Revisiting odd-even effects in *n*- alkane systems

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Overview

n-Alkanes have been widely studied for different applications. Recently, they became even more popular due to their characteristics as Phase Change Materials (PCMs) for Thermal Energy Storage (TES) applications. At the same time, they have been showing intriguing odd-even effects for some thermophysical properties.

This work aims to contribute to a comprehensive view on the predictability of their main solid-liquid phase equilibria characteristics, which is crucial for TES applications.

Our Research

We are focused on new binary systems that can be used as PCMs for TES applications at very low temperatures. Why? For cold storage and transportation of perishable consumables, like vaccines, which is a major logistics challenge for companies that handle this type of goods to minimize the environmental impact of these activities. However, there is still a huge lack of available data for materials that can answer to these challenges.

Our work aims to meet these needs, and, to that end, phase equilibrium studies have been carried out being a key to understand the performance and robustness of the materials as PCMs and also, their characterization with the determination of thermophysical properties. In this context, the present studies are important for the selection of adequate PCMs.

Literature Review

01 Pure *n*-alkanes present polymorphism with distinct characteristics depending on the even or odd number of carbons

02 It is possible to find specific characteristics in the S-L phase diagrams that allow typification based on the even or odd number of carbons for higher alkyl chains

03 For binary mixtures, the S-L phase equilibrium characteristics will depend on the match even/even; even/odd or odd/odd alkanes

H. A. J. Espeau, P., Roblès, L., Mondieig, D., Haget, Y., Cuevas-Diarte, M. A., Oonk, *J.Chim. Phys.*, 1996, 93, 1217-1238. doi: 10.1051/jcp/1996931217.
D. Mondieig, F. Rajabalee, V. Metivaud, H. A. J. Oonk, M. A. Cuevas-Diarte, *Chem. Mater.*, 2004, 16, 786-798. doi:10.1021/cm031169p.
S. N. Gunasekara, V. Martin, J. N. Chiu, *Renew. Sustain. Energy Rev.*, 2017, 73, 558-581. doi: 10.1016/j.rser.2017.01.108

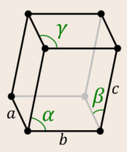
Finding the Differences

n – Alkanes, in general, present polymorphism, which means they have multiple crystal structures. Depending on the odd or even number of carbons in the alkyl chain there is a pattern to the type of polymorphismfound. Let's take a closer look to this!

There are two main solid structures that are adopted by *n*-alkanes which are:

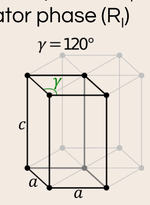
Triclinic Structure (T)

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

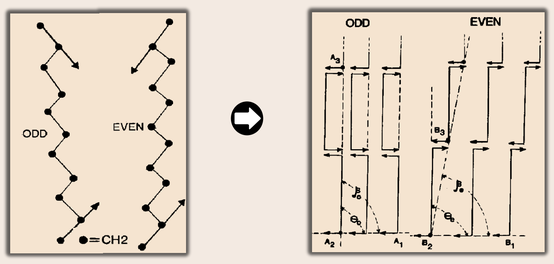


Ortorrombic Structure (O)

- Ordered phase (O_i)
- Rotator phase (R_i)



And why the difference in only one carbon atom can change everything? What is causing these odd-even effects on *n*-alkanes? The answer is quite simple: because of the difference in the odd or even number of carbons, alkanes will have different packaging of the molecules in their crystalline structure.



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

Experimental Work

We already studied four different binary alkane systems: $C_8 – C_{10}$, $C_9 – C_{10}$, $C_9 – C_{11}$ and $C_{10} – C_{12}$ for TES applications at low temperatures. To study their phase equilibrium behavior, three different techniques are used:

01 **Differential Scanning Calorimetry (DSC)** to obtain the melting temperatures and enthalpies of fusion.

02 **Hot Stage Microscopy (HSM)** to visually corroborate the DSC results, mainly for polymorphism events.

03 **Raman Spectroscopy** to corroborate the DSC results both visually and qualitatively.

Afterwords, the construction of the solid-liquid binary phase diagram was possible, that allows understanding if the binary system is a good candidate as PCM. For TES applications there are two types of systems considered ideal PCMs which are the eutectic and congruent melting systems. These two types of diagrams describe a system that behaves ideally as a pure compound where the solid transforms directly into a liquid and vice versa.

