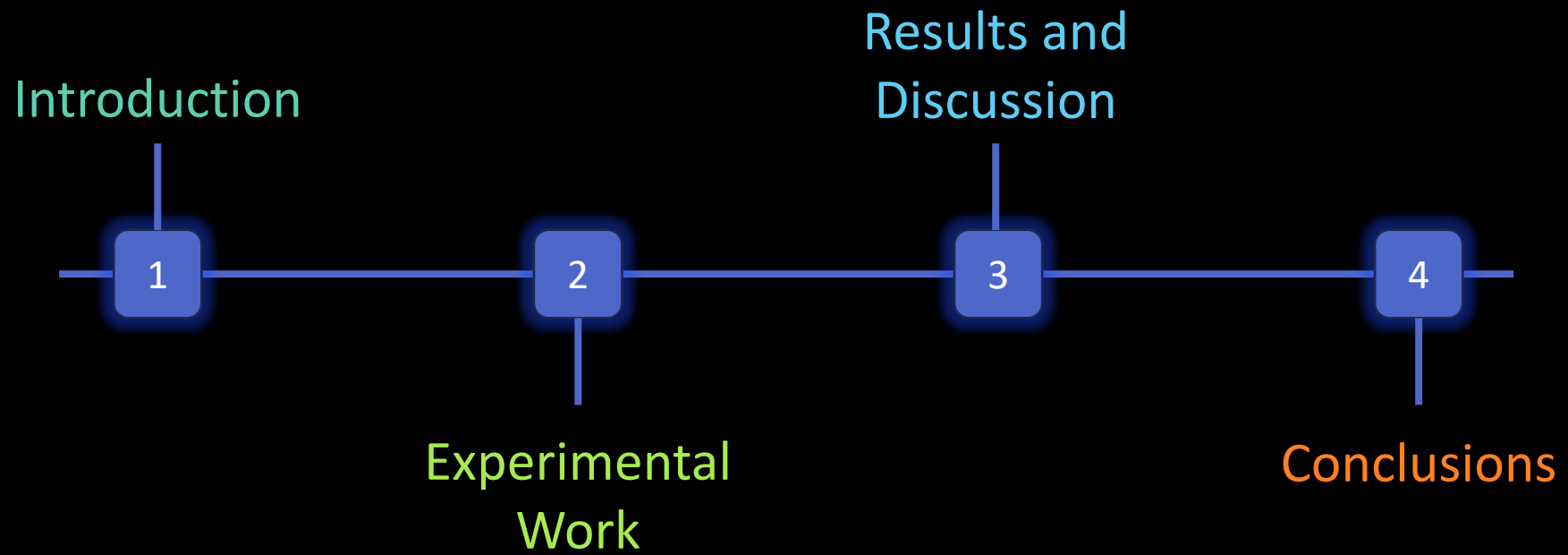


Low temperature energy storage PCM systems

Phase Equilibrium Studies

Maria C. M. Sequeira, Bernardo A. Nogueira, Fernando J. P. Caetano, Hermínio A. P. Diogo, João M. N. A. Fareleira, Rui Fausto



