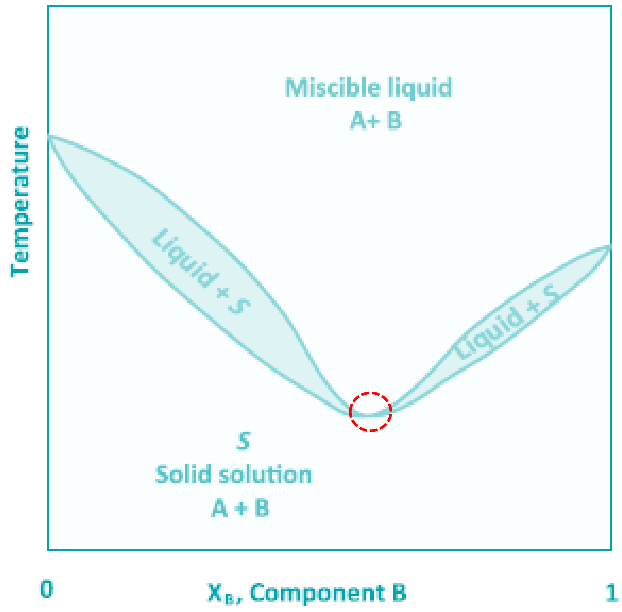
01

Solid – Liquid Phase Equilibrium in TES

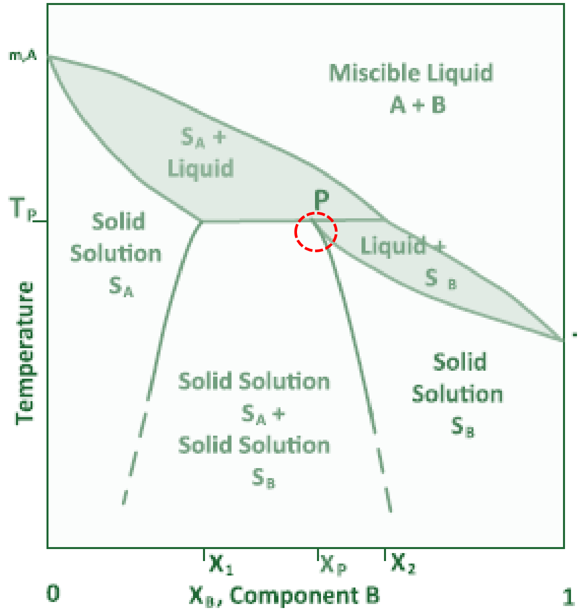
Eutectic System



Congruent Melting System



Peritectic System



S. N. Gunasekara, S. Kumova, J. N. W. Chiu, V. Martin, Int. J. Refrig. 82, 130–140 (2017). https://doi.org/1016/j.ijrefrig.2017.06.003.

