



Thermodynamic assessment of binary erythritol-xylitol phase diagram for phase change materials design



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ARTICLE INFO

Keywords:

Thermal energy storage (TES)
Phase change material (PCM)
Erythritol-xylitol phase diagram
Gibbs free energy minimization
Thermodynamic optimization
CALPHAD

ABSTRACT

Here, the erythritol-xylitol binary system was thermodynamically optimized based on available experimental phase equilibrium data, to explore compositions suitable as phase change materials (PCMs) for thermal energy storage (TES). A previous experimental study revealed that erythritol-xylitol was a partially isomorphous system with a eutectic. In the thermodynamic evaluation, the CALPHAD method was employed coupling the phase diagram and thermodynamic property information. There, both unary and binary systems' experimental data were taken into account, and all phases were described using the substitutional solution model. Finally, a self-consistent thermodynamic description for the erythritol-xylitol system was achieved. The calculated eutectic point is at 76.7 °C and 26.8 mol% erythritol, agreeing well with the experimental data. The calculated phase diagram better-verifies the systems' solidus and the solvus, disclosing the stable phase relations. Based on the Gibbs energy minimization, phase diagrams can be predicted for the binary and higher order systems, provided the component subsystems are thermodynamically assessed beforehand. In conclusion, to move forward beyond e.g. non-isomorphous simple eutectic systems, methods using Gibbs free energy minimization from a fundamental point-of-view such as CALPHAD are essential.

1. Introduction

Improved efficiencies and better management in the energy systems can be realized by integrating thermal energy storage (TES) using phase change materials (PCMs). PCMs can replace fossil-based heating and cooling, by e.g. harvesting excess thermal energy from industries, power plants and like [1,2], for use at different locations and time (e.g. in district heating [3]). TES with PCMs thereby decrease the fossil fuel-based CO₂ emissions [4], while is also attractive for peak shaving and load shifting [5–7]. Material challenges keeping PCMs from reaching commercialization to a large extent include cost, phase separation and supercooling. Bulk blends could serve as cost-effective PCMs, if their phase equilibrium is well established and understood. Thereby, blend compositions that do not phase separate and still have pure material-like sharp phase change (i.e., congruent melting, or, eutectics if supercooling is absent), can be accurately chosen as PCMs [8–10].

Polyols are a renewable material category generally safe for handling, with melting temperatures and enthalpies attractive for cooling and low-temperature heating [11]. They are emerging as PCMs, with

various pure polyols (e.g. [11–18]) as well as blends [19–25] being evaluated as PCMs. These include the binary polyols system erythritol-xylitol, proposed with a non-isomorphous simple eutectic phase diagram [19,20], or with a phase diagram containing a eutectic with solid-solid phase changes implying a partially isomorphous system [21,25]. The non-isomorphous simple eutectic deduction was based on experimental assessments using: Differential Scanning Calorimetry (DSC) [19,20]; Polarized Light thermo-Microscopy (PLM) [19]; X-ray Diffraction (XRD) [19]; Infra-Red thermography (IRT) [20], and theoretical modelling specific to non-isomorphous simple eutectic systems [19,20]. The partially isomorphous system was deduced based on experimental evaluations with the Temperature-History (T-History) method [21,25], complemented with Tammann Plots, XRD and Field-Emission Scanning Electron Microscopy (FESEM) [25].

To complement the experimental evaluations that yielded a partially isomorphous behavior, the erythritol-xylitol binary phase diagram is theoretically evaluated herein. For that, the CALPHAD (CALculation of PHase Diagrams) method [26] based on Gibbs free energy minimization is employed, using the PARROT module in the

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<https://doi.org/10.1016/j.calphad.2017.11.005>

Received 24 July 2017; Received in revised form 9 November 2017; Accepted 19 November 2017
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Nomenclature		Coefficients	
<i>Abbreviations</i>		XRD	X-ray Diffraction
AMPL	2-amino-2-methyl-1,3-propanediol	Xy	Xylitol
CALPHAD	CALCulation of PHase Diagrams	<i>Symbols, subscripts</i>	
DSC	Differential Scanning Calorimetry	config	Configurational
E	Eutectic	c_p	Specific heat at constant pressure (J/(mol/K))
Et	Erythritol	h, H_m	Enthalpy (J/mol)
FESEM	Field-Emission Scanning Electron Microscopy	G_m	Molar Gibbs free energy (J/mol)
IRT	Infra-Red Thermography	${}^E G_m$	Excess molar Gibbs free energy (J/mol)
NPG	Neopentylglycol	γ	Activity coefficient
ORT	Orthorhombic	i, k, j	Any component
PCMs	Phase Change Materials	L	Liquid
PE	Pentaerythritol	${}^0L, {}^1L$	Interaction parameters for excess Gibbs energy
PG	Pentaglycerine	m	Melting/Molar
PLM	Polarized Light Thermo-Microscopy	phys	Physical
SLE	Solid-Liquid Equilibrium	R	Gas constant (J/mol/K)
TES	Thermal Energy Storage	S	Solid
TET	Tetragonal	srf	Surface
T-History	Temperature-History	T	Temperature (K)
TRIS	Tris(hydroxymethyl)aminomethane	tr	Transition
UNIFAC	Universal Quasi Chemical Functional Group Activity	x	Mole fraction

