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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 SrCl₂.6H₂O 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.

Keywords: deep eutectic solvents; choline chloride; calcium chloride hexahydrate; phase change materials; supercooling.

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34 **1. Introduction**

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

42 Recently, a new generation of solvents, namely deep eutectic solvents (DESs) has emerged to
43 overcome some of the principal disadvantages of ILs. In fact, the DESs serve as a low cost
44 alternative to ILs and this is due to the fact that DESs have similar common properties of ILs
45 [6, 7]. Basically, the DESs can be acquired easily by mixing two or more components, which
46 are capable of forming a eutectic mixture through hydrogen bonding or metal halide bond
47 interactions [2, 8]. The compositions of the DESs can manifest four types of DESs. A
48 quaternary salt can be mixed either with a metal salt containing chloride ion (Type I), a metal
49 chloride hydrated salt (Type II) or a hydrogen bond donor (Type III) that can consist of an
50 alcohol, amide or a carboxylic acid [9]. Moreover, mixing a metal chloride salt or a metal
51 chloride hydrated salt with a hydrogen bond donor (HBD) can form type IV DES [10, 11].

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

59 Developing renewable sources of energy plays an important role in reducing the
60 environmental impact related to energy use. Designing thermal energy storage systems is one
61 of the options that can be followed for energy saving and for preserving it for later use.
62 Sensible heat storage (SHS), latent heat storage (LHS) and thermochemical storage (TCS) are
63 the three main thermal energy storage methods [19]. Amongst these, LHS is the most
64 attractive method for storing thermal energy in wide range of applications due to its ability to

65 provide energy storage with high capacity and less temperature fluctuation during the phase
66 change process [20]. Generally, the LHS method is employed to improve the use of energy
67 and conserve it in a number of applications. It is commonly used to improve thermal
68 performance of buildings since it can fulfil the demand for thermal comfort and energy
69 conservation in the buildings [21-23]. In addition, its use covers many other applications [20,
70 24].

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

78 An appropriate PCM for building applications should meet a number of criteria related to the
79 desired thermo-physical, kinetic and chemical properties as well as economics. For the
80 thermal properties, the PCM must have a high latent heat and high thermal conductivity [26].
81 Moreover, they should have a melting temperature slightly above 20 °C to meet the need of
82 thermal comfort of building. According to the ASHRAE (American Society of Heating,
83 Refrigerating and Air-Conditioning Engineers), the suggested comfort room temperature is
84 21.0 - 23.0 °C in winter and 23.5 - 25.5 °C in summer [22]. When it comes to physical
85 properties, the PCM should have a high density that allows more heat to be stored into a
86 limited space and with small volume changes. In terms of the kinetic properties, the PCM
87 must have minimum super-cooling and must have sufficient crystallization rate to form
88 crystals when the heat energy is released. Under the chemical properties, the PCM must have
89 long life time, be compatible with building materials, non-corrosive, non-toxic, non-
90 flammable and show no degradation after numerous cycles. From an economical point of
91 view, the PCM should be readily available in large quantities at low cost [27].

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

97 [22]. However, the thermal conductivity of the organic PCMs can be improved through
98 microencapsulation using different methods [28].

99 Metal salts and hydrated salts are few examples of inorganic PCMs. They have high latent
100 heat of fusion and high thermal storage density. They are cheap compared to organic PCMs,
101 non-flammable and having high thermal conductivity. The main drawbacks of the inorganic
102 PCMs are supercooling and phase segregation. Based on reports in the published literature,
103 the supercooling problem of these PCMs could be eliminated by adding nucleating agent or
104 some impurities, mechanical stirring and encapsulation [24, 29]. Adding thickening agents,
105 using excess of water, mechanical stirring, and PCM encapsulation are available techniques
106 to rectify the phase segregation problem [20, 29, 30]. Amongst the inorganic PCMs, calcium
107 chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) with a large latent heat of fusion (170-190 KJ/Kg) and a
108 low melting temperature (29-30 °C) has been shown as a potential candidate useful in heat
109 storage applications [31]. This hydrated salt is cheap and non-toxic. However, apart from the
110 two serious drawbacks for inorganic PCMs, supercooling and phase segregation, its melting
111 temperature (29 °C) is also too high for use in buildings, which requires much lower melting
112 point in accordance with the human comfort temperature (20-25.5 °C). It is therefore
113 necessary for the eutectic PCMs to be developed for tailored properties from the synergistic
114 effects of various materials.