1. Introduction



Increasing Energy Needs



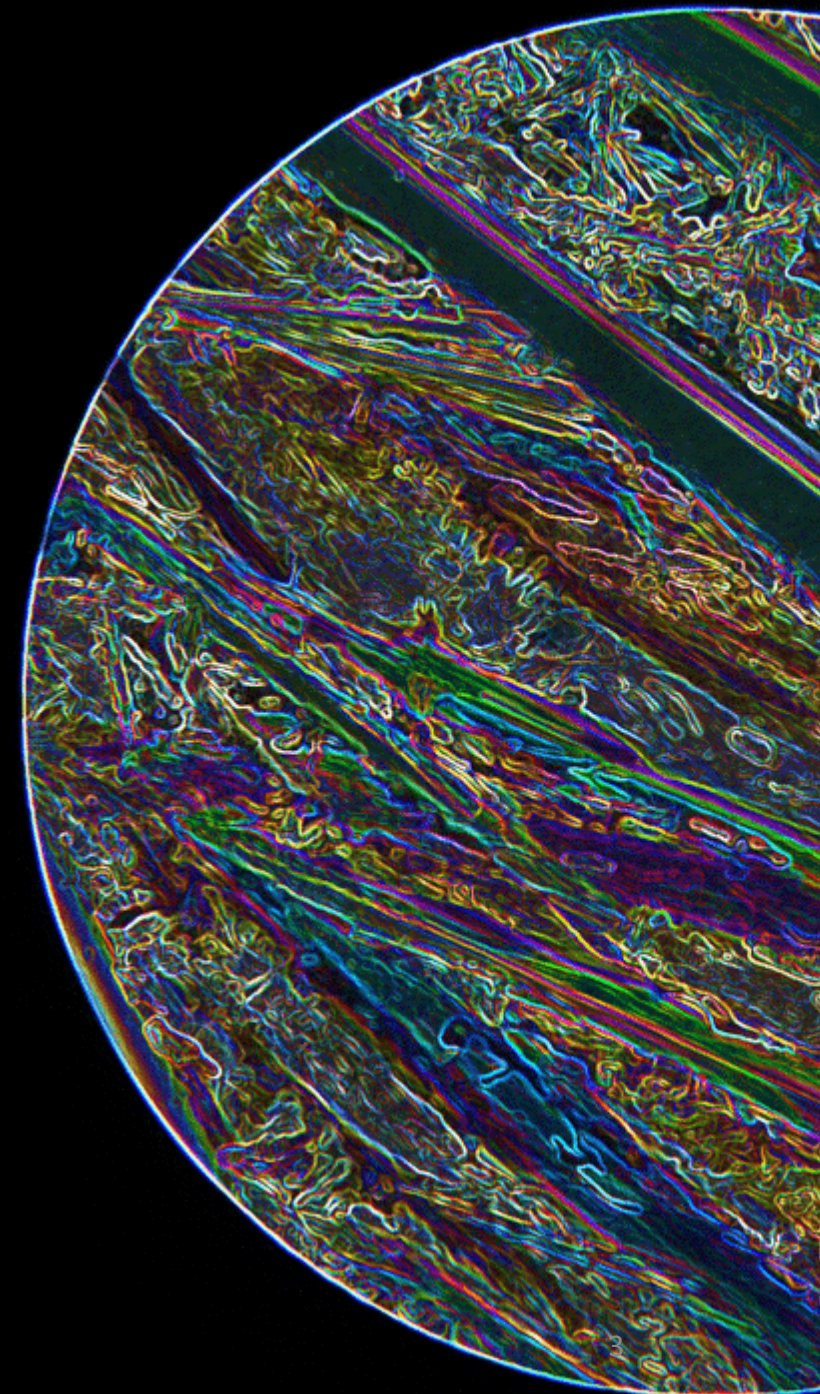
Energy Storage – Thermal Energy Storage

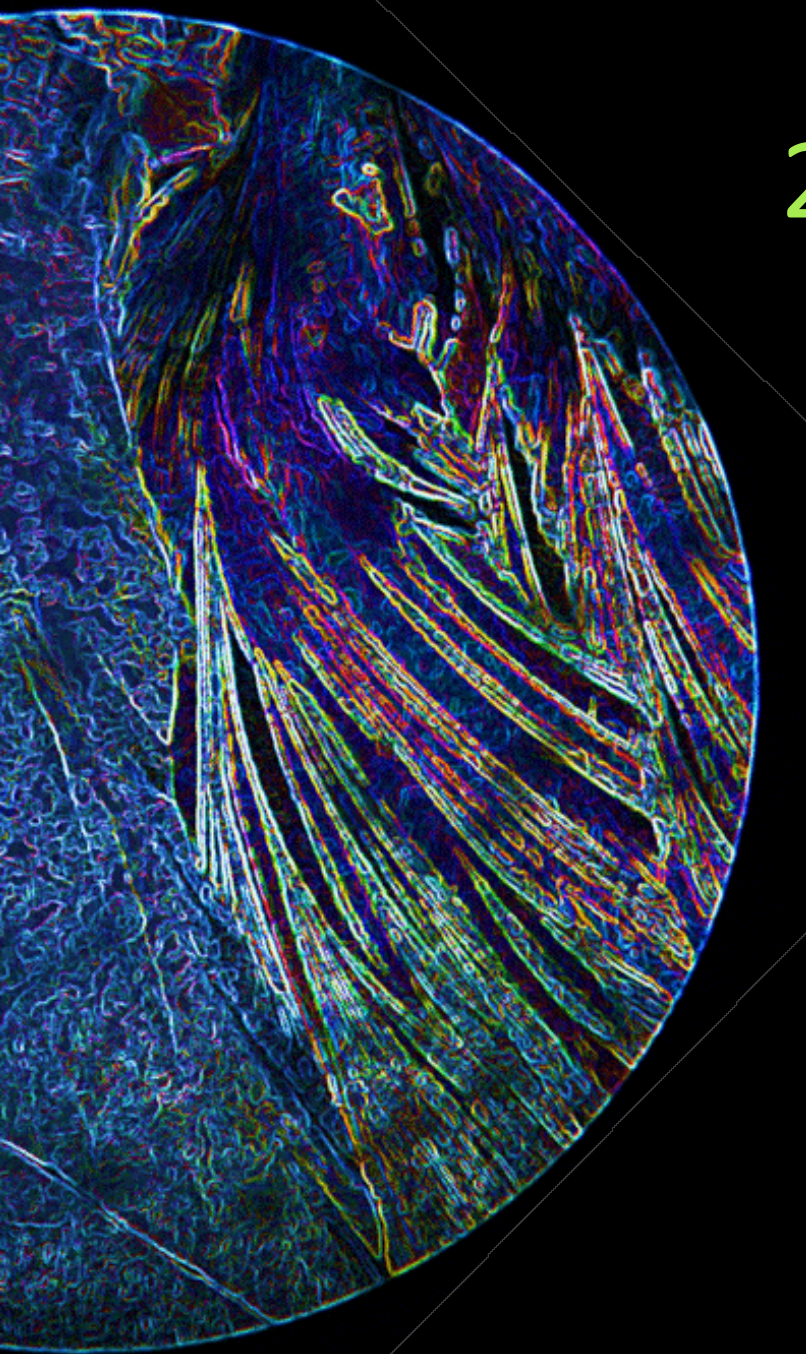


Phase Change Materials – Latent Heat Storage

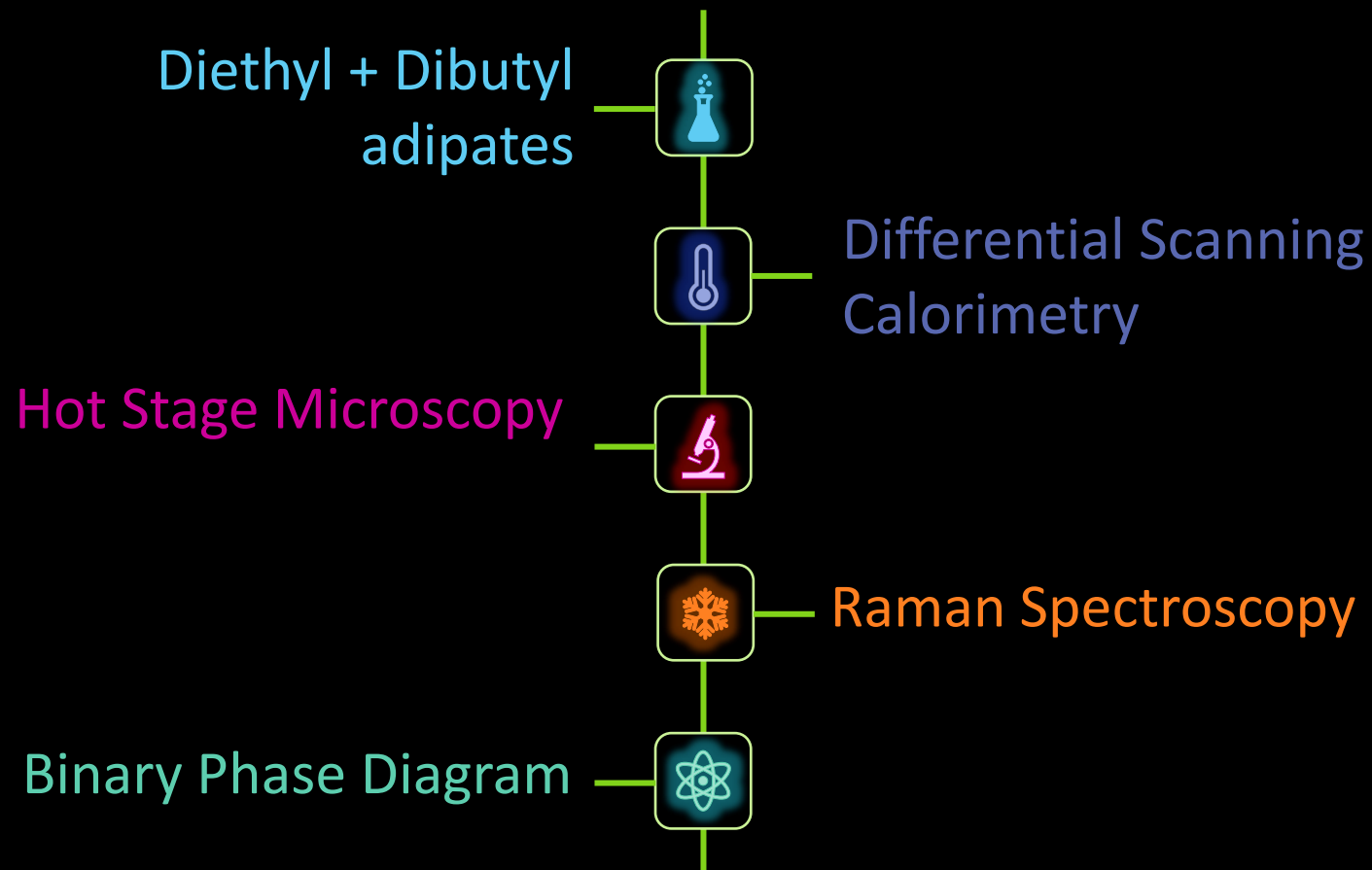


Binary system of n – alkyl - adipates (continuation of the last year's work)





