

Transitions of *n*-Alkanes Above the Melting Point

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Summary

The specific heat capacity of a series of *n*-alkanes was measured in a powercompensated differential scanning Calorimeter with high resolution. Above the melting point the specific heat capacity increases strictly linear with temperature until 430 K. In this region no transition of first, second or third order could be found. Between 450 and 480 K the *n*-alkanes show an exothermic effect bound to the first run with hermetically sealed sample pans. It is assumed that this effect is a pressure induced epitactic ordering phenomenon correlative to the surface of the sample pan.

Introduction

Pietralla and Krüger (1980) showed evidence for a molecular weight dependent transition in the liquid phase of *n*-alkanes, concluded from measurements of Brillouin scattering and viscosity. This gave us the idea to study the thermal behavior of *n*-alkane-melts (especially *n*-Tetracosane which should have a transition at 380 K) in a scanning calorimeter. No effect was found in the interesting temperature region, though the resolution of the calorimeter was driven to 0,2 J/g. In the meantime Denny and Boyer (1981) presented results of DSC-measurements on *n*-alkanes. For low *n*-alkanes they found an endothermic slope change and interpreted it as a transition (of third order). This incited us to measure the variation with temperature of the specific heat capacity of liquid *n*-alkanes with a precision as high as possible.

Experimental

Samples (3 to 5 mg) of very pure *n*-alkanes (GC controlled) in hermetically sealed pans were run in a powercompensated differential Scanning Calorimeter (Perkin - Elmer DSC-2). The heating rate was 10 K/min. The output of the calorimeter was coupled to a computer which was able to store both the baseline (of empty pans) and the heating curve of the sample and to compute the difference between this two runs and the specific heat capacity of the sample. Furthermore the computer allowed to average the results of several runs and to plot them at any given scale. Since the interface between the calorimeter and the computer was able to translate 6 decimal digits with a resolution of 10^{-4} times the adjusted calorime-

tric sensitivity, it was not necessary to change the sensitivity during the run, but we could record all with high sensitivity. Because of the difference in the results between the first and other runs only first runs of different samples were averaged. We also tried to repeat measurements of Denny and Boyer with open sample pans, but a slight covering of alkane in the cold surroundings of the sample holder indicated a partial vaporization of the sample. The heat of vaporization belonging to this process is part of the heat flow measured and should falsify the heat capacity measurements. Therefore we used hermetically closed sample pans taking into the bargain the different thermodynamic conditions (constant volume instead for constant pressure).

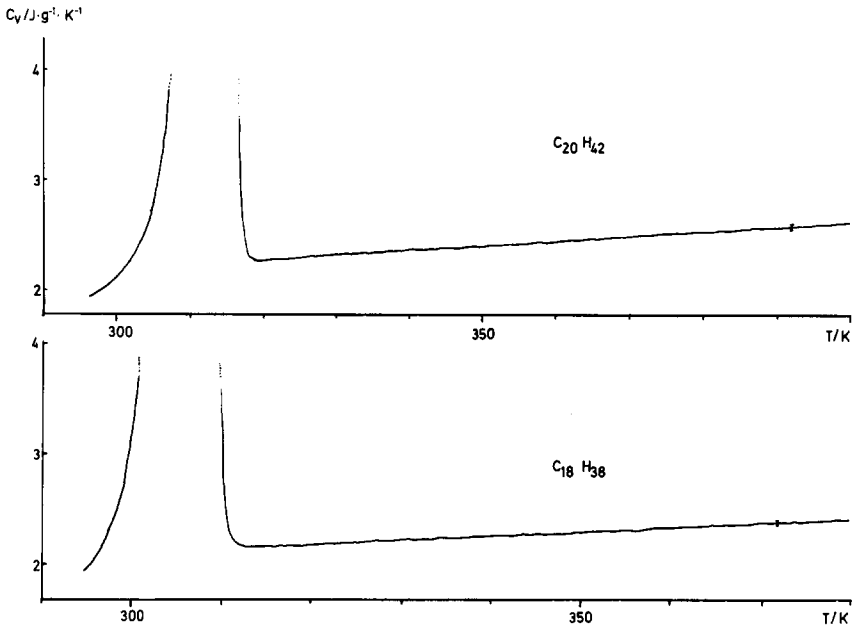


Figure 1: Specific heat capacity of n-Octadecane and n-Docosane

Results

The lower n-alkanes measured show a very linear increase of specific heat capacity (c_v) with temperature. No endothermic peak (1. order transition) nor any endothermic step change (2. order transition) nor any endothermic slope change (3.