Introduction and Purpose

Solid – Liquid Phase Equilibrium in TES

Literature Insights

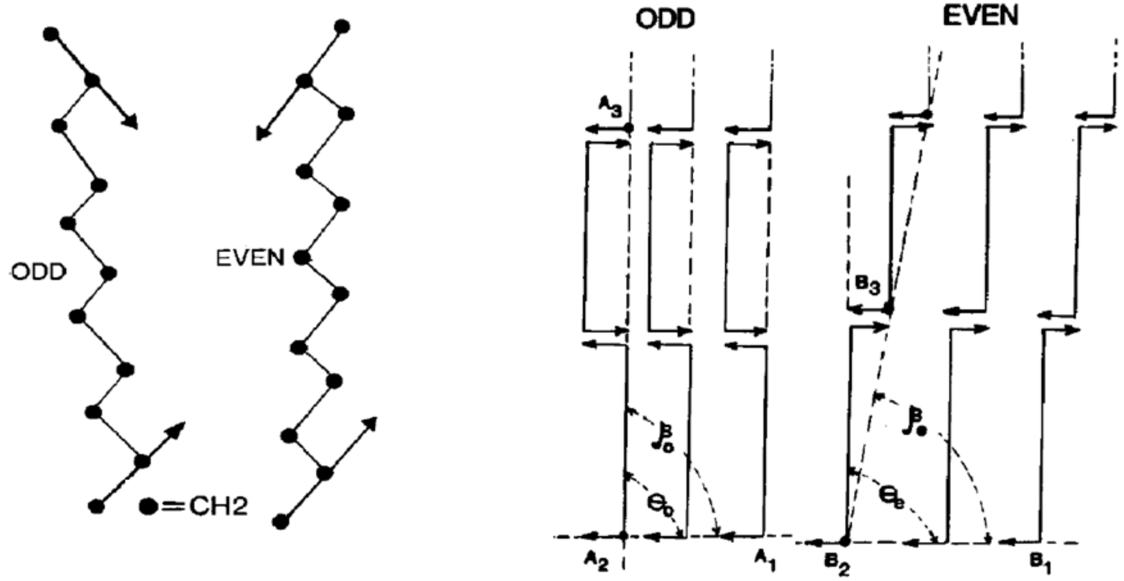
Even + Even Alkanes → **Eutectic**

Odd + Odd Alkanes → **Congruent Melting**

Odd + Even Alkanes → **Peritectic**

But... Why???

01 The packaging:



I. Moradinia, A. S. Teja, *Fluid Phase Equilib.*, 1986, 28, 199-209. doi: 10.1016/0378-3812(86)85079-8.

03 Results and Discussion

Solid – Liquid Phase Equilibrium in TES

Literature Insights

Even + Even Alkanes → **Eutectic**

Odd + Odd Alkanes → **Congruent Melting**

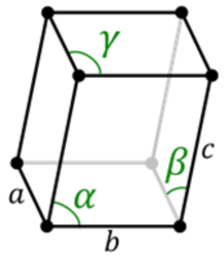
Odd + Even Alkanes → **Peritectic**

But... Why???

02 Different Solid Structures:

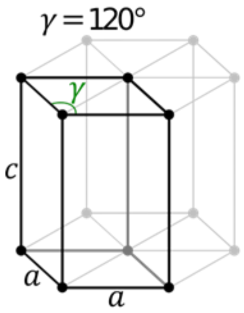
Triclinic Structure (T)

- Even triclinic (T_p) with Z=1 (for even chains)
- Odd triclinic (T_i) with Z=2 (for odd chains)



Orthorhombic Structure (O)

- Ordered phase (O_i)
- Rotator phase (R_I)



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03

Results and Discussion

Solid – Liquid Phase Equilibrium in TES

Literature Insights

Even + Even Alkanes → **Eutectic**

Odd + Odd Alkanes → **Congruent Melting**

Odd + Even Alkanes → **Peritectic**

But... Why???

Even Alkanes

Triclinic (solid state)

↓ No polymorphism

Liquid State

Odd Alkanes

Triclinic (solid state)

↓ Polymorphism

Ordered Orthorrombic (solid state)

↓ Polymorphism

Rotator Orthorrombic (solid state)

