Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supplementary Information**

# Alkane-based Eutectic Phase Change Materials Doped with Carbon Nanomaterials

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## FIGURES

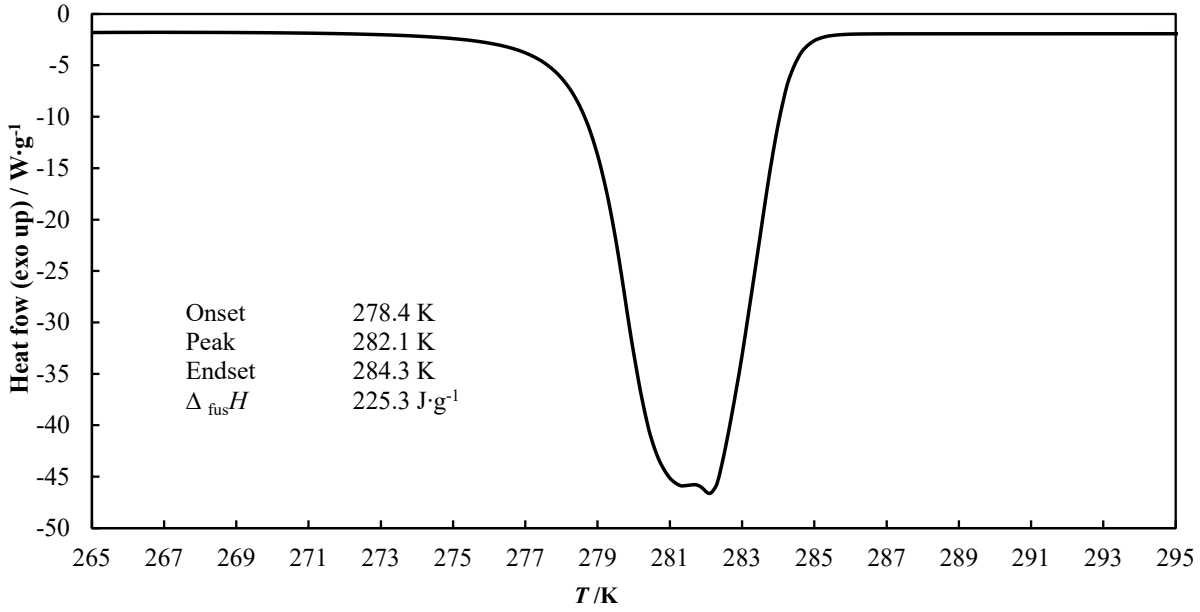



