

INTRODUCTION

Scanning calorimetric techniques allow to obtain continuously the evolution of the heat capacity at constant pressure $C_p(T)$ in terms of the power P and the rate dT/dt .

$$C_p = \frac{dQ}{dT} = \frac{dQ/dt}{dT/dt} = \frac{P}{\dot{T}}$$

In an Adiabatic Scanning Calorimeter (ASC) a constant power P is supplied to the sample and the resulting change in temperature $T(t)$ is measured as a function of time from which the rate dT/dt can be calculated. Combining the rate with the constant power results in $C_p(T)$. Moreover, the enthalpy $H(T)$ is easily obtained from the product of the power P and the time laps between the start of the run at t_0 and the time at which $T(t)$ was reached.

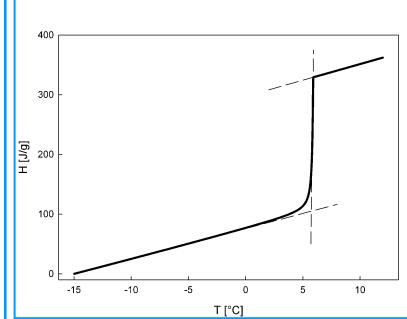
$$H(T) = P[t(T) - t(T_0)]$$

Enthalpy and storage capacity of C14

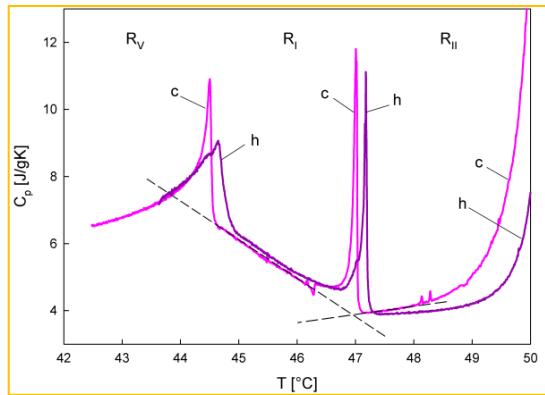
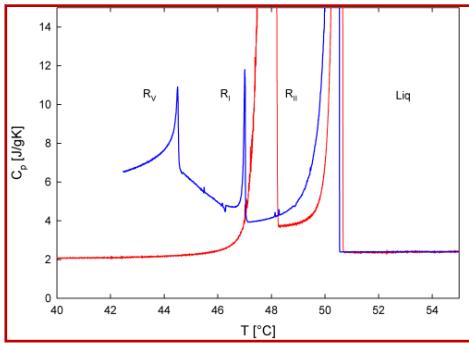
The development of devices that rely on the storage of heat in the phase transitions of phase change materials (PCMs) requires an accurate knowledge of this thermal storage capacity. The quantity of choice to express this storage capacity is the enthalpy, which expresses how much heat an amount of material can store over a given temperature interval. Most PCMs use the large latent heat of a strongly first-order transition, generally the melting/crystallization transition.

C14 melts below 5.95 °C. In the upper figure, the $H(T)$ curve shows a large step at this transition, equivalent to the total heat needed to heat up through the transition and to make the phase conversion, the latter is the latent heat. The total transition heat ΔH is the increase in enthalpy from about 0 °C to 5.95 °C. The latent heat corresponds to the length of the vertical dashed line covered by the $H(T)$ curve. The value for ΔH , 223 ± 2 J/g, corresponds with DSC-determined values (227 J/g [1]), the value for the latent heat, which cannot be separated from the total transition heat with DSC, is 177 ± 13 J/g.

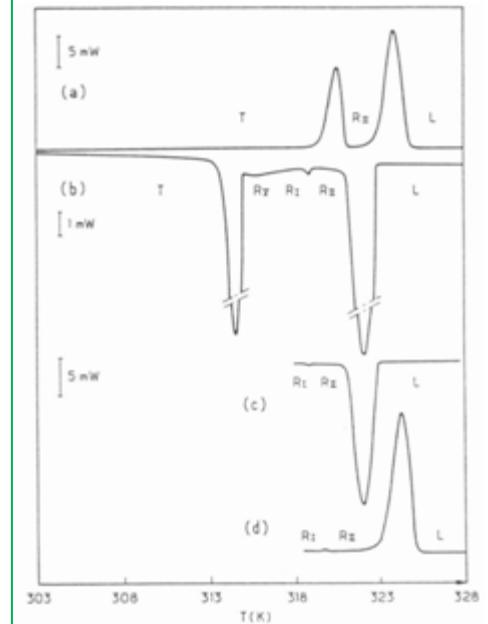
The results are from a 99.5% pure tetradecane sample obtained from Sigma-Aldrich. 66.56 mg C14 was contained in a standard DSC cell and measured with an ASC. Average scanning rate was 6.7 mK/min.



C24 has apart from crystal and liquid phases also several intermediate rotator phases. The figure clearly shows how in a heating run (red) only the R_{II} phase shows up, while in cooling (blue) three rotator phases are detected.



Results from corresponding DSC experiments. (a) and (b). The qualitative phase behaviour is the same as in ASC, but the transitions are severely shifted between heating and cooling, an artificial hysteresis as seen from comparison with the ASC results. All transition peaks are rounded, especially the rotator-to-rotator transitions in the cooling experiments. (c) and (d) Cooling immediately followed by heating from the R_I phase. Again the results from the ASC experiment are qualitatively reproduced, by DSC but the shifts in transition temperature and rounding are enlarged.



The high temperature resolution of ASC is demonstrated by the detection of the transition temperature hysteresis between the cooling and heating runs on the rotator transitions. At the low ASC scanning rates, this is the genuine effect and not a consequence of the operation principle or high scanning rates.

A sample of C24 was cooled (red) down from the liquid phase until the supercooled R_V rotator phase was reached. At 42 °C, a heating run (purple) was started. The figure clearly shows how there is a difference of about 0.2 °C between the rotator transitions in the heating and cooling runs, and a larger difference for the rotator to liquid transition, which is not completely displayed.

The small spikes are the consequence of transitions in small surface layers of the alkane that interact with the walls of measurement cell.

The results are from a 99.9% pure tetracosane sample obtained from Sigma-Aldrich. 59.19 mg C24 was contained in a standard DSC cell and measured with an ASC. Average scanning rate was about 1 K/min both for cooling and heating.

REFERENCES

- [1] Dirand, M., Bouroukba, M., Briard, A.-J., Chevallier, V., Petitjean, D., & Corriou, J.-P. (2002). Temperatures and enthalpies of (solid plus solid) and (solid plus liquid) transitions of n-alkanes. Journal of Chemical Thermodynamics, 34(8), 1255–1277.
- [2] Robles, L., Mondieig, D., Haget, Y., & Cuevas-Diarte, M. A. (1998). Review on the energetic and crystallographic behaviour of n-alkanes. II. Series from $C_{22}H_{46}$ to $C_{27}H_{56}$. Journal De Chimie Physique Et De Physico-Chimie Biologique, 95(1), 92–111. In French..