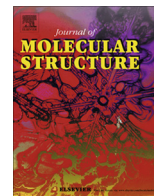




Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

The relationship between orientational disorder and pressure: The case study of succinonitrile

J.Ll. Tamarit^{a,*}, I.B. Rietveld^b, M. Barrio^a, R. Céolin^b^a Grup de Caracterització de Materials (GCM), Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, 08028 Barcelona, Catalonia, Spain^b EAD Physico-chimie Industrielle du Médicament (EA 4066), Faculté de Pharmacie, Université Paris Descartes, 4, Avenue de l'Observatoire, 75006 Paris, France

H I G H L I G H T S

- The effect of pressure on the stability of the plastic phases is compiled and discussed for a broad set of systems.
- The pressure–temperature phase diagram for succinonitrile is established.
- The diffusional barrier increases faster than the rotational one, giving rise to an increase of the plastic phase domain.

A R T I C L E I N F O

Article history:

Received 23 December 2013

Received in revised form 13 March 2014

Accepted 13 March 2014

Available online xxxx

Keywords:

Polymorphism

Orientational disorder

Pressure–temperature

A B S T R A C T

Plastic phases can be considered as an intermediary state between the crystalline state and the liquid state, in which the molecules maintain their positions, but they exhibit orientational disorder. Whereas plastic phases have been studied as a function of temperature, the effect of pressure on these systems is largely unknown. The pressure–temperature phase diagram of succinonitrile has been obtained by a topological approach and by direct measurement. Both approaches demonstrate that the temperature range of the plastic phase increases with pressure. This in first instance counterintuitive result can be explained by a faster increase of the diffusional energy barrier than the rotational barrier with pressure, or in other words, the liquid phase becomes even more unstable than the plastic phase with pressure. These conclusions have been confirmed by comparing the succinonitrile results with a large group of other compounds exhibiting plastic crystal behavior.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Plastic phases are solids with molecules on well-defined positions in a crystal lattice, however their orientation is disordered [1,2]. Although the behavior of plastic phases as a function of temperature is well known, the influence of pressure on these systems is not studied in great detail. A priori, it could be suggested that an increase of pressure reduces the available volume that is required for orientational motions and thus that pressure diminishes the temperature domain of a plastic phase.

After the seminal two-lattice model of Lennard-Jones and Devonshire [3,4] in which melting was treated as a positional order–disorder transition, a lot of effort has been put into understanding the melting phenomenon. By exclusively taking into account positional order, only one order parameter was necessary in the model. Subsequently, the theory was extended to approach the real, more

complex process of melting for molecular systems by taking orientational disorder into account. In first instance, two discrete rotational orientations were combined with the two-lattice model of Lennard-Jones and Devonshire [5,6] and soon after [7] more than two discrete orientations with their respective energy minima were incorporated in the model. In both cases, a non-dimensional, temperature- and volume-independent parameter ν was defined as the ratio between the energy barriers for rotational motion and for diffusion of the molecules through the crystal lattice. In addition, for the extended model [7], a new parameter, D , was introduced accounting for the number of orientations with minimum energy [8]. The main conclusion of this theory is that chemical compounds with ν values higher than 0.325 do not possess a rotational transition (i.e., ordered solid to an orientational disordered phase) and thus their solids melt directly.

Unfortunately, despite the physical significance of these parameters, energy barriers are not known for most molecular materials and D is mainly determined using symmetry considerations requiring information on the crystal structure as well as on dynamic

* Corresponding author. Tel.: +34 934016564; fax: +34 934011839.

E-mail address: josep.lluis.tamarit@upc.edu (J.Ll. Tamarit).

properties that control the occurrence of orientational disorder [8]. This makes a direct comparison with the models' predictions infeasible. To overcome this problem, in the extended model entropy and volume changes at the melting transition, ΔS_m and ΔV_m , have been correlated with the ratio between the transition temperature from purely crystalline to plastic phase (T_t) and the melting temperature (T_m), T_t/T_m [7]. In addition, some pressure–temperature phase diagrams for simple compounds have been calculated with those models showing that the temperature domain of the disordered phase increases with pressure.