**Figure S1.** DSC of *n*-tetradecane, heating rate 5 K·min$^{-1}$.[1]

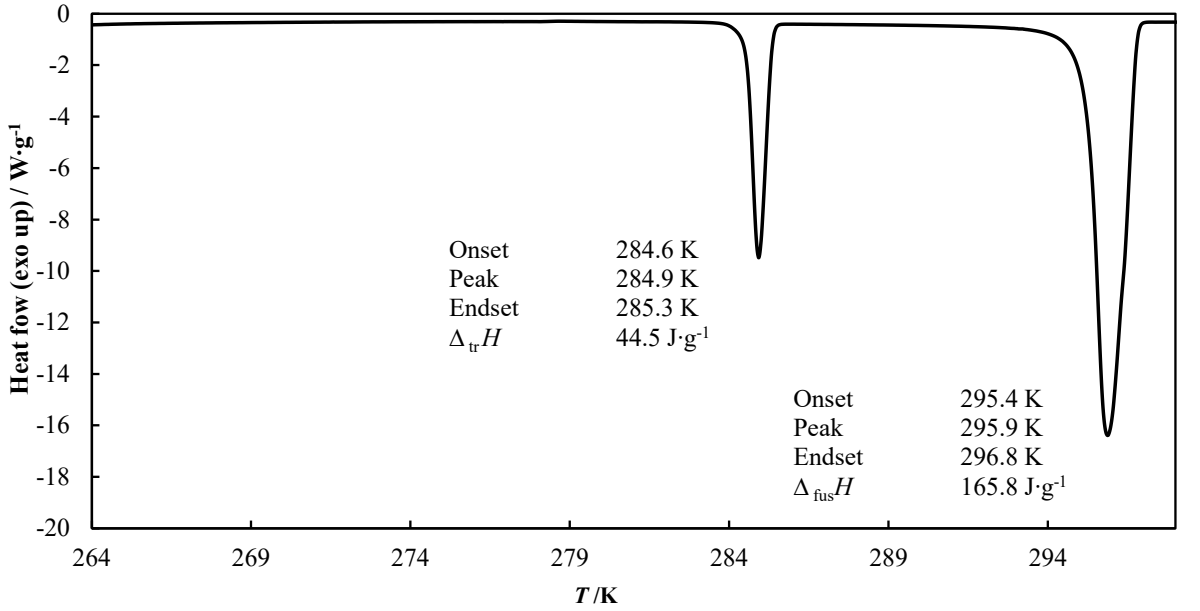



**Figure S2.** DSC of *n*-heptadecane, heating rate 2 K·min$^{-1}$.

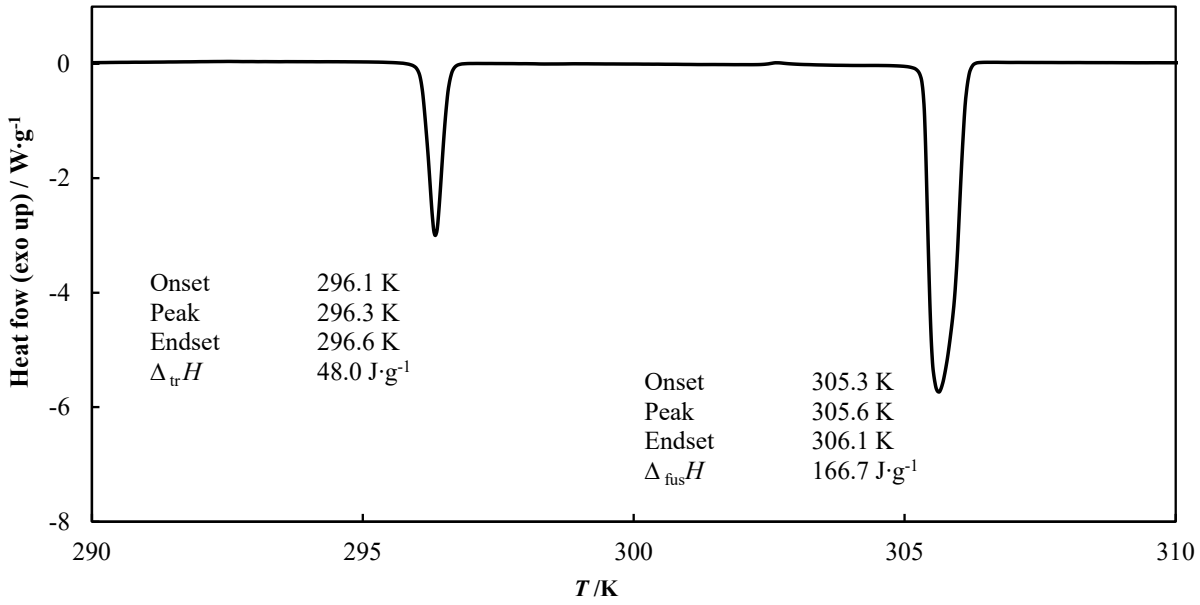



**Figure S3.** DSC of *n*-nonadecane, heating rate 2 K·min$^{-1}$.

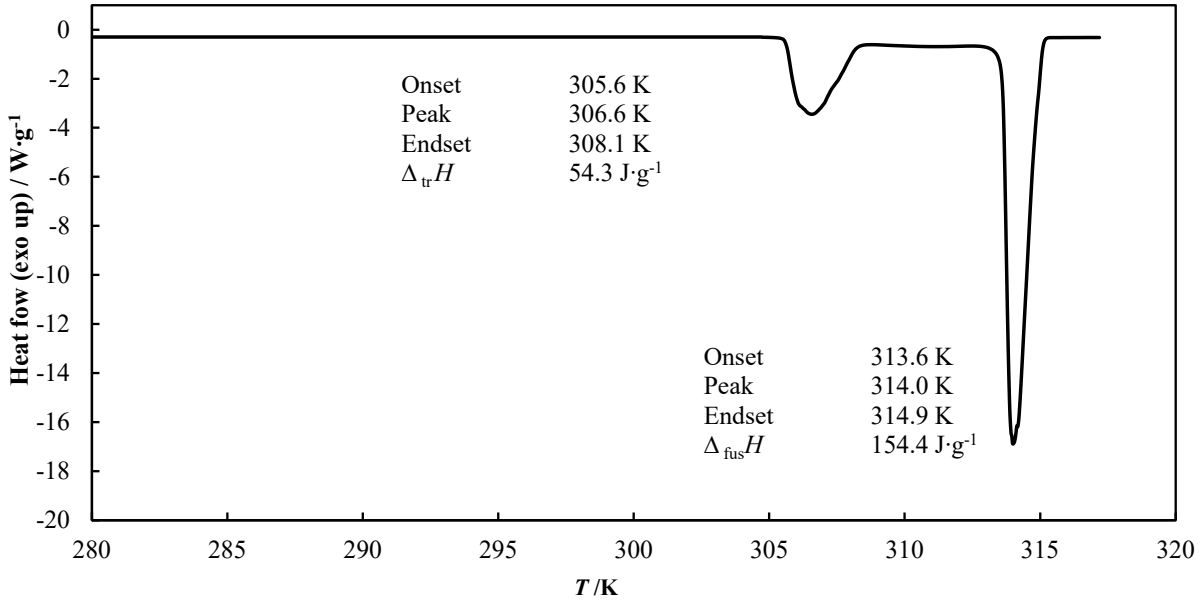