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

122 Carlsson et al. [33] investigated the phase diagram of $\text{CaCl}_2\text{-H}_2\text{O}$ system and also the effect
123 of strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) on the system in order to define
124 compositions and temperature in which the formation of calcium chloride tetrahydrate
125 ($\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$) is prevented. They showed that presence of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ had a significant effect
126 on the phase diagram. Adding $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ can decrease the solubility of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and
127 also shift the peritectic point towards a higher concentration of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. They also found
128 that 2 wt% of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ can avoid the formation of tetrahydrate. Later, Feilchenfeld et al.

129 [34] reported the melting temperature of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ as a nucleating agent
130 and Cab-o-SilR as a thickening agent through 1000 thermal cycles without any signs of the
131 phase segregation. Hiroshi et al. [35] revealed that $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with a slight excess water
132 was stable over 1000 thermal cycles (in a heat cycle of 18-35 °C) in a long vertical glass tube.
133 In addition, it was also reported that NaCl had a nucleating effect to improve the phase
134 change repeatability. Brandstetter [36] stated that $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ can be stabilized against
135 supercooling and incongruent melting using different nucleating agents such as strontium or
136 barium salts and sodium chloride and the formation of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ was inhibited entirely
137 using the extra water principle. Paris et al. [37] studied the $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$
138 as nucleating agents for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and the results showed that 3 wt% $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ revealed
139 a stable thermal behavior with no supercooling. Kaneff and Brandstetter [38] in their patent
140 pointed out that the tetrahydrate formation problem reduces heat storage capacity of
141 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and for solving the problem they proposed the fumed silica as a thickening agent
142 as well as the use of extra water in excess of the stoichiometric composition of the
143 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Moreover, they also suggested other additives such as sodium chloride and
144 potassium chloride to reduce the melting temperature of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

145 Gao and Deng [29] introduced an inorganic PCM based- $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for thermal energy
146 storage with a phase change temperature of 22.6 °C. They revealed that calcium chloride
147 solution containing 5 wt% of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ produced a stable PCM with latent heat of 160
148 KJ/Kg. The results indicated that, by adding 2 wt% $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, the degree of supercooling
149 of the PCM was reduced and no phase segregation was observed. Recently, Li et al. [39]
150 prepared a eutectic hydrated salt based on $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as a new PCM with
151 the phase change temperature and latent heat of 21.41 °C and 102.3 KJ/ Kg. Their results
152 exhibited that 3 wt% $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and 1 wt% SrCO_3 were effective nucleating agents, and 0.5
153 wt% hydroxyethyl cellulose made the PCM stable over 50 thermal cycles. As shown above,
154 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ has long been considered as a low temperature PCM for thermal energy storage
155 and many attempts were made to manipulate its properties and solve the problems associated
156 with its use, yet it has not been applied in real buildings, probably due to the problems
157 mentioned above.

158 The aim of this paper is to introduce a new type III DESs prepared from choline chloride
159 (ChCl) and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Different compositions of the ChCl salt and hydrated salt were
160 prepared and characterized. Furthermore, the prepared DESs were investigated as potential

161 PCMs for building applications by measuring their properties such as freezing temperature,
162 latent heat of fusion, degree of supercooling and thermal stability. Most previous researchers
163 used extra water to ensure the long-term stability of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. From the phase diagram
164 of $\text{CaCl}_2\text{-H}_2\text{O}$ system [33], it is clear that adding water above the degree of hexahydrate can
165 reduce the concentration of CaCl_2 . Consequently, the melting temperature of composition
166 decreases and no tetrahydrate is formed. However, any loss of the water due to improper
167 encapsulation would initiate the problems of phase separation. In this work, using extra water
168 was not proposed and the thickening agents were examined for stability of the synthesized
169 DESs as PCMs.

