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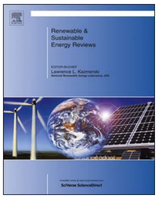

Phase equilibrium in the design of phase change materials for thermal energy storage: State-of-the-art

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ABSTRACT

This paper presents a review of phase equilibrium as a tool for accurately identifying suitable blended phase change materials (PCMs) to be used for thermal energy storage (TES). PCM storage increases the overall energy efficiency for many applications, however, high cost and complex phase change phenomena in blends often undermine the benefits. The study of phase equilibrium as derived from phase diagrams is the key to solve these issues. It enables the evaluation of PCM-suitability through indication of temperature-composition points, e.g. congruent melting compositions, eutectics and peritectics. To clearly stake out the opportunities of a phase equilibrium-based design methodology, this paper reviews the state-of-the-art based on findings from four decades (1977–2016). On one hand, eutectics, salts-based systems, fatty acids, and alkanes dominate the existing PCM literature. Here peritectics have often been erroneously praised as suitable PCMs despite the many problems depicted from a phase equilibrium point of view. On the other hand, the most PCM-ideal congruent melting systems, as well as the blends of polyols, fats, metal alloys and organic-inorganic combinations lack full attention. This work brings forward the knowledge on these insufficiently explored yet extremely suitable phase equilibrium characteristics. In addition, comprehensive PCM-design thermal properties of these various blends are presented, as a basis to further extensive explorations, and material category-based predictions.

1. Introduction

Cost-effective and technically robust thermal energy storage (TES) is an essential part of a sustainable energy system. Latent heat-based phase change materials (PCMs) are one storage solution. Some applications are commercially available (e.g., hand/pocket-warmers [1,2], and in pharmaceuticals transportation container insulations [3]). However large-scale implementation in energy systems is still lacking. To aid in readying PCM-based TES-technology for commercial storage applications, the advancements in PCMs is one important factor. The PCM must be cheap, non-toxic, originate from a sustainable source, and remain stable over many thousands of phase change cycles. Some recent examples of research into PCM properties and functions are: supercooling of PCM in a vertical container [4]; suppression of supercooling in microencapsulated PCM [5]; microencapsulated hydrated salts [6]; polyols blends as PCM [7]; and the study of non-eutectic $NaNO_3$-KNO_3 mixture [8].

Instead of high-purity single component PCMs, industrial blends can be realized as cost-effective PCMs, if they come with robust phase change over the long-run. To develop and choose blended PCMs, a thorough understanding of their phase changing behavior is essential, with phase equilibrium being a central part. Here, a phase diagram is an important tool for depicting phase equilibrium like the phase changing temperature or the interval, the number of phases present at each instant, as well as the composition and the proportion of all phases [9]. Moreover, a phase diagram provides information on incongruent melting with phase separation, as well as on metastable states (e.g. that occur under supercooling[1]) [10]. As a whole, the phase diagram indicates the robustness of the PCM blend. Engineering new PCM blends to achieve a desired melting temperature can also be done systematically through phase equilibrium studies, e.g. [11–18].

The expected phase change behavior of a novel candidate PCM blend can be predicted based-on the information on known PCM systems made of similar chemical components. This requires a compendium of phase equilibrium knowledge per material category. This potential has been recognized by early stage PCM research, evaluating various material systems with phase diagrams of PCM TES importance, e.g. [10,19–22]. Many investigations aim at understanding the material behaviors, e.g.: identifying the suitability as a PCM [19,23]; evaluating specific categories as PCM, like fatty acids

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[1] As also at these metastable states the phase rule and the liquidus, solidus principles are valid [10].

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Nomenclature

Abbreviations

aq	Aqueous
BA	Benzoic acid
CA	Capric (decanoic) acid
CBA	o-chlorobenzoic acid
CLA	Caprylic (Octanoic) acid
CFD	Computational Fluid Dynamics
CSP	Concentrated Solar Power
DSC	Differential Scanning Calorimetry
EEP	Ethyl palmitate
EES	Ethyl stearate
EPMA	Electron Probe Micro-analysis
FT-IR	Fourier Transform Infra-red
LA	Lauric (Dodecanoic) acid
MA	Myristic (Tetradecanoic) acid
MEO	Methyl oleate
MEP	Methyl palmitate
MES	Methyl stearate
NA	Not available
NMR	Nuclear Magnetic Resonance
NPG	Neopentylglycol
OA	Oleic (*cis*-9-Octadecenoic) acid
PA	Palmitic (Hexadecanoic) acid
pBCB	p-bromochlorobenzene
PCM	Phase change materials
p-CNB	p-chloronitrobenzene
pDBB	p-dibromo-benzene
pDCB	p-dichlorobenzene
PE	Phase equilibrium
SA	Stearic (Octadecanoic) acid
SAT	Sodium acetate trihydrate
SEM	Scanning Electron Microscope
SLE	Solid-liquid equilibrium
SSPCM	Solid-solid phase change materials
SR-XRD	Synchrotron radiation XRD
TAGs	Triacylglycerols
TES	Thermal Energy Storage
TG	Thermogravimetric Analyses
T-History	Temperature-History
TME	Trimethylolethane
TMP	Trimethylolpropane
w/w	By weight (fraction)
XRD	X-ray Diffraction