**Figure S4.** DSC of *n*-heneicosane, heating rate 2 K·min$^{-1}$.

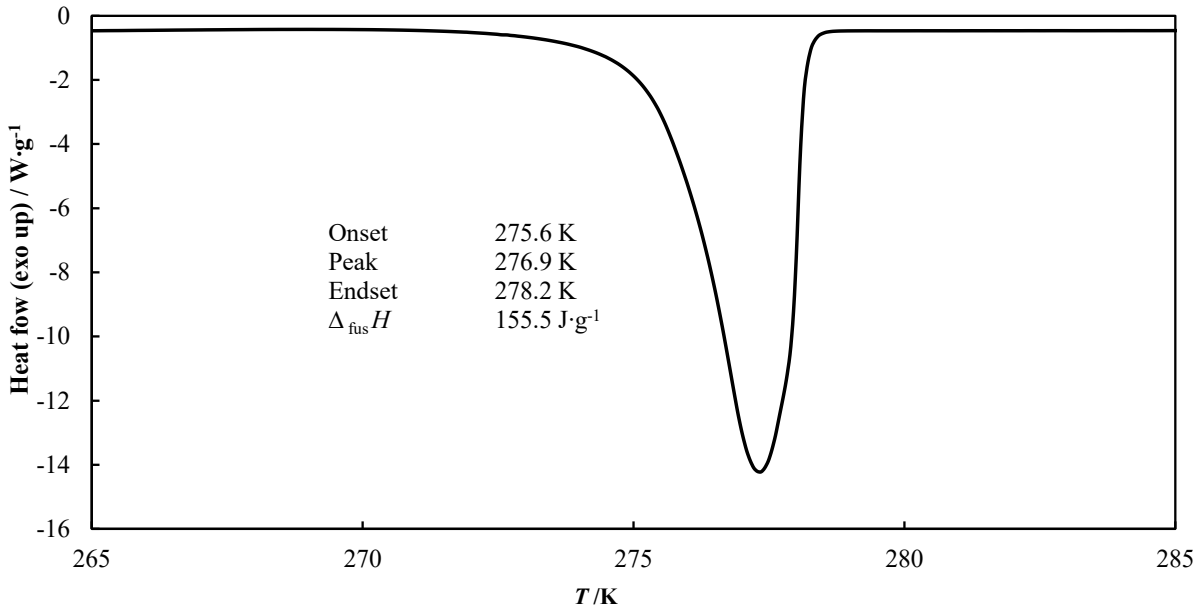



**Figure S5.** DSC of {*n*-tetradecane (1) + *n*-heptadecane (2)} eutectic mixture, $x_1$= 0.8149, heating rate 2 K·min$^{-1}$.