iterative optimization software Thermo-Calc [27]. The CALPHAD method is considered as a suitable choice to evaluate the erythritol-xylitol phase diagram, as this method can evaluate multi-component systems of different chemical origin (organic or inorganic) with various phase equilibrium. This is in contrast to the previous theoretical approaches employed on the system, which were restricted to a non-isomorphous simple eutectic. With the thermodynamic assessment, it is expected herein to further confirm the erythritol-xylitol system's phase equilibrium behavior forming a eutectic in a partially isomorphous system.

1.1. Background

The previous theoretical assessments of the erythritol-xylitol phase diagram were conducted using solid-liquid equilibrium (SLE) expressions expressed with respect to the activity coefficients of the components [19,20]. There, the correction terms for the solid-solid transitions of the components and for the specific heat (c_p) difference between the liquid and solid were neglected, as these are small compared to the activity coefficients' uncertainties [19,20]. Based on the experimental results indicating a non-isomorphous simple eutectic behavior (thus considering that the solid components are immiscible), the solid-state activity coefficients were assumed to be equal to unity [19,20]. Then, to determine the SLE, in one approach, the liquid-state activity coefficients were determined by employing the modified UNIFAC (Universal quasi-chemical functional group activity coefficients) method [19]. In another approach, ideal liquid solutions were assumed, and hence assuming the liquid-state activity coefficients also as equal to unity [19,20]. Overall, these theoretical assessments conducted on the erythritol-xylitol phase diagram so far are restricted to non-isomorphous simple eutectic systems. Hence, such specific theoretical methods cannot be used to thermodynamically evaluate the partially isomorphous behavior with a eutectic identified on the erythritol-xylitol system [21,25]. Therefore, for the thermodynamic assessment of the erythritol-xylitol system based on this new understanding of its phase equilibrium, the CALPHAD method was chosen as a suitable approach, as it can evaluate any material type and any phase change behavior.

With the CALPHAD method, the Gibbs free energy of a system is minimized to find its equilibrium phases. By employing the CALPHAD method, numerous organic and inorganic multicomponent phase

diagrams with complex phase change characteristics have been optimized thermodynamically (e.g. [10,28–44]). For that, various optimizer tools have been used, such as LIQFIT combined with Prophase on binary systems (e.g. [28–33]); TXY-CALC on ternary systems (e.g. [29–31]); FactSage (OptiSage module) on binary-quaternary systems (e.g. [42]) or, Thermo-Calc on numerous multicomponent systems (e.g. [10,34–41,43]). In these CALPHAD-based assessments, a part of the total molar Gibbs free energy (G_m) of the system was expressed in-terms of the excess molar Gibbs free energy (${}^E G_m$). There, the excess molar Gibbs free energy was often expressed in the form of a Redlich-Kister polynomial for binary [10,29–31,34–41,43,44], ternary [10,37,38] and quaternary ([42]) systems. In certain ternary systems evaluations, the excess molar Gibbs free energy was expressed according to the Kohler's method¹ (e.g. [29–32]).

By employing the CALPHAD method together with Thermo-Calc (PARROT module), the phase diagrams of: the binary polyol systems 2-amino-2-methyl-1,3-propanediol (AMPL)–neopentylglycol (NPG) [34,36], pentaerythritol (PE)–AMPL [35,36], and AMPL–pentaglycerine (PG) [43]; the binary amine-polyol systems tris(hydroxymethyl)aminomethane (TRIS)–NPG [36], TRIS–AMPL [39], and TRIS–PG [43]; and the ternary polyol systems PE–PG–NPG [10,37] and PE–NPG–AMPL [38]; have been thermodynamically assessed. These phase diagrams contain complex phase equilibrium features including eutectics, peritectics, eutectoids and peritectoids. The phase diagrams of the AMPL–NPG [34,36], PE–AMPL [35,36], and AMPL–TRIS [39], TRIS–PG, AMPL–PG [43], PE–PG–NPG [10], and PE–NPG–AMPL [38] systems were thermodynamically optimized, obtaining satisfactory agreements with the experimental data. For the TRIS–NPG system, an unoptimized phase diagram using ideal solutions assumption was found to have reasonable agreements with the experimental data, possibly because the excess molar Gibbs free energy parameters of the system were small by magnitude [36]. In these organic systems, different liquid and solid solution phases were thermodynamically described by employing: regular and sub-regular solution models [10,34,35,37,38,43]; substitutional solution models [10,37,38]; and ideal solution models [34].

Evidently, the CALPHAD method is an attractive choice for modeling a materials system's deviations from the ideal behavior, unlike e.g.

¹ Refer Saunders and Miodownik [26] for details.

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