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A novel calcium chloride hexahydrate-based deep eutectic solvent as a phase change materials

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ABSTRACT

Deep eutectic solvents (DESs) are gaining interest in various applications due to their tuneable properties and affordable preparation cost. Developing low cost new DESs is vital for some potential industrial applications. This work introduces a new type III DESs based on choline chloride as a quaternary ammonium salt (QAS) and calcium chloride hexahydrate as a hydrated salt. The prepared DESs were characterized by measuring some of their important physical and chemical properties. Furthermore, the applicability of the new DESs as a possible phase change material (PCM) that can be used for building applications was investigated. The experimental results manifested that the DESs in the molar ratios of 1:6 and 1:8 (QAS: hydrated salt) have the potential to be utilized as PCMs in building applications with large latent heat (127.2–135.2 kJ Kg^{-1}) and suitable phase change temperature (20.65–23.05 °C), However, they suffered from supercooling and phase segregation. In order to overcome these problems, 2 wt% of $SrCl_2 \cdot 6H_2O$ as nucleating agent and fumed silica as thickener were used during the 100 thermal cycling test. The cycling results showed the degree of supercooling of the DESs was significantly reduced and the phase change temperatures of the DESs remained unchanged.

1. Introduction

In 1990 s when the concept of green chemistry was introduced, ionic liquids (ILs) received a significant attention because of their favorable features such as being environmentally friendly, non-volatile, easily designable, high solvating, non-flammable, thermally stable, and also having simple regeneration processes [1]. However, some ILs are very toxic and poorly biodegradable [2,3]. Furthermore, the synthesizing process of ILs is complicated, expensive and non-environmentally friendly since it demands a large amount of salts and solvents to allow the anions to exchange completely [4,5].

Recently, a new generation of solvents, namely deep eutectic solvents (DESs) has emerged to overcome some of the principal disadvantages of ILs. In fact, the DESs serve as a low cost alternative to ILs and this is due to the fact that DESs have similar common properties of ILs [6,7]. Basically, the DESs can be acquired easily by mixing two or more components, which are capable of forming a eutectic mixture through hydrogen bonding or metal halide bond interactions [2,8]. The compositions of the DESs can manifest four types of DESs. A quaternary salt can be mixed either with a metal salt containing chloride ion (Type I), a metal chloride hydrated salt (Type II) or a hydrogen bond donor (Type III) that can consist of an alcohol, amide or a carboxylic acid [9]. Moreover, mixing a metal chloride salt or a metal chloride hydrated salt with a hydrogen bond donor (HBD) can form type IV DES [10,11].

Generally, the physico-chemical properties of DESs can be further adapted to tailor particular application by altering the characteristics of constituting components. In the last decade, DESs as affordable green solvents have been successfully demonstrated in various applications such as electrochemical processes [12], biological catalysis [13], synthesis of solar cells [14], separation and purification processes [15–17], nanotechnology [18] and many other potential applications [9]. In addition, the potential of DESs usage in some new applications can be examined due to their unique features.

Developing renewable sources of energy plays an important role in reducing the environmental impact related to energy use. Designing thermal energy storage systems is one of the options that can be followed for energy saving and for preserving it for later use. Sensible heat storage (SHS), latent heat storage (LHS) and thermochemical storage (TCS) are the three main thermal energy

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storage methods [19]. Amongst these, LHS is the most attractive method for storing thermal energy in wide range of applications due to its ability to provide energy storage with high capacity and less temperature fluctuation during the phase change process [20]. Generally, the LHS method is employed to improve the use of energy and conserve it in a number of applications. It is commonly used to improve thermal performance of buildings since it can fulfill the demand for thermal comfort and energy conservation in the buildings [21–23]. In addition, its use covers many other applications [20,24].

Phase change material (PCM) is the main representative of the LHS method. The theory of PCM use in buildings is quite simple. When the indoor temperature of a building increases, the PCM is changed from solid to liquid, absorbing heat being an endothermic process. Likewise, decreasing the temperature in the building solidifies the PCM which releases the heat it absorbed. The use of PCMs in buildings enhances the energy storage capacity of the building envelope and can justify the use of renewable and nonrenewable energies more efficiently [25].

An appropriate PCM for building applications should meet a number of criteria related to the desired thermo-physical, kinetic and chemical properties as well as economics. For the thermal properties, the PCM must have a high latent heat and high thermal conductivity [26]. Moreover, they should have a melting temperature slightly above 20 °C to meet the need of thermal comfort of building. According to the ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers), the suggested comfort room temperature is 21.0–23.0 °C in winter and 23.5–25.5 °C in summer [22]. When it comes to physical properties, the PCM should have a high density that allows more heat to be stored into a limited space and with small volume changes. In terms of the kinetic properties, the PCM must have minimum super-cooling and must have sufficient crystallization rate to form crystals when the heat energy is released. Under the chemical properties, the PCM must have long life time, be compatible with building materials, non-corrosive, non-toxic, non-flammable and show no degradation after numerous cycles. From an economical point of view, the PCM should be readily available in large quantities at low cost [27].

The PCMs used in buildings and other applications can be classified into three different types, namely: organic, inorganic and eutectic. For examples, paraffin, fatty acids and fatty acid ester lie under the organic class. The main advantages of organic PCMs are their moderate heat of fusion at low temperature, small volume changes and do not undergo super-cooling. But they usually have poor thermal conductivity and expensive for use in buildings [22]. However, the thermal conductivity of the organic PCMs can be improved through microencapsulation using different methods [28].