↓

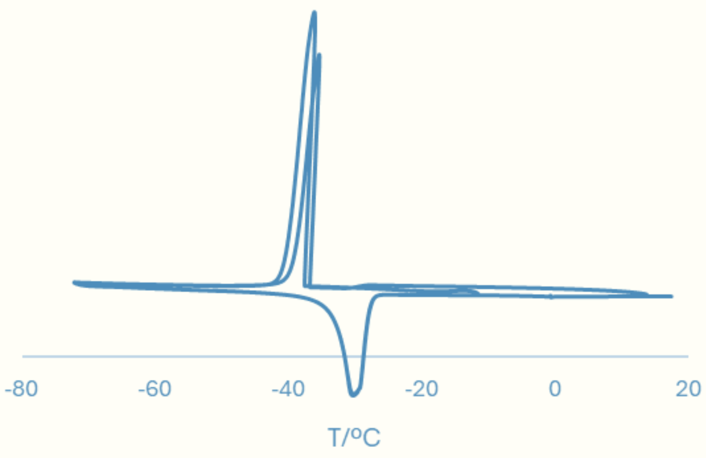
Liquid State

Experimental Work

02

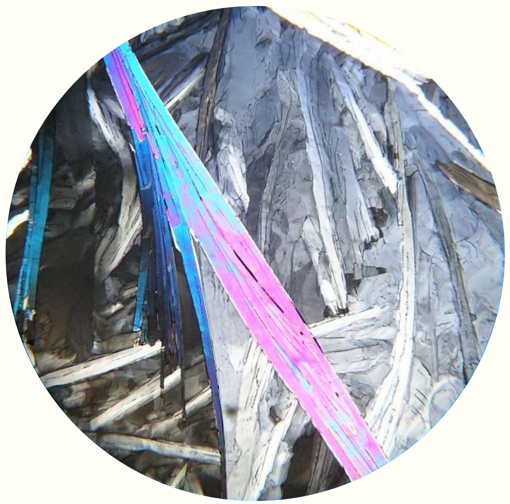
Experimental Techniques

Differential Scanning Calorimetry



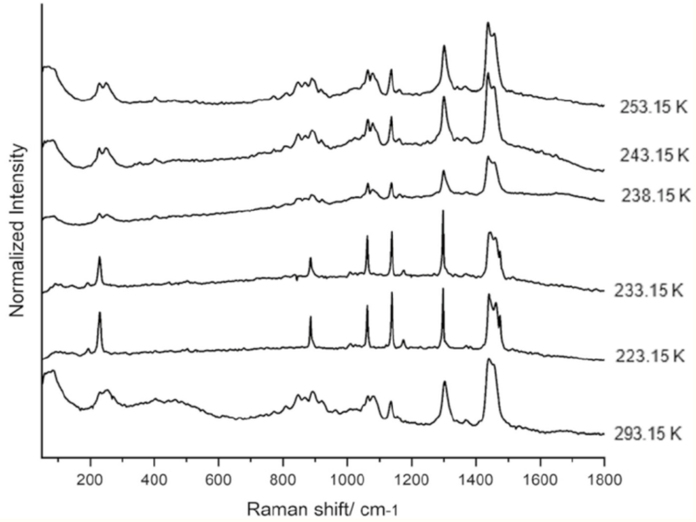
- Pure compounds
- Binary mixtures
- Temperatures of fusion
- Enthalpies of fusion

Hot Stage Microscopy



- Pure compounds
- Binary mixtures
- Visual interpretation of the DSC results

Raman Spectroscopy



- Pure compounds
- Binary mixtures
- Temperature – variation
- Understand the different phases

03

Results and Discussion

Solid – Liquid binary phase diagrams[1]