Our systems revealed the same tendency found in the literature for higher alkyl chains, which can be very helpful in the future for further studies, since it is possible to predict in some way the phase equilibrium properties of these binary systems. ¾ systems studied revealed ideal PCM behavior as they turned out to be eutectic and congruent melting systems.

Figs. 1, 2 and 3 show the binary phase diagrams of the systems with ideal PCM behavior. Fig. 4 shows the results for the system $C_9 – C_{10}$, which preliminary results evidenced a peritectic system. The latest situation, although is not an ideal PCM behavior, also in line with the literature indication, which once again boosted the predictability of the phase equilibria for these compounds.

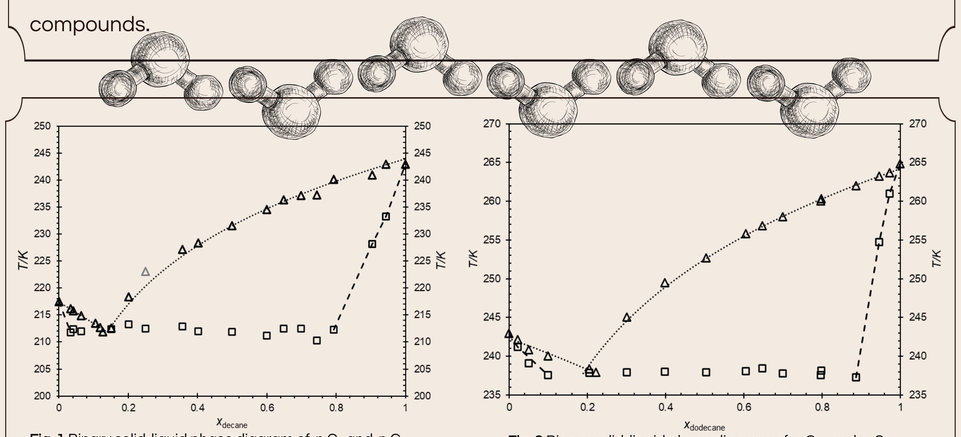


Fig. 1 Binary solid-liquid phase diagram of *n*-C_8 and *n*-C_{10}. doi:10.1007/s10765-023-03317-9.

Fig. 2 Binary solid-liquid phase diagram of *n*-C_{10} and *n*-C_{12}. doi:10.1007/s10765-023-03317-9.

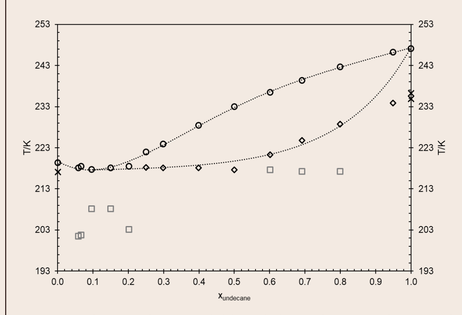


Fig. 3 Preliminary binary solid-liquid phase diagram of *n*-C_9 and *n*-C_{11}. Submitted for publication in *Int. Journal of Thermophysics*.

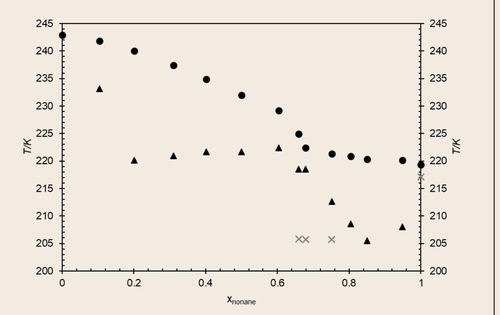


Fig. 4 Preliminary binary solid-liquid phase diagram of *n*-C_9 and *n*-C_{10}.

Conclusions

01 Even and Odd alkanes exhibit different packaging which results in different crystal structures inducing polymorphic diversity.

02 The solid-liquid equilibrium is specially affected by this behaviour. This feature seems predictable specially for lower alkyl chains.

03 These experimental results confirm this predictability and this issue is specially important to anticipate and understand which systems have potential to be used as PCMs.

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