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Thermodynamic assessment of orientationally disordered organic molecular crystals: Ternary system pentaerythritol–neopentylglycol–2-amino-2methyl-1,3, propanediol (PE–NPG–AMPL)

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ABSTRACT

Organic crystals such as pentaerythritol [PE-C$(CH_2OH)_4$], neopentylglycol [NPG-$(CH_3)_2C(CH_2OH)_2$] and 2-amino-2methyl-1,3,propanediol [AMPL-$(HOCH_2)_2C(NH_2)CH_3$] store a large amount of thermal energy in their solid state high temperature phases with orientational disorder. There are very few pure compounds of these polyalcohol and amine family that are commercially available exhibiting these properties, leading to limited choices of energy storage materials. Binary and ternary solid solutions allow a wider selection of materials with different phase transition temperature, heat content, and compositions for practical applications. Thermodynamic calculations of the PE–NPG–AMPL system are presented that provide critical thermodynamic data for energy storage systems. Substitutional solution model is used for optimization of interaction parameters. Activities of binaries, ternary isotherms of PE–NPG–AMPL at various temperatures, and pseudo-binary isopleth are presented.

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1. Introduction

The driving force behind the development of renewable energy source is the emission of greenhouse gases and increasing fuel prices. Researchers are continually in search of new and alternative energy solutions, and solar radiation is considered to be one of the most promising sources of energy. One of the options is the development of energy storage devices, which are equally important as developing new energy sources. The development of thermal energy storage materials is important as a passive system in which energy stored during the day from solar radiation and utilized at later periods of time. Thermal energy can be stored as either sensible heat or as latent heat, in which heat is stored and released as these materials undergo phase transitions at nearly constant temperature. In general, "Phase Change Materials" (PCMs) can exhibit solid–liquid, liquid–gas or solid–solid phase transitions. Materials such as paraffins and salts store energy while undergoing solid–liquid phase transitions, but have a propensity to leak in containers, as well as exhibit super cooling effects [1]. In this study, we present a special class of energetic solid–solid phase change materials, with high entropy of solid–solid and low entropy of solid–liquid phase changes, referred to as

"Orientationally Disordered Organic Molecular Crystals. These crystalline organic molecular materials are classified as "Plastic Crystals" in which portions of a molecules can rotate around one or several axes [2]. The formation of plastic crystals is attributed to the ability of the pseudospherical molecules to arrange themselves in a cubic array (FCC /BCC) over a particular range of temperature [3]. They also undergo thermal rotatory displacements at the same time, so that there is no long range orientational order between the molecules [4,5]. This phase is also referred to as ODIC (Orientational Disorder in Crystals) [6]. At the upper temperature limit of this orientational disordered phase the liquefaction occurs with breakdown of the long range positional order with only a small entropy variation, generally smaller than 21 J mol^{-1} K^{-1} a characteristic value to classify these compounds and plastic crystal from a thermodynamic point of view [7]. Fig. 1 shows the structures of the compounds studied in this work. The advantage of these materials is that they utilize the heat capacity as well as the solid–solid latent heat of phase transitions. The focus of this research is the potential use of these materials in thermal energy storage and systems for solar and other applications, owing to the large entropy variation in the phase transitions.

Pentaerythritol and related organic crystals undergo solid–solid phase transformations, from low temperature α or β layered or chained structures (tetragonal, monoclinic, orthorhombic) to isotropic disordered high temperature cubic ODIC (FCC or BCC) phases. Examples of these 'plastic crystals' include pentaerythritol [PE: C
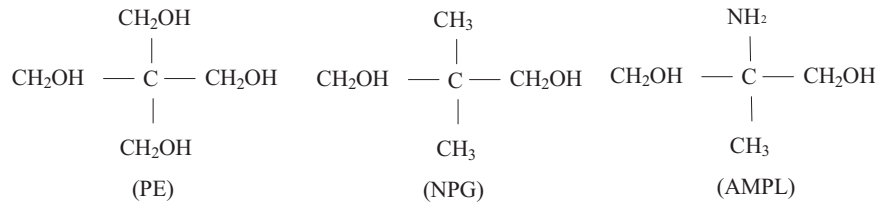
Fig. 1. Structure of PE, NPG and AMPL.

$(CH_2OH)_4$, 2-amino-2methyl-1,3, propanediol [AMPL: $(HOCH_2)_2C(NH_2)CH_3$], pentaglycerine [PG: $(CH_3)_2C(CH_2OH)_3$], neopentylglycol [NPG: $(CH_3)_2C(CH_2OH)_2$], and tris(hydroxymethyl)aminomethane [TRIS: $(NH_2)C(CH_2OH)_3$]. The thermodynamic parameters and crystallographic details for a number of such pure compounds and their binary system have been reported in the literature. Calculated phase diagrams for most of the systems have been reported by various investigators. To our knowledge, no ternary phase diagrams have been reported in these types of systems. This work aims at creating a calculated PE–NPG–AMPL ternary phase diagram. Nitta and Watanabe [8] reported crystallographic properties of the PE compound. Chandra et al. [9] used high resolution Guinier diffraction and reported high temperature structural details of PE and NPG. These polyalcohols when combined to form solid solutions undergo a variation in the phase transition temperatures. The solid solutions can then be used to suit particular applications [10]. To study the alloying effect on the solid–solid phase transitions, Benson et al. [11] investigated binary systems such as PE–PG, PE–NPG, and PG–NPG for thermal energy storage in solar buildings. Font et al. [12] carried out calorimetric studies of the mixtures of PE–NPG and PG–NPG and Barrio et al. [13] conducted an investigation of heat storage applicability of PE–PG, PG–NPG, and PE–NPG binary systems. Chandra et al. [14,15] reported a reduction in the transition temperature of PE by alloying it with PG and NPG. Several research groups have reported partial and complete phase diagrams of PG–NPG [16,17], PE–NPG [18–23], TRIS–NPG [24,25], PE–PG [26], TRIS–PG [27], TRIS–PE [28], TRIS–AMPL [29], and PE–AMPL [30]. Sturz et al.[31], Witusiewicz et al. [32], and Lopez et al. [33] reported thermodynamic assessment of similar systems that were carried out by other research groups to determine multicomponent phase equilibria.