2. Experimental Work





3. Results and Discussion



Differential Scanning Calorimetry

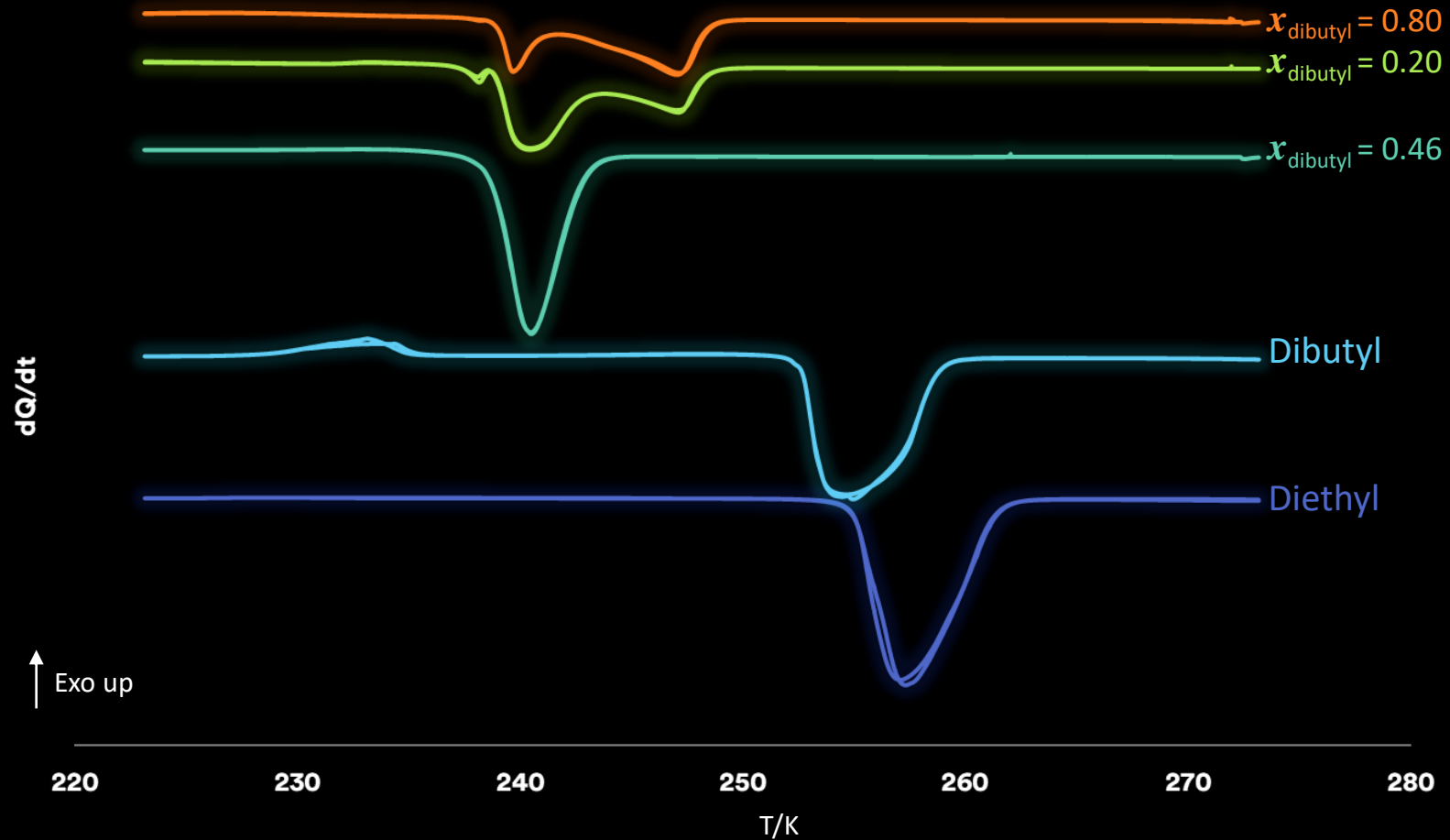
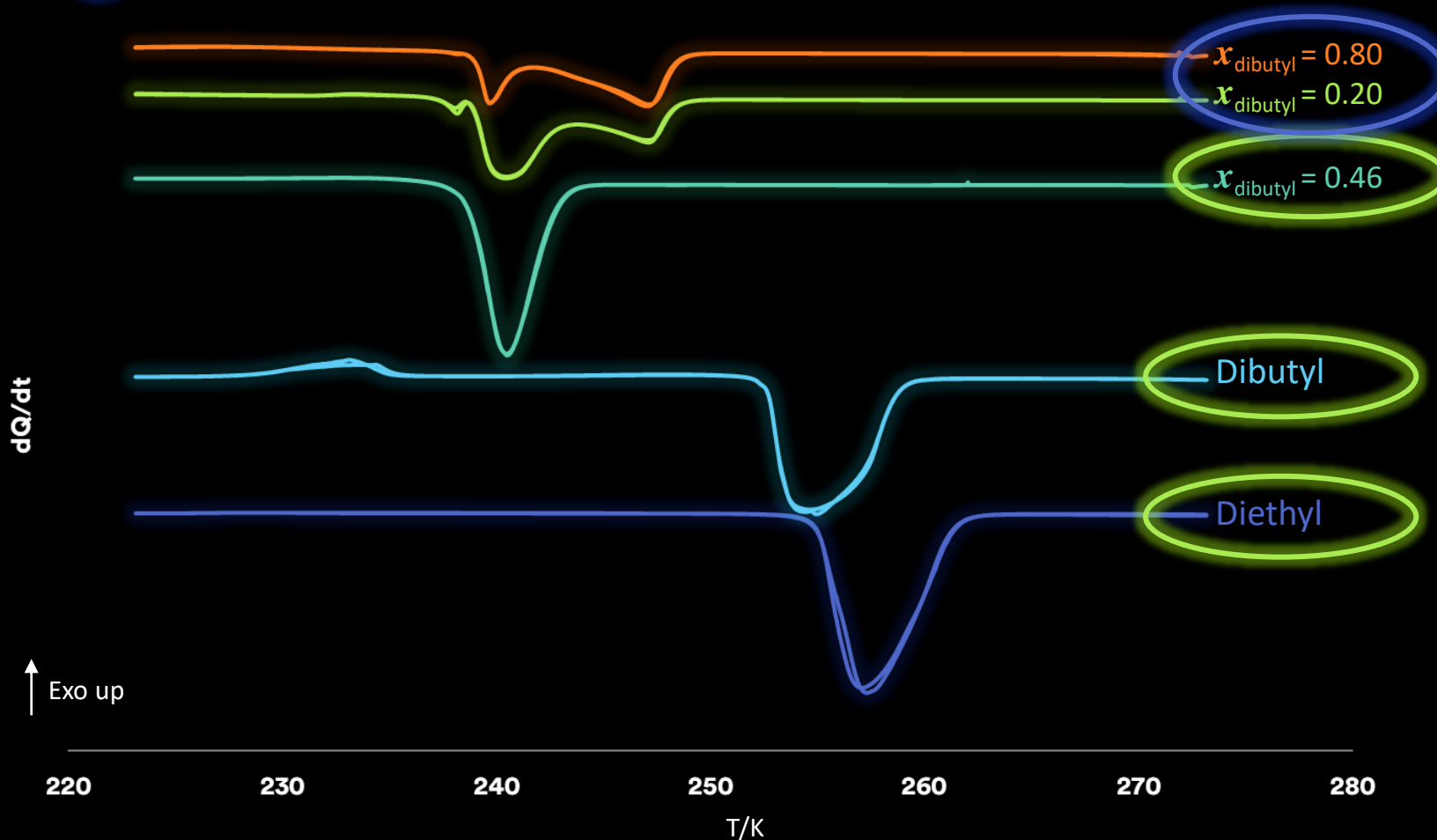


