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The low-temperature heat capacities, phase transitions and thermodynamic properties of 1,3-dimethyladamantane and 1-ethyladamantane

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Abstract

The heat capacity of the crystalline and liquid phases of 1,3-dimethyladamantane (1,3-DMA) and 1-ethyladamantane (1-EA) have been measured by vacuum adiabatic calorimetry over the temperature range (8 to 373) K. 1,3-DMA and 1-EA were found to exist in two and one crystalline phases, respectively. The temperatures, enthalpies and entropies of solid-to-solid transition and fusions have been determined. The $\Delta_{fus}S$ is less than the gas constant for 1,3-dimethyladamantane, indicates that this compound, as well as 1,3,5-trimethyladamantane (1,3,5-TMA) studied previously, forms a plastic crystalline phase before being fused. The temperature dependencies of the lattice modes were determined with Raman spectroscopy for all three substances. The thermodynamic functions obtained calorimetrically for 1,3-DMA, 1-EA and 1,3,5-TMA were corroborated through adequate accord between the calorimetric and spectroscopically determined entropy.

Keywords: Calorimetry; Ramans spectroscopy; Heat capacity; Thermodynamic functions

1. Introduction

1,3-Dimethyladamantane{1,3-dimethyltricyclo(3,3,1,1^{3,7})-decane} and 1-ethyladamantane {1-ethyltricyclo(3,3,1,1^{3,7})-decane} are saturated tricyclic hydrocarbons with two methyl and one ethyl groups joined to the tertiary carbon atoms, respectively. Adamantane and some of its derivatives [1–4] form disordered, so-called plastic crystalline phases. The fusion of such substances occurs in two stages. First, an orientational disorder proceeds in the crystalline lattice, and then the plastic crystals fuse owing to a translational molecular motion at higher temperature. In this case, the magnitudes of enthalpy and entropy of the solid-to-solid transition are several times larger than those of fusion. In accordance with Timmerman's empirical criterion [5], the $\Delta_{fus}S$ for the plastic crystals are usually less than 20 $J \cdot mol^{-1} \cdot K^{-1}$. There are two modifications of the plastic crystals with different molecular reorientations, isotropic and anisotropic [6]. Some substances are known to form both of them [7,8]. The nature of the molecular mobility in the plastic crystals can be revealed by probing the low-frequency modes in crystals with Raman spectroscopy [7].

In reference [9], the order–disorder transition and fusion properties of the nine 1-halogenadamantanes and methyladamantanes, including 1,3-DMA and 1,3,5-TMA, were investigated by differential scanning calorimetry (d.s.c.). The results were used to define empirical relationships between the values of the entropy of

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transition and the temperature interval of the orientationally disordered phase, $(T_m - T_{tr})$, as well as between these quantities and the molecular shape. However, such relationships gave erroneous results for 1,3-DMA and 1,3,5-TMA, since the calculated values of $(T_m - T_{tr})$ were seven times larger than the experimental ones.

This paper reports a continuation of our work [1,10,11] that is devoted to the precise study of the thermodynamic of alkyladamantanes. In reference [10] the enthalpies of formation of 1,3-DMA, 1,3,5-TMA, and 1-EA at $T = 298.15$ K were determined by calorimetric measurements of the enthalpies of combustion. The thermodynamics of vaporization of 1,3-DMA and 1,3,5-TMA was studied in reference [11] by both experimental and calculation over a wide temperature range. Reference [1] reports our determination of the thermodynamic quantities of the solid-to-solid transition and fusion of 1,3,5-TMA by adiabatic calorimetry. In this paper we report application of this method to 1,3-DMA and 1-EA compounds and the use low-frequency Raman spectroscopy to determine the phase transitions in these molecules. For the 1,3-DMA we obtained essentially the same result as given by the previous Raman study [2]; the temperature dependence of the 1,3,5-TMA and 1-EA photon spectra clearly indicate the formation of the plastic crystalline phase by the former substance and the absence of the solid-to-solid transition in the latter compound. The thermodynamic functions of all the substances in the series were calculated on the basis of their molecular parameters and compared with those obtained from the combined experimental data.