Chandra et al. [34] determined the complete phase diagram for the AMPL–NPG binary. Barrio et al. [35] also reported on the AMPL–NPG binary, but there were significant differences between these two phase diagrams of Chandra et al. and Barrio et al. Salud et al. [36] performed further experimental studies on the AMPL–NPG system in 1997 including a calculated phase diagram. Chellappa et al. also published calculated phase diagrams for AMPL–NPG [37] and PE–AMPL [38]. AMPL–NPG phase diagrams have also been calculated by Witusiewicz et al. [32] using the CALPHAD method. A thermodynamic assessment of the ternary system PE–PG–NPG has been calculated using the CALPHAD method [39].

This work involves thermodynamic assessments of the PE–NPG, AMPL–NPG and PE–AMPL binary systems utilizing the CALPHAD method. In the case of NPG–AMPL system, we made two different calculations based on by Witusiewicz et al. [32], and Raja et al. [37]. These calculated binary phase diagrams are then used to compute the PE–NPG–AMPL ternary system.

2. Computational procedure

In order to compute phase equilibria and calculate the phase diagrams, certain thermodynamic parameters need to be calculated. This section describes the determination of thermodynamic properties (enthalpies and entropies of formation for PE, NPG

and AMPL, Gibbs free energies of the stable and metastable phases, etc.).

2.1. Calculation of thermodynamic properties

Joback's group contribution method has been used to calculate the enthalpy and entropy of formation. Since, the organic plastic crystals (e.g. PE, NPG, AMPL) are not pure elements; their enthalpy of formation is not zero. These thermophysical quantities can be calculated using group contribution methods, which takes into account the smallest constituents (atoms/groups), and in this case, the functional groups (which may be composed of few atoms and bonds). Data for the functional groups is taken from Marrero and Gani [40]:

<u>AMPL</u> $(NH_2)(CH_3)C(CH_2OH)_2$

$$\Delta H_{AMPL} = \begin{pmatrix} -22.01 \\ -76.5 \\ 82.23 \\ -20.64 \\ -208.4 \end{pmatrix}, k = (1 \; 1 \; 1 \; 1 \; 2), \quad \Delta G_{AMPL} = \begin{pmatrix} 14.07 \\ -43.96 \\ 116.02 \\ 8.42 \\ -189.2 \end{pmatrix}$$

$$\Delta H_{0_{AMPL}} = (68.29 + k.\Delta H_{AMPL}) \times 10^3 = -406,030 \text{ kJ/mol}$$

$$\Delta G_{0_{AMPL}} = (53.88 + k.\Delta G_{AMPL}) \times 10^3 = -221,550 \text{ kJ/mol}$$

$$S_{0_{AMPL}} = \frac{\Delta H_{0_{AMPL}} - \Delta G_{0_{AMPL}}}{298} = -619.06 \text{ kJ/mol K}$$

<u>NPG</u> $(CH_3)_2C(CH_2OH)_2$

$$\Delta H_{NPG} = \begin{pmatrix} -76.45 \\ 82.2 \\ -20.64 \\ -208.04 \end{pmatrix}, k = (2 \; 1 \; 2 \; 2)$$

$$\Delta H_{0_{NPG}} = (68.29 + k.\Delta H_{NPG}) \times 10^3 = -459,770 \text{ kJ/mol}$$

$$\Delta G_{0_{NPG}} = (53.88 + k.\Delta G_{NPG}) \times 10^3 = -279,580 \text{ kJ/mol}$$

$$S_{0_{AMPL}} = \frac{\Delta H_{0_{NPG}} - \Delta G_{0_{NPG}}}{298} = -604.66 \text{ kJ/mol K}$$

2.2. Thermodynamic modeling of solution phases

The low temperature phases of pure compounds are referred to as "Phase III" or "Phase II,' and the high temperature phases as "Phase I." The nomenclature used for low temperature phases is α, β or δ phases, and for high temperature phases as γ, ε or η, in the multicomponent system. For simplicity PE is represented by "A," NPG as "B" and AMPL as "C." Table 1 shows list of symbols used to describe the various phases in the PE–NPG–AMPL ternary system.

A CALPHAD type optimization using regular and sub-regular solution model is considered to be adequate to describe the Gibbs energies of different phases. If the reference state for each phase is taken to be that of the pure components in that phase, then the Gibbs energy of a solution phase ϕ ($\phi = \alpha, \beta, \delta, \gamma, \varepsilon, \theta, \eta, L$) can be represented as follows (unit of Gibbs energy is J mol^{-1} throughout