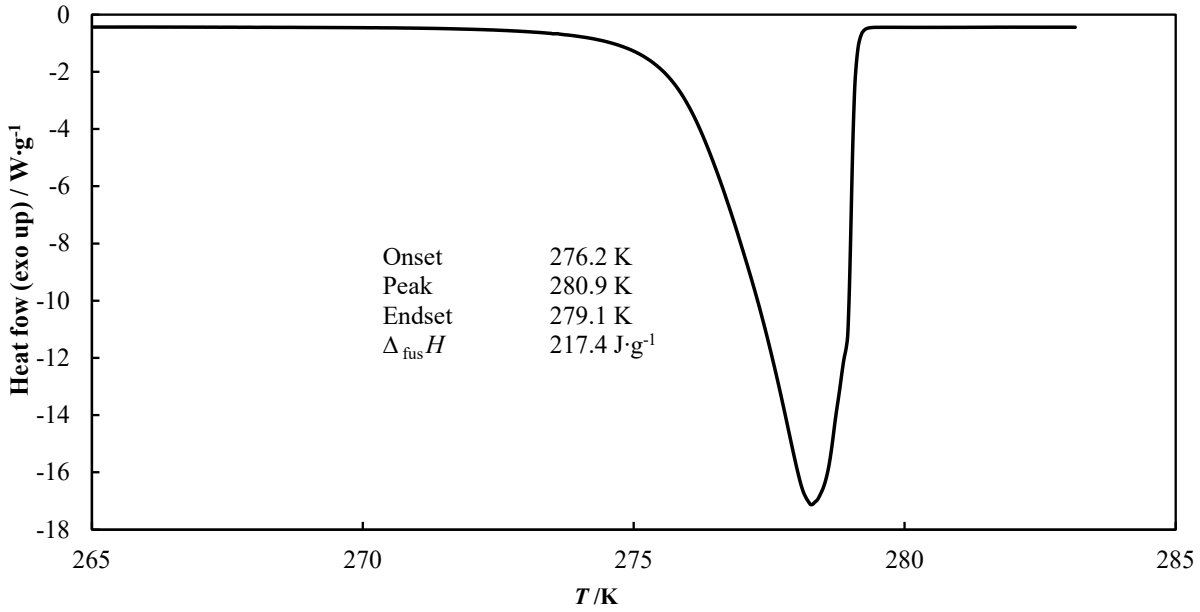



**Figure S6.** DSC of {*n*-tetradecane (1) + *n*-nonadecane (2)} eutectic mixture, $x_1$= 0.8963, heating rate 2 K·min$^{-1}$.