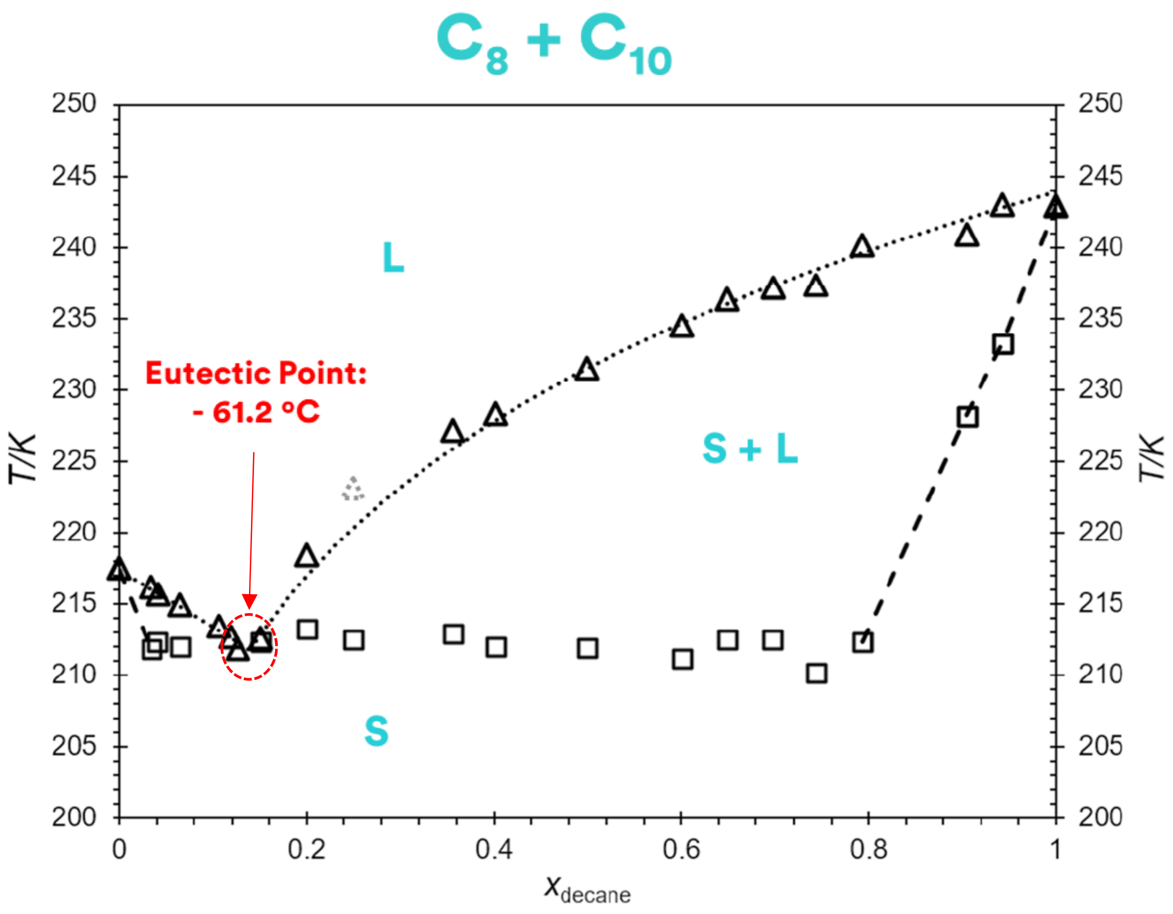


Fig.8 – Binary solid-liquid phase diagram of *n*-octane and *n*-decane.