Fig. 1 – DSC heating curves of pure diethyl, dibutyl, and of selected binary mixtures, with dibutyl molar fraction x_{dibutyl} .



Differential Scanning Calorimetry



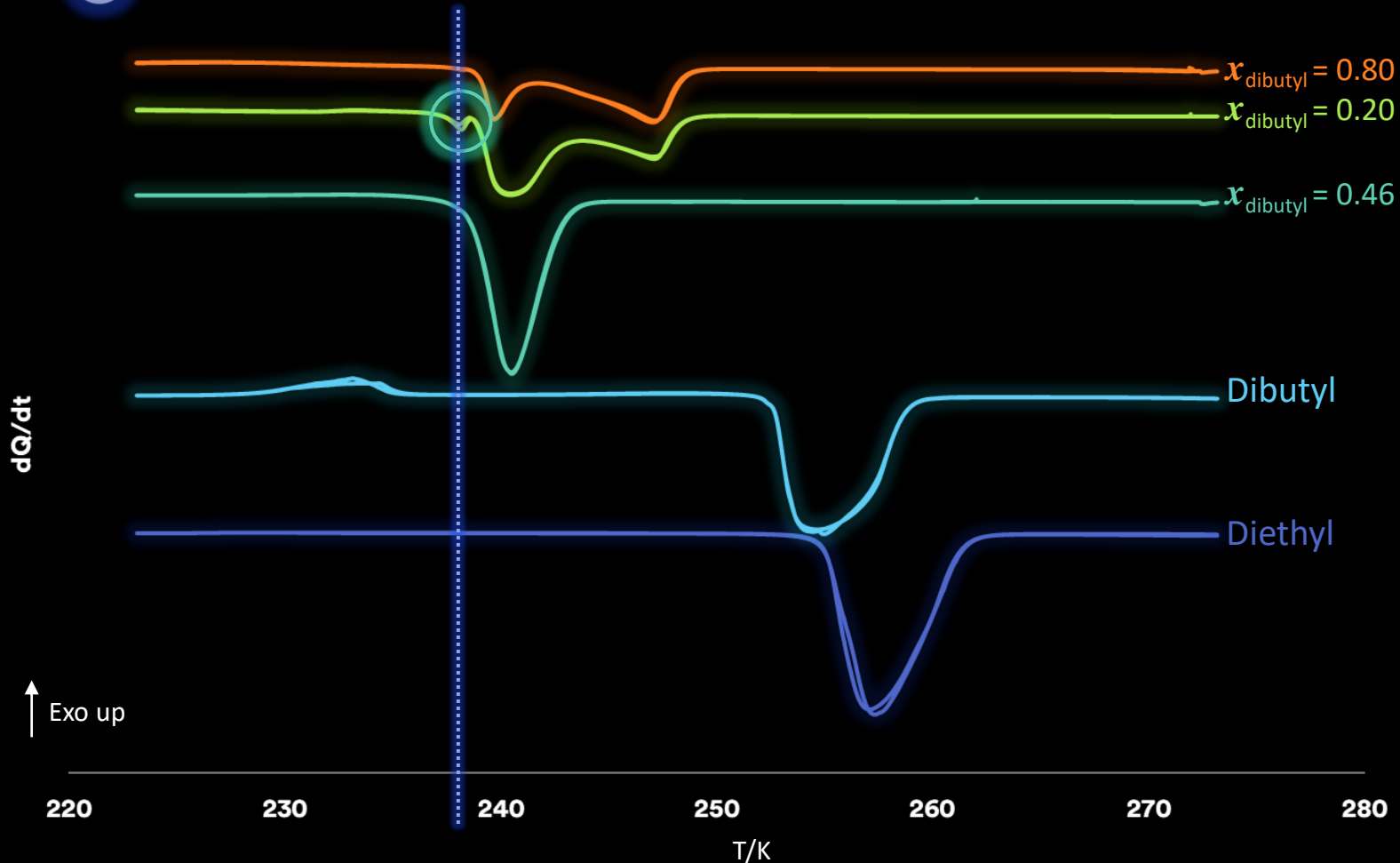
For **pure compounds** and the **eutectic mixture**: only a single peak for the phase transition

For **binary mixtures** ($x_{\text{dibutyl}} = 0.20$ and 0.80): two peaks for the phase transition

Fig. 1 – DSC heating curves of pure diethyl, dibutyl, and of selected binary mixtures, with dibutyl molar fraction x_{dibutyl} .