Recent approaches have applied more sophisticated methods to study the behavior of phase transitions as a function of the ν parameter with similar results [9–11]. The common feature of all these models is the appearance of an intermediate orientationally disordered phase between the low-temperature crystal phase and the liquid state for values of ν smaller than ca. 0.3. Moreover, for a restricted (model-dependent) range of ν it emerges that the temperature domain of the disordered phase increases with pressure.

Several physical correlations result from the aforementioned studies. First, both ΔS_m and ΔV_m appear to decrease with the increase of the T_t/T_m parameter. Second, the temperature domain of the plastic phase, accounted for by the T_t/T_m parameter, increases with pressure. Fig. 1a and b shows the entropy and volume changes for the melting process at normal pressure as a function of the T_t/T_m parameter for several series of materials exhibiting plastic phases. It can be seen that for all series, both thermodynamic

quantities increase with the increasing temperature range of the disordered phase. At present, a reasonable number of experimental pressure–temperature phase diagrams for plastic phases has been obtained by Würflinger at the Ruhr Universität, Bochum, and by the group of Materials Characterization at the Universitat Politècnica de Catalunya, Barcelona.

The different groups presented in the figures are the following:

- (1) Cyclic molecules, those derived or related to cyclohexane (red squares in Fig. 1) such as Cl-cyclohexane, F-cyclohexane, cyclohexanone, cyclopentanol, cycloheptanol, cyclooctanol; the data are from the Würflinger group [12–29].
- (2) Tetrahedral or tert-butyl molecules (blue circles in Fig. 1) such as $(\text{CH}_3)_3\text{CX}$, $\text{X} = \text{NO}_2, \text{NH}_2, \text{Cl}, \text{Br}$ [30–35].
- (3) Alcohols such as some derivatives of neopentane (pink triangles in Fig. 1) ($(\text{C}(\text{CH}_3)_4$), as $(\text{CH}_3)_3\text{CNO}_2$, $(\text{CH}_3)_2\text{CNO}_2\text{CH}_2\text{OH}$, $(\text{CH}_3)_2\text{CNH}_2\text{CH}_2\text{OH}$, $\text{C}(\text{CHOH})_4$, $\text{NH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ [36,37].
- (4) Chlorine–bromine tetrahedral molecules (green stars in Fig. 1) such as CCl_4 , CBrCl_3 , CBr_2Cl_2 , $(\text{CH}_3)_2\text{CCl}_2$, $(\text{CH}_3)\text{CCl}_3$, CBr_4 [38–47].
- (5) Inorganic XF_6 molecules (vertically half-filled circles in Fig. 1) such as WF_6 , MoF_6 , SeF_6 . The values are reported in the book of Parsonage and Staveley [2].
- (6) A number of molecules such as ethane, succinonitrile, C_2F_6 (horizontally half-filled circles in Fig. 1) [2].

Experimental studies indicate that the temperature domain of the plastic phase increases with pressure in all series, as is predicted by the models. This implies a decrease of T_t/T_m with pressure and may also imply an increase of entropy and volume changes with pressure. These latter implications have never been verified and we will demonstrate in the discussion section that they are not valid for the systems that have been experimentally studied so far.

In the present paper, the experimental pressure–temperature phase diagram of one of the most well-known compounds exhibiting a plastic phase, succinonitrile, $\text{C}_2(\text{CN})_2$ is presented in order to demonstrate how pressure–temperature phase diagrams are constructed by (1) a topological approach and (2) a pure experimental approach. The thermodynamic properties of succinonitrile are discussed together with those of a number of similarly structured molecules in relation to the pressure dependence of these properties for plastic crystals.