order transition) in specific heat capacity could be found in the interesting temperature region 300 to 500 K. Figure 1 for example shows the results of the specific heat measurements for n-Octadecane ($C_{18}H_{38}$) and n-Docosane ($C_{22}H_{46}$). Both measurements are averaged of three samples each. By this procedure the thermal noise is reduced and the fluctuations of the measurement curve are lower than 0.02 J/gK . The reproducibility and relative accuracy is about ± 0.03 , the absolute accuracy of the c_v value is about 5% or $\pm 0.1 \text{ J/gK}$. The deviation from linear increase is lower than 0.05 J/gK per 100 K . The heat capacities of the other measured n-alkanes are written in table 1.

Figure 2 shows the averaged results of measurements on n-Tetracosane ($C_{24}H_{50}$) in a hermetically sealed or in an open sample pan. For the case of open pans the endothermic slope change is explicable by the heat of vaporization of about 0.1 mg Tetracosane which was found on the cold surroundings of the sample holder after each run. (The area of the rectangle in fig. 2 represents this heat).

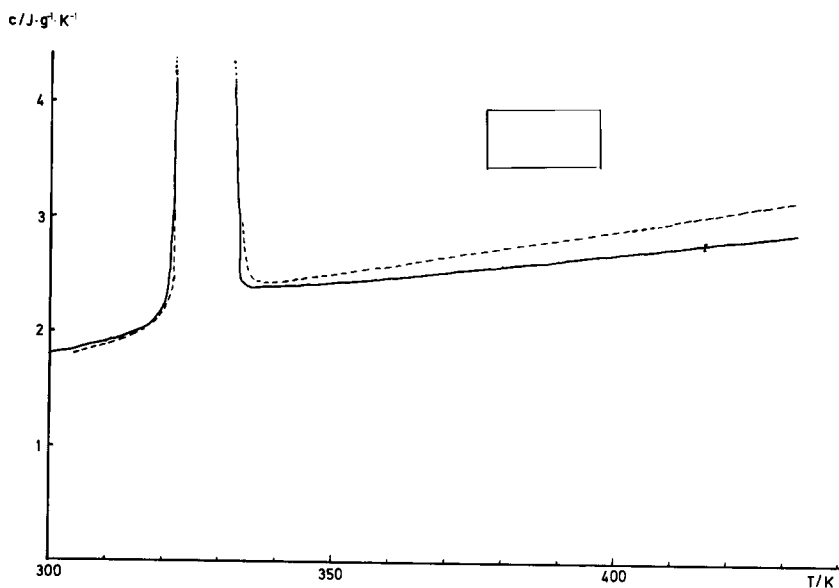


Figure 2: Specific heat capacity of n-Tetracosane in a hermetically sealed pan (—) and in a open pan (---). The area represents the heat of vaporization of 0.1 mg of substance.

TABLE

n-alkane	$c_v / J g^{-1} K^{-1}$ at a temperature of									
	300 K	325 K	350 K	375 K	400 K	425 K	450 K	475 K	500 K	
$C_{18}H_{38}$	-	2.20	2.29	2.38						
$C_{20}H_{42}$	-	2.32	2.41	2.52	2.66					
$C_{22}H_{46}$	1.48	1.84	1.86	1.91	2.00	2.09	2.20	2.31	2.44	
$C_{24}H_{50}$	1.75	-	2.33	2.43	2.53	2.64				± 0.07
$C_{30}H_{62}$	1.30	-	1.95	1.97	2.02	2.10	2.20			
$C_{32}H_{66}$	1.77	-	2.20	2.25	2.27	2.33	2.44	2.50		
$C_{36}H_{74}$	1.64	2.05	-	2.31	2.38	2.45	2.53	2.61	2.73	

At higher temperatures all n-alkanes showed an exothermic effect (of about - 10 to - 30 J/g at 450 to 480 K) for the case of first runs in closed sample pans (see fig. 3). Neither the use of open pans at various pressure nor other than first runs gave similar results. n-Dotriacontane has a particular acute effect which looks like an exothermic transition, hence we especially were engaged in this alkane. We realized the effect being connected to the size of the surface but not the material of the sample pan.