2. Experimental

1-Ethyladamantane was synthesised from methyl-1-adamantylketone [10], while 1,3-dimethyladamantane was prepared by $AlCl_3$-catalyzed isomerization of the perhydroacenaphtene [11]. The samples were purified by double rectification on a column with the efficiency of 20 theoretical plates. The mole fractions of the impurities were determined chromatographically and found to be $5 \cdot 10^{-4}$ for both compounds. The total amount of impurities, N_2, was determined by calorimetric fractional melting as described in reference [12]. The presence of the solid-to-soluble impurities was not indicated. Table 1 lists the single experiments to determine of the equilibrium melting temperatures T_i of 1,3-DMA and 1-EA as the functions of inverse fractions of the sample melted, $1/F_i$. The mole fractions N_2, the triple point temperatures T_{tp}, and the cryoscopic constants A_{cr} and B_{cr} were estimated as the mean values from 3 and 4 experiments for 1,3-DMA and 1-EA, respectively. The results are listed in table 2. The values of the mole fractions of impurities defined by the cryoscopic and chromatografic methods were in good agreement.

TABLE 1
Equilibrium melting temperatures T_i[a], reciprocal of the sample fraction melted $1/F_i$[a], the $T_{i(calc.)}$ values calculated from the linear dependence of T_i on $1/F_i$ for 1,3-dimethyladamantane and 1-ethyladamantane

T_i/K	q_i[b]/J	$1/F_i$	$T_{i(calc.)}$/K
	1,3-DMA		
245.058	6.576		
246.023	6.576		
246.979[a]	6.575	7.979[a]	246.982
247.428[a]	4.936	3.732[a]	247.419
247.563[a]	4.935	2.345[a]	247.563
247.627[a]	4.935	1.663[a]	247.634
247.677[a]	4.935	1.262[a]	247.676
247.737	4.935	1.000	247.703
248.152	4.935		
248.871	4.935		
249.589	4.935		
		0.000	247.806
	1-EA		
225.406[a]	10.499	5.986[a]	225.406
225.483[a]	10.465	2.993[a]	225.482
225.507[a]	10.464	1.998[a]	225.507
225.519[a]	10.464	1.499[a]	225.520
225.527[a]	10.463	1.200[a]	225.527
225.542	10.461	1.000	225.532
		0.000	225.557

[a] The T_i and $1/F_i$ values were used for calculation of N_2 and T_{tp} in the range of $1/F_i$ from 1.2 to $\leqslant 10$ according to [13].

[b] The q_i denotes a quantity of energy used for melting of the F_i substance's fraction.

The heat capacities of the substances under study were measured in a fully automated setup described elsewhere [14,15] that consisted of a vacuum adiabatic calorimeter, data acquisition and control system, and a personal computer. The temperature of the calorimeter was measured with an accuracy of $\pm 5 \cdot 10^{-3}$ K by means of (rhodium + iron) resistance thermometer ($R_O \approx 100$ Ω) calibrated on ITS-90. The temperature difference between the calorimeter and the adiabatic shield was measured by a four-junction (copper + 0.001 mass fraction iron) – chromel thermocouple. The data acquisition system controlled the adiabatic experiment with a stability of 1 mK throughout the whole temperature interval. The calorimeter was tested with *n*-heptane and copper as standard reference materials [1]. The accuracy of

TABLE 2
The values of total amount of impurities, N_2, triple point temperatures, T_{tp}, and cryoscopic constants A_{cr} and B_{cr} for 1,3-dimethyladamantane and 1-ethyladamantane

Compound	1,3-DMA	1-EA
N_2/mol	$(2.7 \pm 0.4) \cdot 10^{-4}$	$(7 \pm 1) \cdot 10^{-4}$
T_{tp}/K	247.79 ± 0.01	225.56 ± 0.02
A_{cr}/K^{-1}	$(3.02 \pm 0.01) \cdot 10^{-3}$	$(26.53 \pm 0.06) \cdot 10^{-3}$
B_{cr}/K^{-1}	$(6.33 \pm 0.02) \cdot 10^{-3}$	$(2.38 \pm 0.01) \cdot 10^{-3}$