Theoretical background

If temperature T and pressure P are chosen as independent variables (among the thermodynamic variables P , T , volume V and entropy S), the energy for the three states (crystalline solid, liquid and vapor) of what Gibbs named a “body” is given by the function G . This function changes monotonously with its variables. Therefore, each state can be defined by a monotonous surface in the three-dimensional $G(P,T)$ space. Those surfaces intersect each other only along a single curve in the G – P – T space corresponding to equilibria involving two states. The three curves intersect each other at a single point (the so-called triple point), which corresponds to the equilibrium involving three states.

The projection of this topology onto the P – T plane leads to the well-known P – T diagram describing the stability domains of the three states of matter for a given body. As the $G(P,T)$ surfaces are monotonous, they intersect only once resulting in a single triple point in the P,T diagram.

If a given body possesses two crystalline states (called dimorphism), a fourth $G(P,T)$ surface is present in the G – P – T space and the projection of the intersecting curves on the P – T plane leads

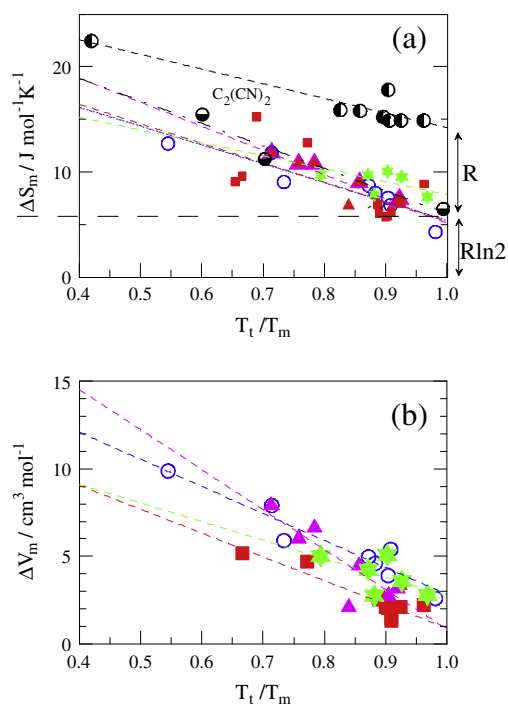


Fig. 1. Entropy (ΔS_m , top panel) and volume (ΔV_m , bottom panel) changes at the melting transition as a function of the T_t/T_m parameter, T_t and T_m being the low-temperature crystal to plastic phase and the melting of the plastic phase temperatures, respectively. Blue circles, tert-butyl molecules ($(\text{CH}_3)_3\text{CX}$, $\text{X} = \text{CH}_3, \text{Br}, \text{Cl}, \text{NO}_2, \text{NH}_2, \text{COOH}, \text{CH}_2\text{OH}, \text{SH}$); Red squares, cyclic molecules (cyclohexane, cyclohexane- X , $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{CN}, \text{O}, \text{OH}, \text{OD}, \text{NH}_2$; cyclohexene, cyclopentane, cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, isocyanocyclohexane); green stars, methyl-chloro-bromine-methane derivatives, $(\text{CH}_3)_{4-n-m}\text{CBr}_n\text{Cl}_m$; pink triangles, tetrahedral polyalcohols ($(\text{CH}_3)_3\text{C}(\text{CH}_2\text{OH})$, $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$, $(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_3$, $\text{NO}_2(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})$, $\text{NO}_2(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_2$, $\text{NH}_2(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_2$, $\text{NO}_2\text{C}(\text{CH}_2\text{OH})_3$); black vertically half-filled circles, XF_6 molecules ($\text{X} = \text{S}, \text{Mo}, \text{W}, \text{Re}, \text{Os}, \text{Ir}, \text{Pt}, \text{Xe}$); black horizontally half-filled circles, C_2X_6 molecules ($\text{X} = \text{CN}, \text{F}, \text{Cl}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/7809862>

Download Persian Version:

<https://daneshyari.com/article/7809862>

[Daneshyari.com](https://daneshyari.com)