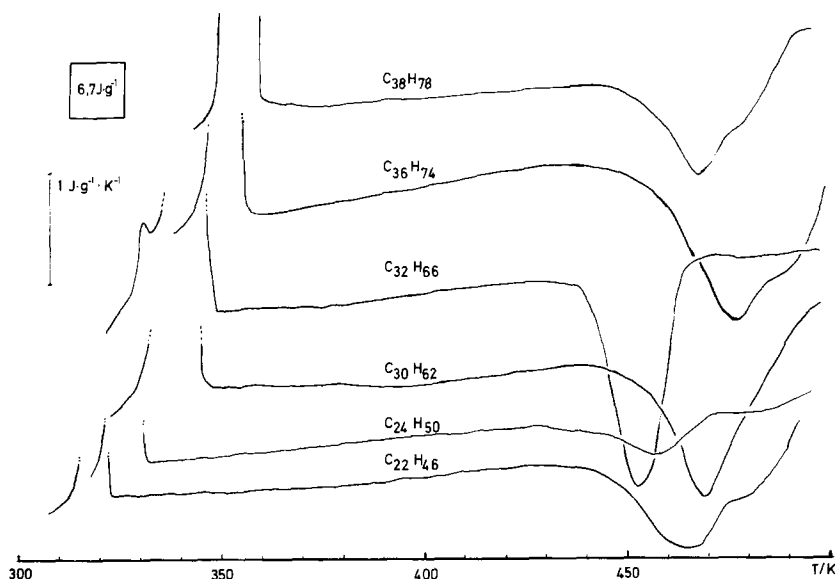


Figure 3: Normalized heating curves (1. run) of various n-alkanes in hermetically closed pans

Large area pans gave an increasing effect but aluminium steel of tefloncovered pans with equal area gave the same results. A very little hole in the top of the tight sample pan completely prevents the effect.

We tried to produce the effect once more in samples which had been run already and succeeded by putting the sample (with the pan) in liquid nitrogen one night. Another successful method was to open the pan and to scrape the sample into a new one and seal it up. Pulverizing the sample increases the exothermic effect.

Discussion

A transition in the liquid phase of n-alkanes discussed by Krüger et al. (1980) and Pietralla and Krüger (1980) based on their measurements of Brillouin scattering and of viscosity

could not be found in our measurements. The temperature dependence of the specific heat capacity c_V is fully normal in the named temperature region. A *thermodynamic phase transition* of first, second or third order is accompanied by a peak, a step or a slope change in specific heat capacity, which can be, however, very weak. Indications to such a transition of liquid n-alkanes found by Denny and Boyer (1981) during the first runs in open sample pans may be explained by the slope change caused by the beginning of vaporization of the alkanes (which is temperature dependent) or by the change of the heat conductivity of the alkanes, or both. From the Brillouin measurements of Krüger et al. (1980) resulting in a slope change of sound velocity and attenuation as well as a step change of the Grüneisen-parameter one can conclude that there should occur a step change, at least a slope change of thermal conductivity at the named temperatures. (Pietralla, private communication). This effect often causes a step of slope change in DSC curves from calorimeters of heat-flux type like du Pont 990-910 used by Denny and Boyer (1981). A power compensated scanning calorimeter which we used is not sensitive to changes in heat conductivity.

The exothermal effect found at 450 to 480 K is corresponding with a decrease of entropy, therefore the liquid alkane must change from lower to higher order. We suppose that the n-alkane is building a well ordered layer at the surface of the sample pan. This gives an advantage in volume and the system makes way for the increasing pressure in the closed pan. This interpretation explains the behaviour of the n-alkanes relative to the exothermic effect named above. If this interpretation is right, the heat of melting at constant pressure should decrease with increasing pressure. First measurements show this behaviour, we intend to report the results in another paper.

In spite of the fact that there so called T_U -temperatures can well be detected and reproduced by various experimental methods including NMR-measurements of T_1 (Krüger et al. 1981), a calorimetric effect at these temperatures remains questionable since it must be detectable by any type of sensitive calorimeter.

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