Metal salts and hydrated salts are few examples of inorganic PCMs. They have high latent heat of fusion and high thermal storage density. They are cheap compared to organic PCMs, nonflammable and having high thermal conductivity. The main drawbacks of the inorganic PCMs are supercooling and phase segregation. Based on reports in the published literature, the supercooling problem of these PCMs could be eliminated by adding nucleating agent or some impurities, mechanical stirring and encapsulation [24,29]. Adding thickening agents, using excess of water, mechanical stirring, and PCM encapsulation are available techniques to rectify the phase segregation problem [20,29,30]. Amongst the inorganic PCMs, calcium chloride hexahydarte ($CaCl_2 \cdot 6H_2O$) with a large latent heat of fusion (170–190 kJ/Kg) and a low melting temperature (29–30 °C) has been shown as a potential candidate useful in heat storage applications [31]. This hydrated salt is cheap and non-toxic. However, apart from the two serious drawbacks for inorganic PCMs, supercooling and phase segregation, its melting temperature (29 °C) is also too high for use in buildings, which requires much lower melting point in accordance with the human comfort temperature (20–25.5 °C). It is therefore necessary for the eutectic PCMs to be developed for tailored properties from the synergistic effects of various materials.

A eutectic PCM could be a combination of different materials including organic-organic, organic-inorganic and inorganic-inorganic which can produce a mixture that has a specifically designed property such as melting point and latent heat of fusion [32]. Hence, there is no limit to the number of eutectic PCMs that can be synthesized from available organic and inorganic chemicals. For instance, a new eutectic PCM can be synthesized by mixing an inorganic compound that has a great energy storage capacity with an organic compound to adjust the melting temperature for a particular application.

Carlsson et al. [33] investigated the phase diagram of $CaCl_2$-H_2O system and also the effect of strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) on the system in order to define compositions and temperature in which the formation of calcium chloride tetrahydrate ($CaCl_2 \cdot 4H_2O$) is prevented. They showed that presence of $SrCl_2 \cdot 6H_2O$ had a significant effect on the phase diagram. Adding $SrCl_2 \cdot 6H_2O$ can decrease the solubility of $CaCl_2 \cdot 6H_2O$ and also shift the peritectic point towards a higher concentration of $CaCl_2 \cdot 6H_2O$. They also found that 2 wt% of $SrCl_2 \cdot 6H_2O$ can avoid the formation of tetrahydrate. Later, Feilchenfeld et al. [34] reported the melting temperature of $CaCl_2 \cdot 6H_2O$ with $SrCl_2 \cdot 6H_2O$ as a nucleating agent and Cab-o-SilR as a thickening agent through 1000 thermal cycles without any signs of the phase segregation. Hiroshi et al. [35] revealed that $CaCl_2 \cdot 6H_2O$ with a slight excess water was stable over 1000 thermal cycles (in a heat cycle of 18–35 °C) in a long vertical glass tube. In addition, it was also reported that NaCl had a nucleating effect to improve the phase change repeatability. Brandstetter [36] stated that $CaCl_2 \cdot 6H_2O$ can be stabilized against supercooling and incongruent melting using different nucleating agents such as strontium or barium salts and sodium chloride and the formation of $CaCl_2 \cdot 4H_2O$ was inhibited entirely using the extra water principle. Paris et al. [37] studied the $Ba(OH)_2 \cdot 8H_2O$ and $SrCl_2 \cdot 6H_2O$ as nucleating agents for $CaCl_2 \cdot 6H_2O$, and the results showed that 3 wt% $SrCl_2 \cdot 6H_2O$ revealed a stable thermal behavior with no supercooling. Kaneff and Brandstetter [38] in their patent pointed out that the tetrahydrate formation problem reduces heat storage capacity of $CaCl_2 \cdot 6H_2O$ and for solving the problem they proposed the fumed silica as a thickening agent as well as the use of extra water in excess of the stoichiometric composition of the $CaCl_2 \cdot 6H_2O$. Moreover, they also suggested other additives such as sodium chloride and potassium chloride to reduce the melting temperature of $CaCl_2 \cdot 6H_2O$.

Gao and Deng [29] introduced an inorganic PCM based-$CaCl_2 \cdot 6H_2O$ for thermal energy storage with a phase change temperature of 22.6 °C. They revealed that calcium chloride solution containing 5 wt% of $Mg(NO_3)_2 \cdot 6H_2O$ produced a stable PCM with latent heat of 160 kJ/Kg. The results indicated that, by adding 2 wt% $SrCl_2 \cdot 6H_2O$, the degree of supercooling of the PCM was reduced and no phase segregation was observed. Recently, Li et al. [39] prepared a eutectic hydrated salt based on $CaCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ as a new PCM with the phase change temperature and latent heat of 21.41 °C and 102.3 kJ/Kg. Their results exhibited that 3 wt% $SrCl_2 \cdot 6H_2O$ and 1 wt% $SrCO_3$ were effective nucleating agents, and 0.5 wt% hydroxyethyl cellulose made the PCM stable over 50 thermal cycles. As shown above, $CaCl_2 \cdot 6H_2O$ has long been considered as a low temperature PCM for thermal energy storage and many attempts were made to manipulate its properties and solve the problems associated with its use, yet it has not been applied in real buildings, probably due to the problems