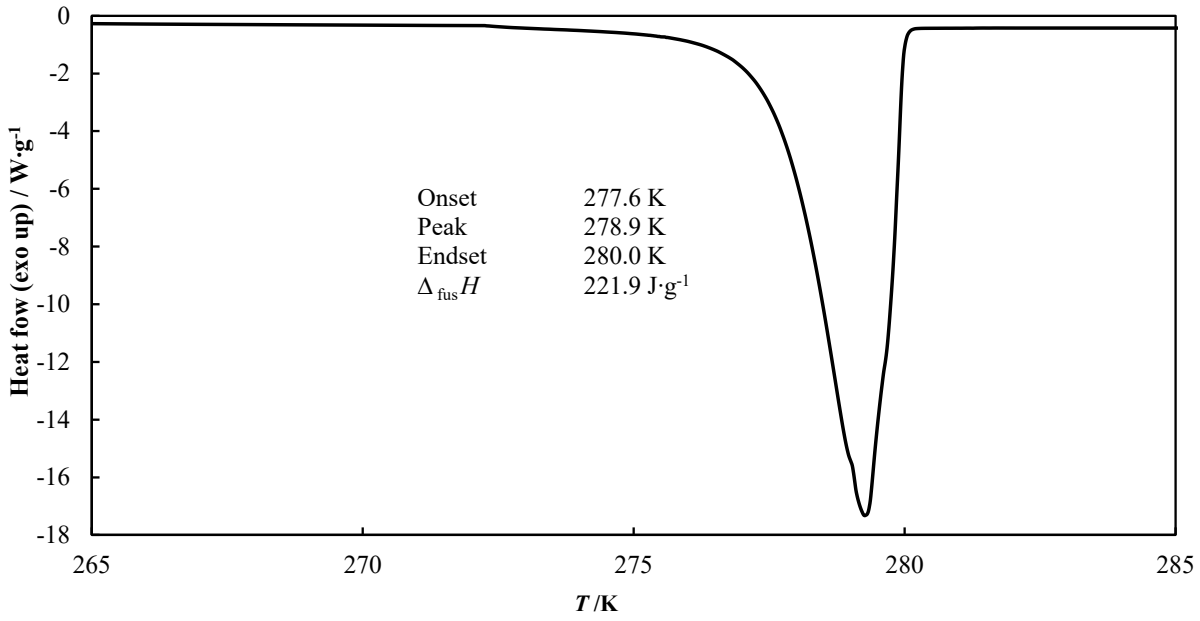



**Figure S7.** DSC of {*n*-tetradecane (1) + *n*-heneicosane (2)} eutectic mixture, $x_1$= 0.9574, heating rate 2 K·min$^{-1}$.