170 **2. Experimental details**

171 *2.1 Chemicals*

172 Choline chloride ($\text{C}_5\text{H}_{14}\text{ClNO}$), calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), strontium
173 chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$), hydroxyethyl cellulose and fumed silica (SiO_2) with
174 average particles size of 0.2-0.3 μm were purchased from Sigma-Aldrich (St. Louis, USA).
175 All chemicals were of synthesis grade (purity > 98%) and were used without further
176 purifications.

177 *2.2 Preparation of DESs*

178 The DESs in this work were prepared based on the method described in previous work [5].
179 The mixture of ChCl as quaternary ammonium salt (QAS) and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ as hydrated salt
180 at different mole fractions were mixed mechanically into 150 ml Schott bottle at 400 rpm
181 using magnetic stirrer. The synthesis temperature was maintained at 90 °C. The DES is said
182 to be fully prepared when the mixture turns into homogeneous liquid phase without any solid
183 precipitation. For the purpose of preventing moisture absorption, the DESs' bottles were
184 sealed with Parafilm. Table 1 shows the $\text{ChCl} : \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ combinations used in this work
185 along with their mole fractions. Abbreviations were given to each DES for convenient
186 identification.

187 *2.3 Characterization of DESs*

188 Freezing temperature of DESs was determined using the temperature history method. The
189 freezing performance of DESs was conducted using a programmable cycling water bath
190 (PolyScience, US). 10 ml of each DES was added in a glass vial. Subsequently, a type K

191 thermocouple was inserted at the center of DES, and the vial was placed in a water bath at 40
192 °C. After 15 min, the sample was cooled to -15 °C. The thermocouple was connected to a
193 temperature data logger (Pico TC-08, UK) to record the temperature of DES at time interval
194 of 5 seconds. The thermal cycling test was also carried out using the above procedure for 100
195 melting and freezing cycles with the following temperature program: held at 40 °C for 15 min
196 then cooling from 40 to 5 °C, held at 5 °C for 15 min and heating from 5 to 40 °C.

197 The latent heat of the synthesized DESs was measured using a Shimadzu Differential
198 Scanning Calorimetry instrument (DSC-60). A small amount of sample was placed in an
199 aluminum pan with lid and subjected to the DSC furnace. The DSC measurements were
200 carried out at a heating rate of 1 °C min⁻¹. Octadecane and tetradecane were used to calibrate
201 the DSC instrument, which allowed latent heat to be measured with uncertainty better than ±
202 2 kJ.kg⁻¹.

203 Densities of synthesized DESs were determined using an Anton Paar DMA 500 vibrating-
204 tube density meter. The accuracy of the density meter was checked using distilled water and
205 air. The measured values were compared with the corresponding values in the density tables,
206 showing measurements accuracy of ±0.0001g cm⁻³. Density measurements were performed at
207 temperatures from 15 to 40 °C with 5 °C intervals and three replicates for each reading.

208 Viscosity measurements were conducted at different temperatures using a controlled stress
209 AR-G2 rheometer (TA Instrument Ltd, US). The rheometer was fitted with a conical
210 concentric cylinder geometry and was calibrated using an oil standard. Viscosity values were
211 taken between 15 to 40 °C at 5 °C intervals. The temperature was controlled by an external
212 water bath and circulator. The uncertainty in the viscosity measurements was ± 0.02 Pa·s.

213 **3. Results and discussion**

214 In this work ChCl as quaternary ammonium salt and CaCl₂.6H₂O as hydrated salt were
215 selected to prepare the new type III DESs. This was accomplished by mixing the quaternary
216 salt and the hydrated salt at different mole fractions. Accordingly, five DESs based on
217 CaCl₂.6H₂O were prepared from these mixing experiments (Table 1) and their fundamental
218 physico-chemical properties including density, viscosity, freezing temperature and latent heat
219 were measured. It should be pointed out that in order to obtain the eutectic point and also
220 study the influence of ChCl on freezing temperature of the DESs, five mole fractions of ChCl
221 (0.09, 0.11, 0.14, 0.20, 0.34) were selected in this work. All synthesized DESs at the selected

222 mole fractions were homogeneous colorless liquids at room temperature, however, at higher
223 mole fractions of ChCl (>0.34) prepared mixtures were solid at ambient conditions.