Differential Scanning Calorimetry



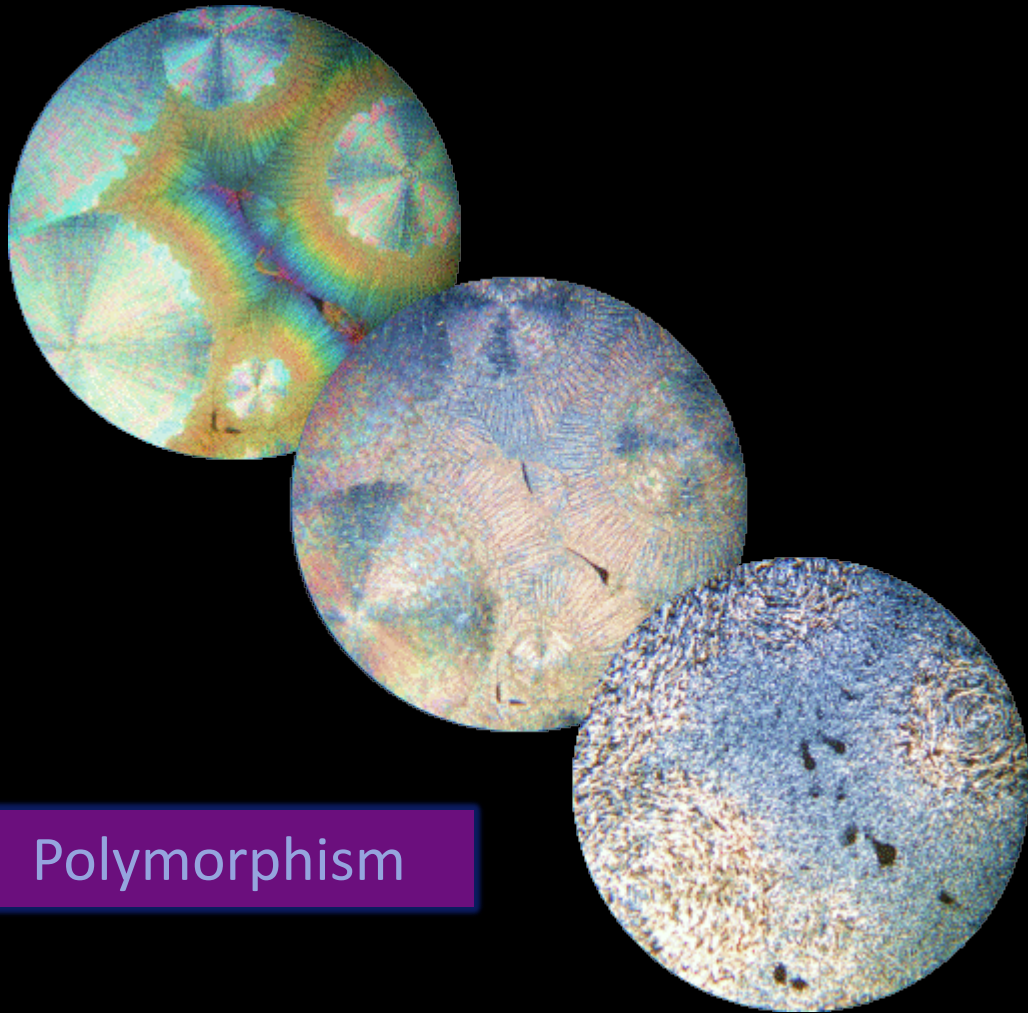
Polymorphism: is detectable for the mixture $x_{\text{dibutyl}} = 0.20$ and for other mixtures.

Polymorphism occurs always at the **same T** without compromising the solid-liquid phase transition

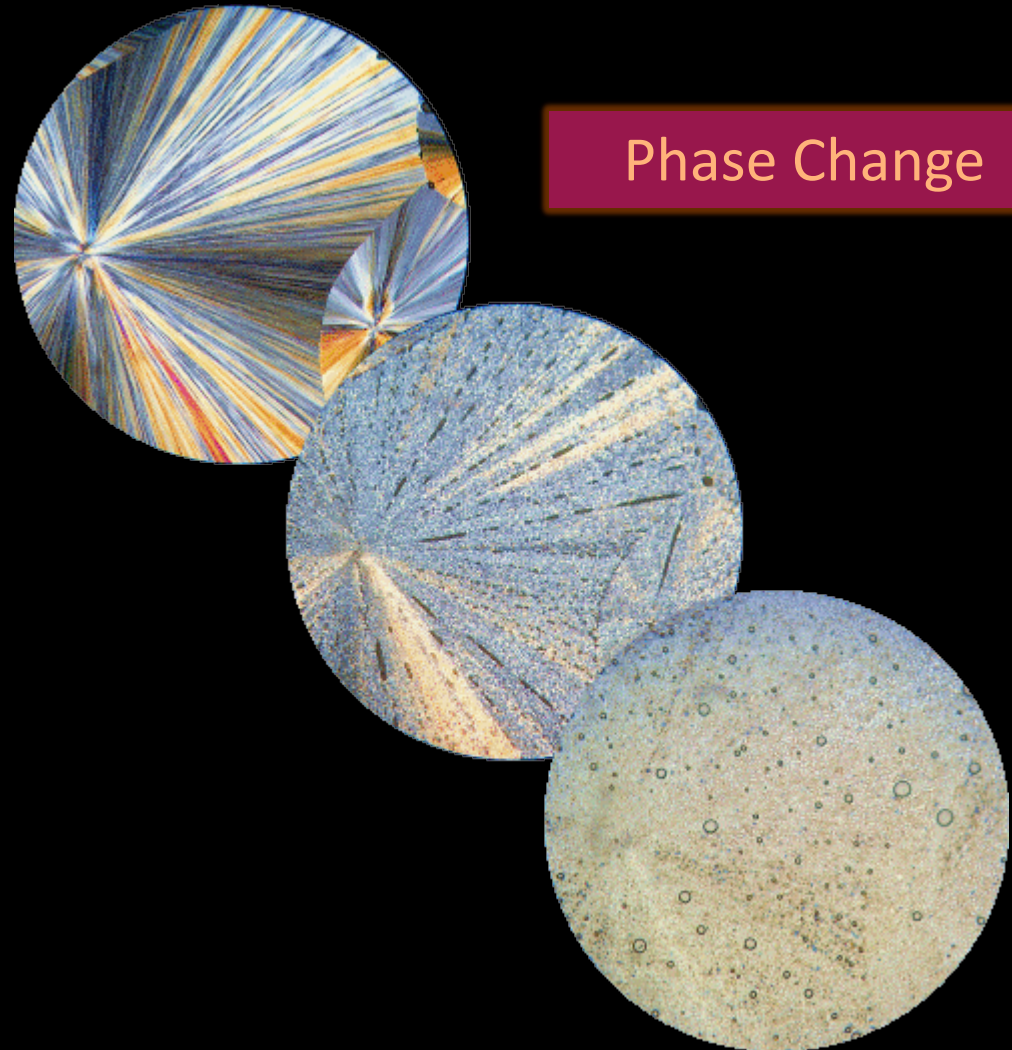
Fig. 1 – DSC heating curves of pure diethyl, dibutyl, and of selected binary mixtures, with dibutyl molar fraction x_{dibutyl} .