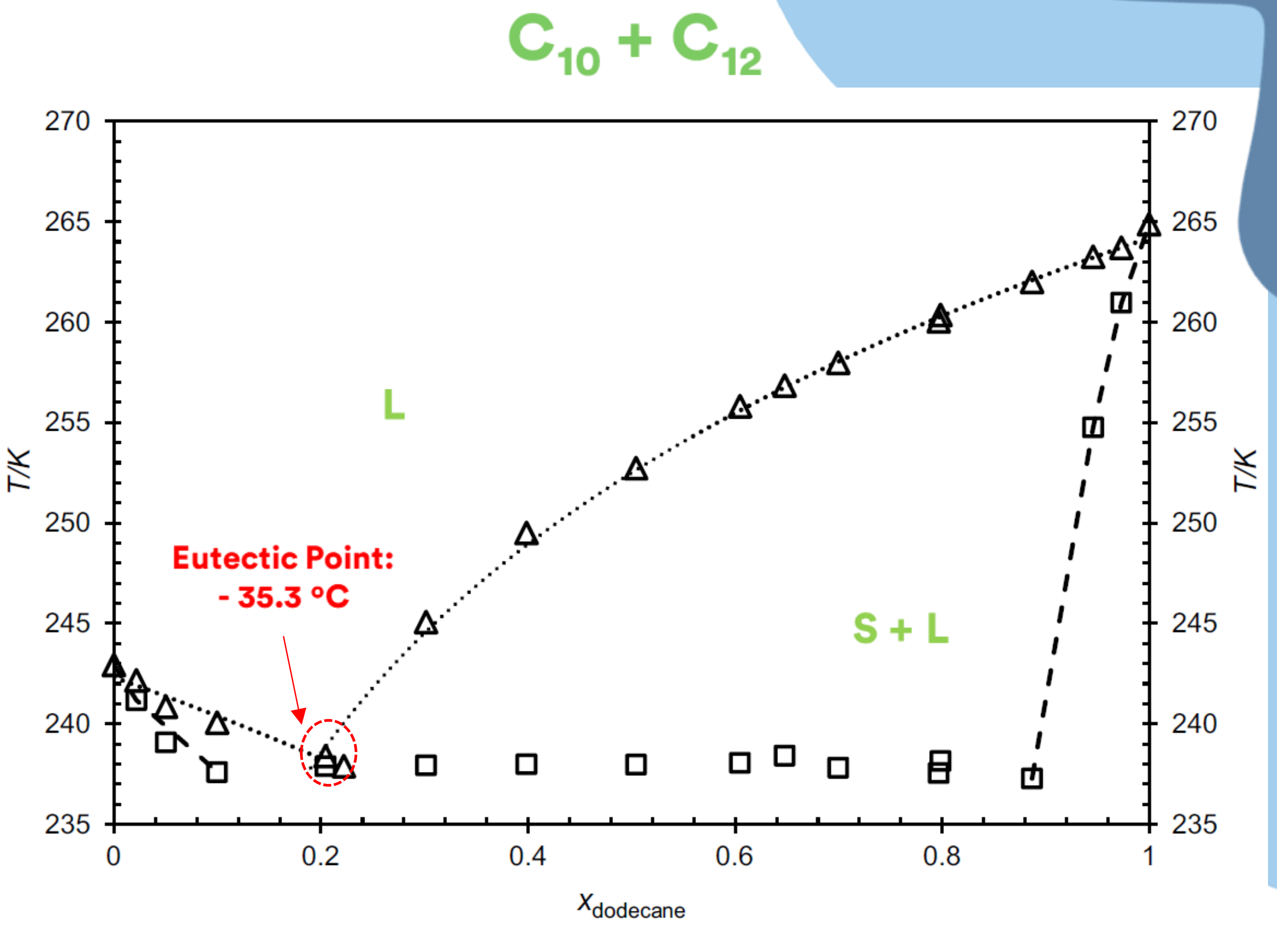


Fig. 9 – Binary solid-liquid phase diagram of *n*-decane and *n*-dodecane.

[1]Results published in the International Journal of Thermophysics. DOI: 10.1007/s10765-023-03317-9

Results and Discussion

Solid – Liquid binary phase diagrams[2]