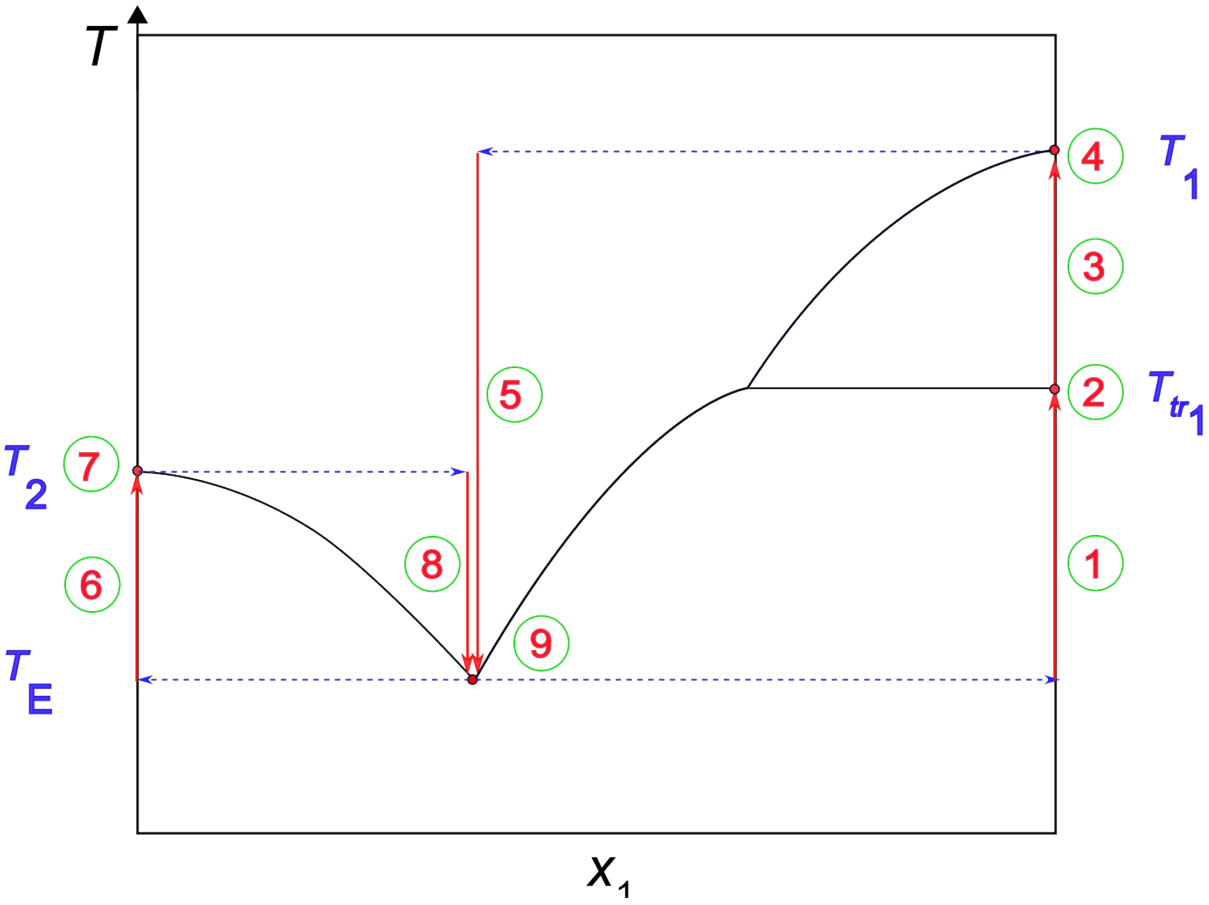
## TABLES

**Table S1.** List of UNIFAC (Do) subgroups and their group surfaces and volumes.[2]

| Subgroup | Main group No. | *R* | *Q* |
|---|---|---|---|
| CH3 | 1 | 0.6325 | 1.0608 |
| CH2 | 1 | 0.6325 | 0.7081 |

## CALCULATIONS

Eutectic mixture melting enthalpy balance in a simple eutectic system (with polymorphic transition A→B) based on the following thermodynamic cycle.




$$\Delta H_1 = x_1 \cdot \int_{T_E}^{T_{tr}1} C_{p\,1A}^{S} dT \qquad \Delta H_6 = x_2 \cdot \int_{T_E}^{T_2} C_{p\,2}^{S} dT \qquad (1), (2)$$

$$\Delta H_2 = x_1 \cdot \Delta_{tr} H_1 \qquad \Delta H_7 = x_2 \cdot \Delta_{fus} H_2 \qquad (3), (4)$$

$$\Delta H_3 = x_1 \cdot \int_{T_{tr\,1}}^{T_1} C_{p\,1B}^{S} dT \qquad \Delta H_8 = x_2 \cdot \int_{T_2}^{T_E} C_{p\,2}^{L} dT \qquad (5), (6)$$

$$\Delta H_4 = x_1 \cdot \Delta_{fus} H_1 \qquad \Delta H_9 = \Delta H^{mix} \qquad (7), (8)$$

$$\Delta H_5 = x_1 \cdot \int_{T_1}^{T_E} C_{p\,1}^{L} dT \qquad \Delta_{fus} H_E = \sum_{i=1}^{9} \Delta H_i \qquad (9), (10)$$

For the ideal system $\Delta H_9 = 0$, while taking into account the non-ideality of the system related to the interactions between the components, this value will correspond to the excess enthalpy of mixing, $\Delta H^E$. The requirement for the application of the above calculations is that the investigated compound pairs

form simple eutectic systems, i.e. systems in which no solid solutions are present. In the case of a phase transformation in a solid in the temperature range under study, the expression should be supplemented with the enthalpies of the polymorphic transition. Due to the negligible difference in the heat capacity of the two solid phases of the same compound, it is justified to omit this factor. Then the expression for the enthalpy of melting of the eutectic will take the form:

$$\Delta_{fus} H_E = \sum_{i=1} x_i \left[ \Delta_{fus} H_i + \Delta_{tr} H_i + \left( C_{p\,i}^{L} - C_{p\,i}^{S} \right) \cdot \left( T_E - T_{fus\,i} \right) \right] + \Delta H^E$$

## REFERENCES


(1) Więckowski, M.; Królikowski, M. Designing and Characterization of Low-Temperature Eutectic Phase Change Materials Based on Alkanes. *J. Chem. Eng. Data* **2022**. https://doi.org/10.1021/acs.jced.1c00783.

(2) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178–193.