Hot Stage Microscopy



Polymorphism



Phase Change



Raman Spectroscopy

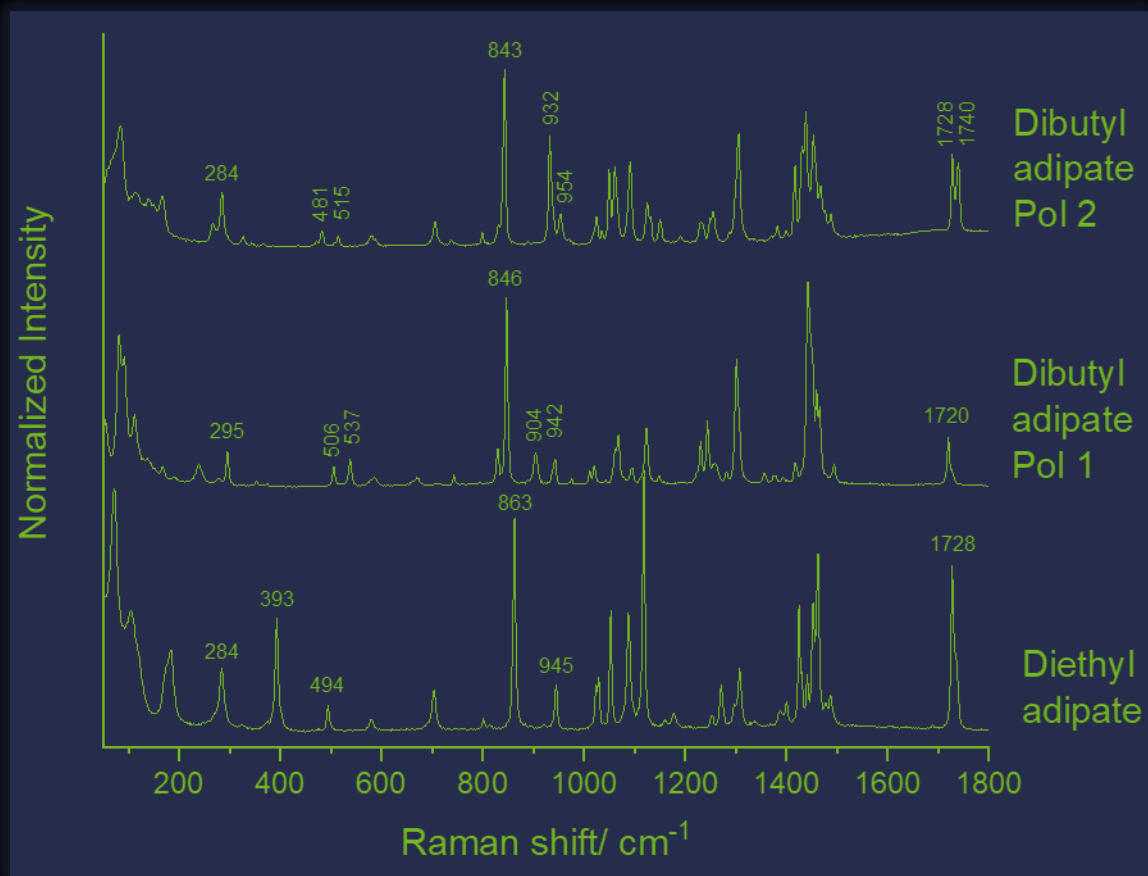


Fig. 2 – Raman spectra of the solid-state pure diethyl adipate and dibutyl adipate samples.

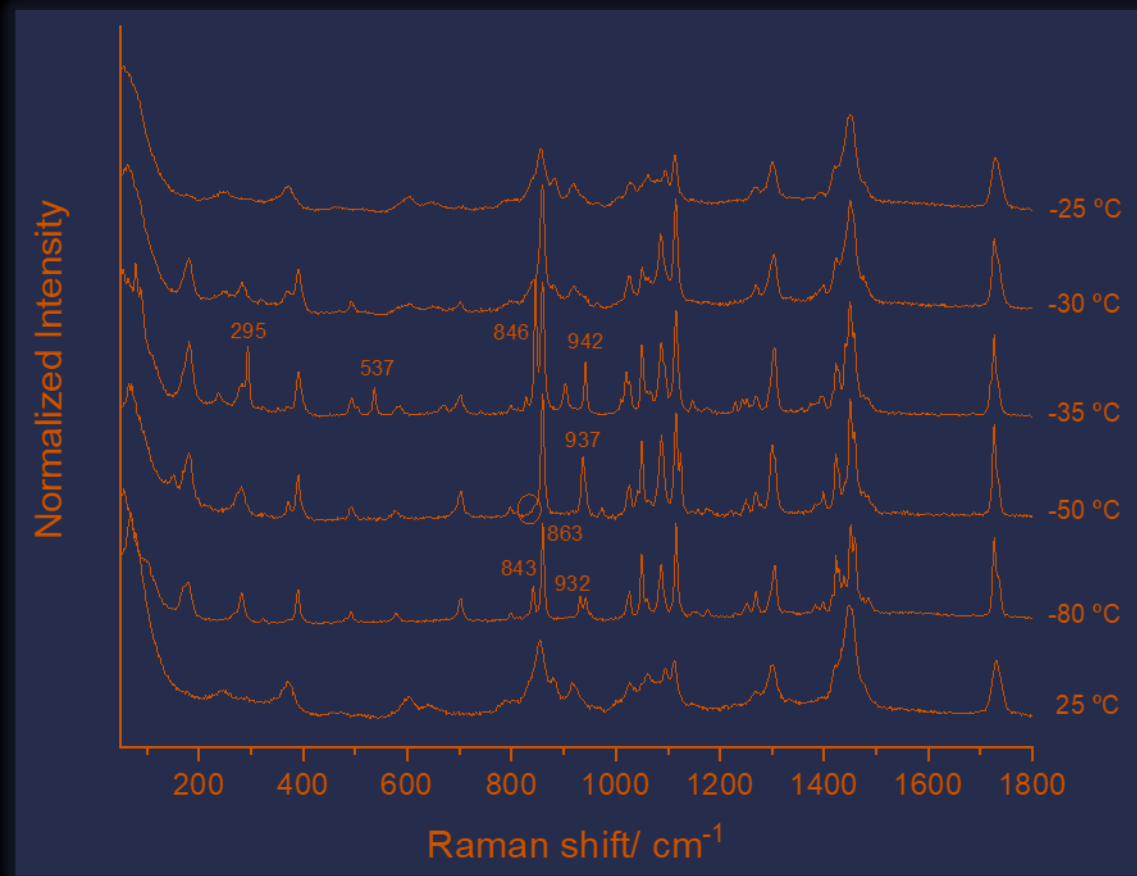
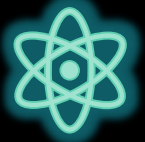


Fig. 3 – Temperature-variation Raman spectra the 80:20 diethyl adipate:dibutyl adipate mixture sample.