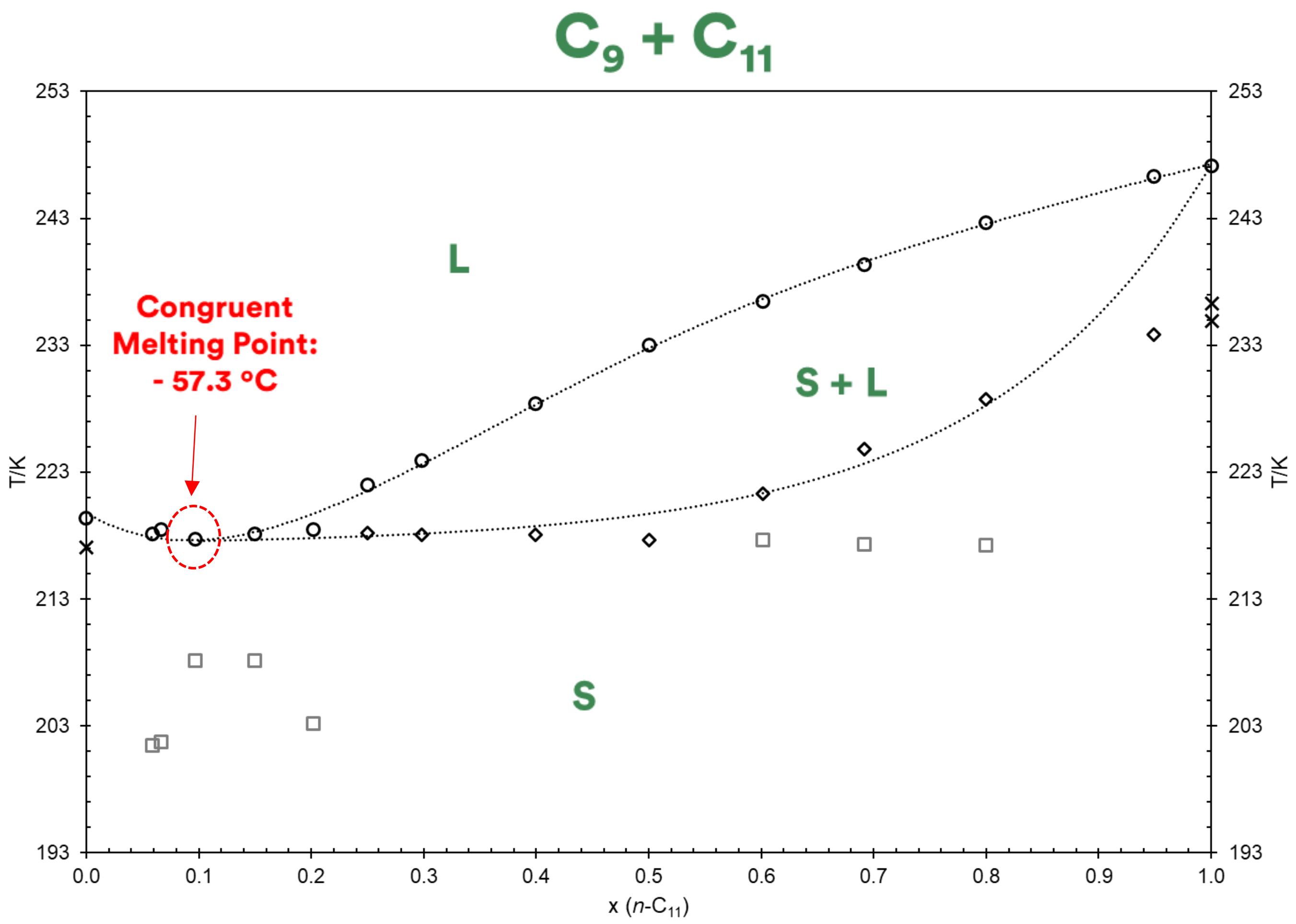


Fig. 10 – Binary solid-liquid phase diagram of *n*-nonane and *n*-undecane.

[2]Results submitted to the International Journal of Thermophysics.