Subscripts/superscripts

A, B	any component A, any component B
E, E1, E2	Eutectic, Eutectic 1, Eutectic 2
P	Peritectic
W	Water

Symbols

α, β	Solid phases
Δ	Difference
CC	Congruent melting compound
E	Eutectic
G	Gibbs free energy of the system (kJ)
l	Liquid
P	Peritectic
s	Solid
S	Solid solution
T	Temperature (°C/K, as mentioned)
X	Mole fraction

[24,25], salt hydrates [21,26], and alkanes [27,28], as well as for melting point adjustments [12,29]. In addition, some phase equilibrium studies are found on solid-solid PCM design [30].

Although the published materials contain interesting findings, the results mainly focus on identifying and predicting eutectic blends. Very little attention is given to other PCM-relevant equilibrium characteristics. For example only a few studies on congruent melting systems were found, even if such mixtures are ideally suited as PCMs as compared to eutectics and peritectics. Furthermore, very little has been done to use the knowledge of phase equilibrium to avoid phase separating blends, or at least to understand supercooling and incongruent phase change. Instead, phase separation and supercooling are being addressed in a preventive manner using techniques like mixing, gelling and thickening [31], micro/macro encapsulation, e.g. [32–35], and crystallization initiation via techniques like the addition of nucleators [31,36], and with Peltier elements [31].

In this paper, the state-of-the art on phase diagrams and phase equilibrium for precise design of blended PCMs is presented and comprehensively analyzed. A resulting databank entails PCM-favorable phase equilibrium characteristics and shows requirements in designing latent heat-based TES, serving as a basis for extensive future explorations of blended PCM.

2. Phase equilibrium concepts – a theoretical background

Chemical systems exhibit various phase equilibrium characteristics which can be depicted in several types of phase diagrams. In PCM-based TES design, some of these characteristics are of major interest since they lead to favorable phase changing characteristics as applied to storage design. To complement general phase equilibrium studies, e.g. [9,20,37–43] this work puts the focus specifically on the PCM design context.

Material systems may consist of a number of components. The simplest system is made of one single pure component1F, where a phase change occurs at a specific temperature. The simplest mixture is a binary system, and hence is the starting point of a multicomponent study. A number of binary systems have desirable phase equilibrium characteristics suitable for PCM and are briefly presented here in the PCM-context, as a background for the analysis and discussion in this paper. Fig. 1 illustrates nine types of phase equilibrium systems with PCM-desirable phase changes. All of these are completely miscible in the liquid state, and are condensed systems considered at constant pressure and ignoring vapor phase.

Generally, in binary solid mixtures, three types of phases are possible: solid solution3F[2] phase, eutectic phase and compounds4F[3] [44]. The

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[2] A *solid solution* consists of atoms of at least two different types, with guest (solute) atoms occupying either substitutional or interstitial positions in the host (solvent) crystal lattice, while maintaining the crystal structure of the host. The composition of a solid solution is rather the same throughout, i.e., homogeneous [9,45,46]. A *solution* (liquid or solid) is a single phase made of more than one component, while a *mixture* is a material composed of more than one phase [44,47].

[3] A *compound* is also made of atoms of more than one element, but in a fixed stoichiometric proportion to each other. The atoms in a compound are bonded chemically and are arranged in space in definite arrangements for each of the atoms [45]. Comparing, atoms in solid solutions may exist in a variable ratio, while in a compound atoms ratio is fixed. For instance, if a compound is A_xB_y, here x and y are the fixed stoichiometric coefficients, while for a solid solution A_xB_y, x and y are variable within a range. Also, in a solid solution even though the crystal lattice of host (solute) is retained, atoms' spatial arrangement is variable. Then a compound always has the same atomic spatial arrangement that is characteristic to the compound. A solid solution can be separated by physical means while a compound can only be separated by chemical means [10,45].