Binary Phase Diagram

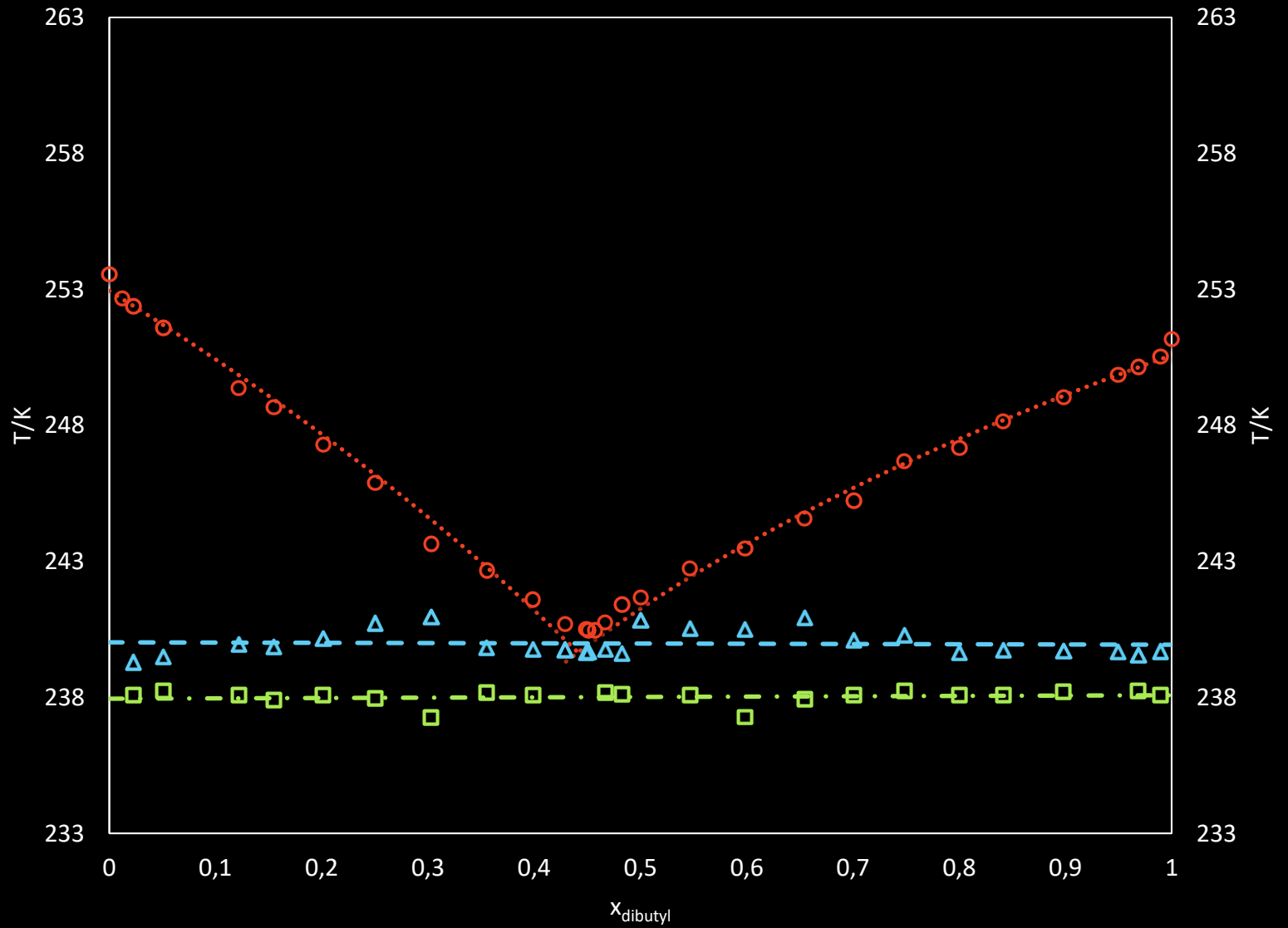


Fig. 4 – Binary solid-liquid phase diagram of the system of diethyl and dibutyl adipates.