03 Results and Discussion

Solid – Liquid binary phase diagrams

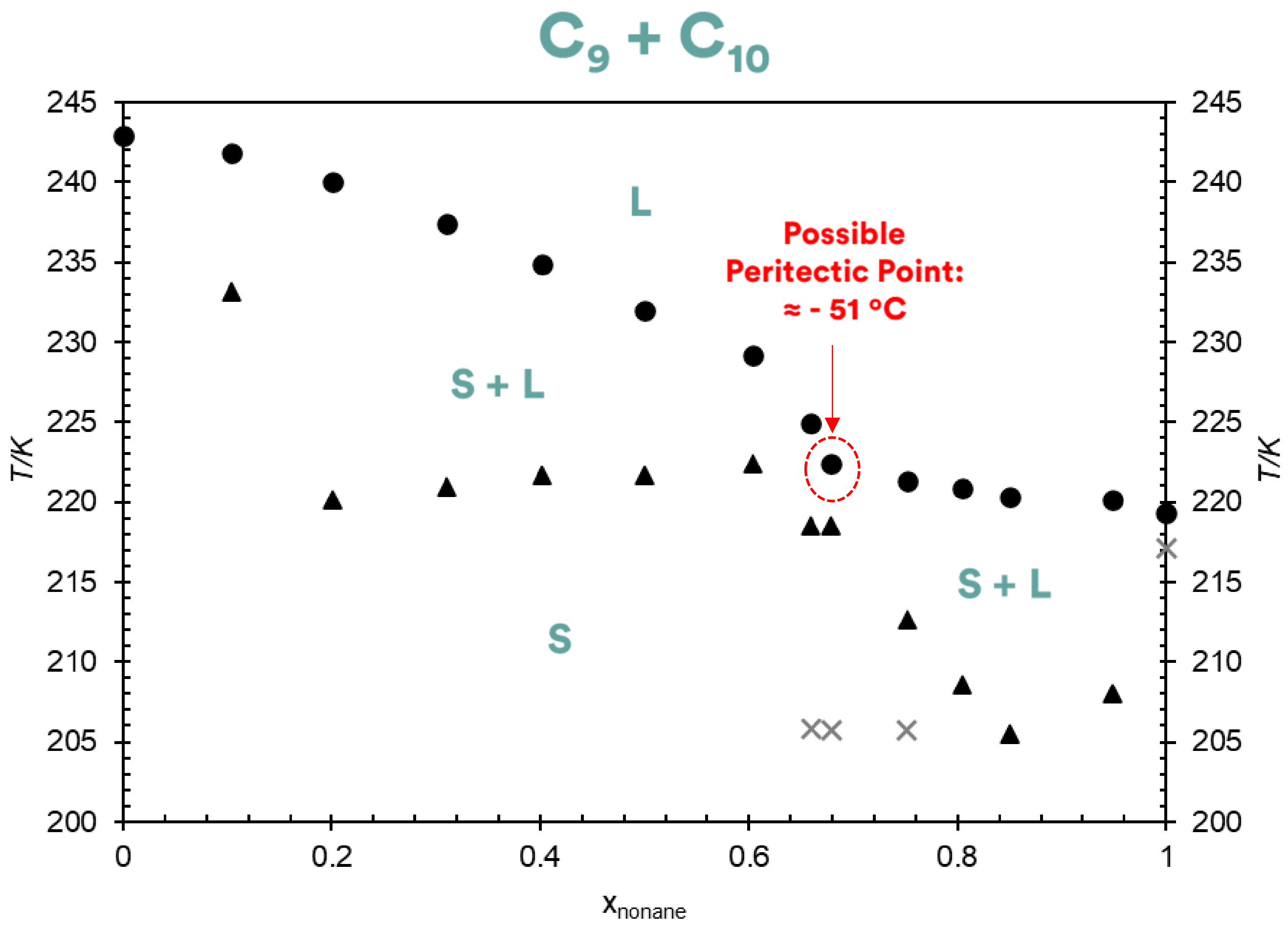


Fig. 11 – <u>Preliminary</u> binary solid-liquid phase diagram of *n*-nonane and *n*-undecane.

04 Conclusions

Different packaging and, consequently different **solid structures** for odd and even alkanes

Solid-liquid phase equilibrium behaviour is affected for odd and even alkanes and for their binary mixtures differently

It is possible to **predict** their **phase equilibrium properties** by the odd or even molecules involved in the mixture

This **predictability** is very important to **understand** which systems should be investigated as **potential new PCMs**

n-alkanes have proven to be **good candidates** as **PCMs** for **very low temperature TES** applications

3/4 studied systems **exhibit ideal PCM** behaviour with: $-61.2\ °C < T_{fus} < -35.3\ °C$ and similar energy storage performance

Acknowledgements

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Supp. Information

Eutectic Point (octane + decane):

$\boldsymbol{x}_{decane}$ = 0.13
T_{fus}= -60.6 ºC
$\boldsymbol{\Delta_{fus}H}$ **= 138.7 J·g⁻¹**

Eutectic Point (decane + dodecane):

$\boldsymbol{x}_{dodecane}$ = 0.22
T_{fus}= -35.3 ºC
$\boldsymbol{\Delta_{fus}H}$ **= 136.6 J·g⁻¹**

Eutectic Point (nonane + undecane):

$\boldsymbol{x}_{undecane}$ = 0.10
T_{fus}= -57.31 ºC
$\boldsymbol{\Delta_{fus}H}$ **= 103.9 J·g⁻¹**