Binary Phase Diagram
obtained with 30 mixtures
and 2 pure compounds

1 Liquid zone
2 Biphasic zones
2 Solid zones (because of
the polymorphism)

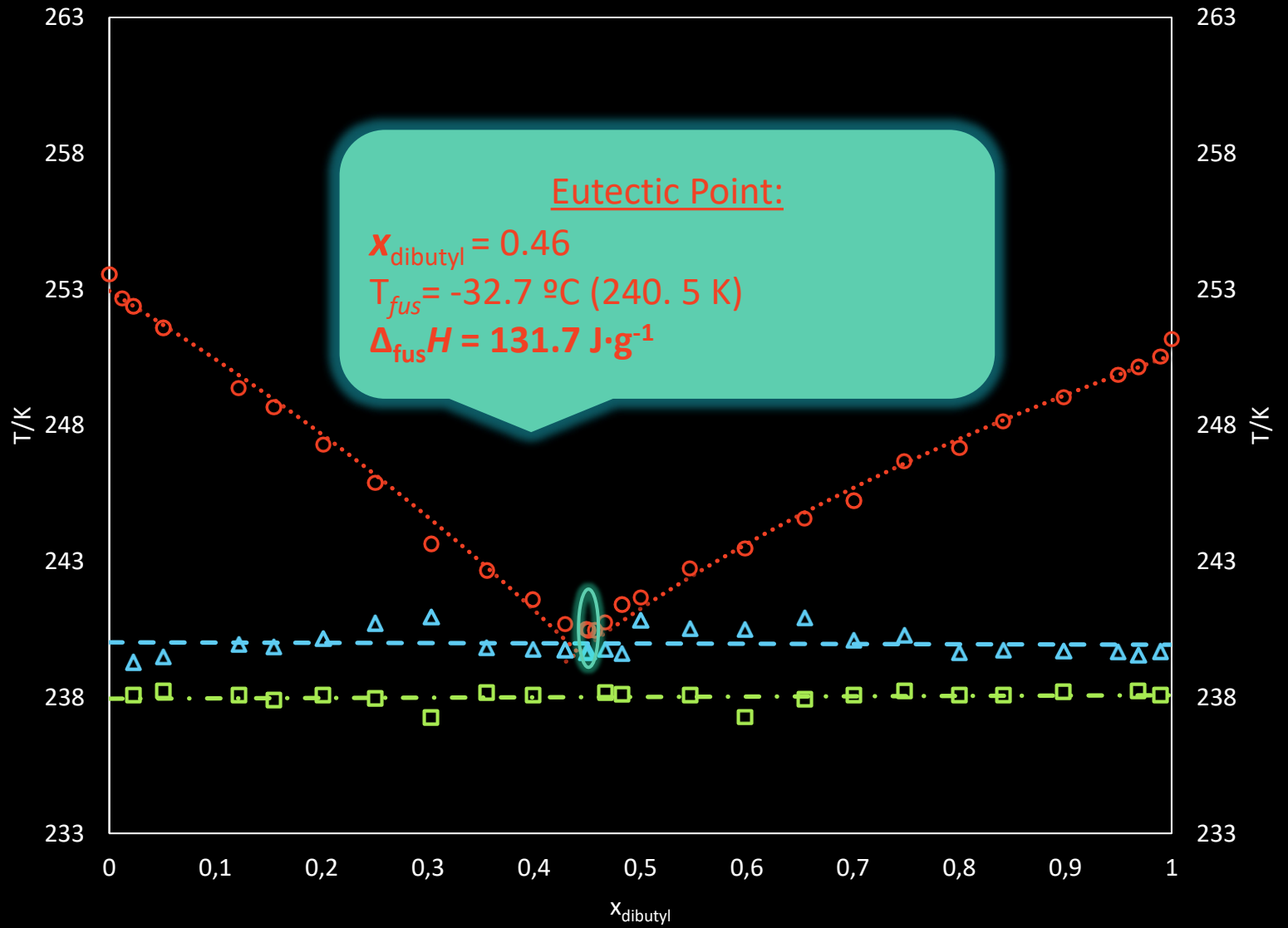


Fig. 4 – Binary solid-liquid phase diagram of the system of diethyl and dibutyl adipates.

Freezing-point depression curve¹

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

Characterize the *liquidus* line of a solid-liquid binary phase diagram

Fitted Eutectic Point:

$$x_{\text{dibutyl}} = 0.44$$

$$T_{\text{fus}} = -33.4 \text{ }^{\circ}\text{C} \text{ (239.8 K)}$$

-- 0.54 °C abs. Deviation --

(Max. Abs. Deviation ±1.5 °C)

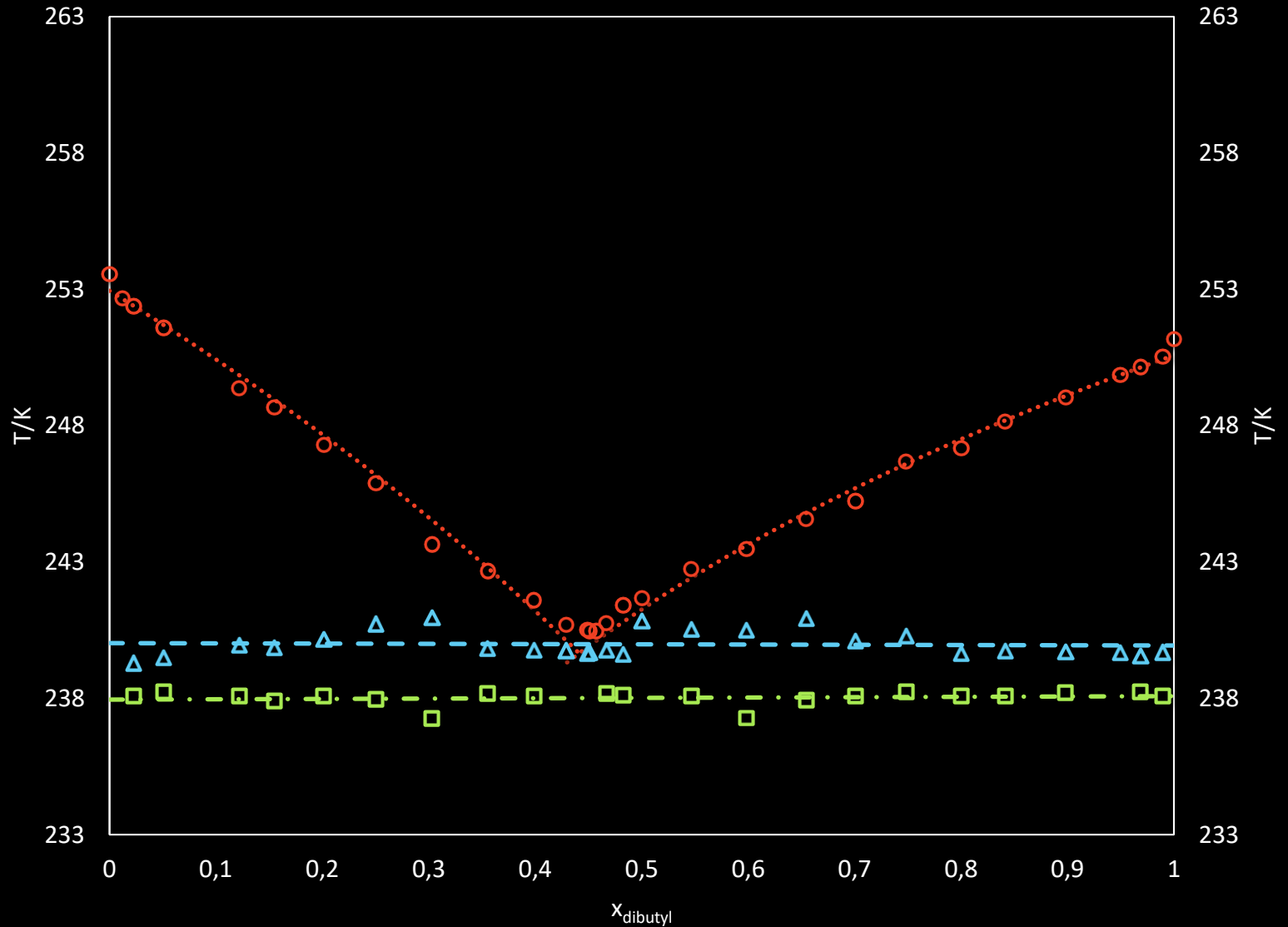


Fig. 4 – Binary solid-liquid phase diagram of the system of diethyl and dibutyl adipates.

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

5. Conclusions

Binary System of two di-*n*-alkyl adipates: Diethyl and Dibutyl

Construction of the Solid-Liquid Binary Phase Diagram

Eutectic Behaviour for Low Temperatures

Eutectic Point: $x_{\text{dibutyl}} = 0.46$; $T_{\text{max}} = -32.7 \text{ }^\circ\text{C}$ (240.5 K); $\Delta_{\text{fus}}H = 131.7 \text{ J}\cdot\text{g}^{-1}$

Good Candidate for Low Temperature Energy Storage Applications

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.

M.C.M. Sequeira acknowledges the PhD grant funded by FCT ref. UI/BD/152239/2021.