224 Density is an important and useful physical property for the DESs. The knowledge of this
225 property plays an important role in many engineering application designs of DESs. The
226 densities of all synthesized DESs (DES1 to DES5) were measured at temperatures from 15 to
227 40 °C in 5 °C intervals and at atmospheric pressure. The results of the measured densities of
228 DES1 to DES5 are presented in Fig. 1. As expected, the liquid densities of all DES exhibit a
229 temperature-dependent behavior and decreased linearly with the increase in temperature due
230 to thermal expansion of the DESs. The DESs' densities also increased linearly with the
231 decrease in mole fraction of ChCl. The following liner equation was found to fit the measured
232 DESs' densities as a function of temperature:

$$\rho = aT + b \quad (1)$$

233 where ρ and T are density ($\text{g}\cdot\text{cm}^{-3}$) and temperature ($^{\circ}\text{C}$), respectively, while a and b are
234 empirical constants as tabulated in Table 2 (a depends on type of DES and b depends on mole
235 fractions of constituting components).

236 The viscosity is another important property in the early design stage of any processes
237 employing new DESs. Viscosity data for many types of DESs was reported in the literature as
238 part of new DESs characterization studies [40, 41]. In this work, viscosity of all $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$ -
239 based DESs (DES1 to DES5) was measured experimentally at a temperatures range of 15 to
240 40 °C and its values were plotted against temperature in Fig. 2. As expected, the viscosity of
241 the DESs decreased with temperature. In addition, the viscosity of DES1 was much higher
242 than that of DES2, DES3, DES4 and DES5. This could be attributed to the stronger hydrogen
243 bonding between ChCl and $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$ in DES1 as shown by its low freezing temperature,
244 (Table 3). As a result, the mole fraction of ChCl has an obvious effect on the viscosity of
245 DESs. The DES with lower mole percentage of ChCl has lower viscosity at any temperature.
246 The viscosity values of each DES were fitted with a high accuracy by an Arrhenius-like
247 equation [40], given below:

$$\mu = \mu_o e^{\frac{E_o}{RT}} \quad (2)$$

248 where μ is viscosity (Pa.s), μ_o is a constant (Pa.s), E_o is activation energy (Pa.m³.mol⁻¹), R is
249 the gas constant (Pa.m³.mol⁻¹.K⁻¹) and T is the temperature in Kelvin. The values of μ_o and E_o
250 are given in Table 2.

251 The melting/freezing temperature is of utmost importance in defining the liquidity range of
252 the newly prepared DESs. Moreover, this property plays a key role in the selection of PCM
253 for a particular application. The freezing temperatures of all studied DESs were measured
254 using the temperature history method described in the earlier section. The reason for using
255 this method in this work is that it offers true and precise information about melting/freezing
256 temperature of a sample as compared to DSC, especially in the presence in supercooling
257 which is very common for both ILs and DESs. This method is able to provide a very slow
258 heating/cooling rate in comparison with DSC analysis. In addition, it gives a better simulation
259 in the real use of PCMs in building applications. Table 3 presents the measured freezing
260 temperatures for DES1 to DES5. As can be seen, the freezing temperatures of all synthesized
261 DESs were less than the freezing temperatures of their constituting components, which is a
262 main character of DESs. Results also show that the freezing temperature of DES is a function
263 of mole fraction of ChCl. The freezing temperature gradually decreased with increasing ChCl
264 mole fraction and eutectic temperature occurred at DES1 with a freezing temperature of 2.7
265 °C. As above-mentioned, the ideal phase change temperature of PCMs used in building
266 application should be in accordance with the human comfort temperature. DES3, DES4 and
267 DES5 satisfied this expectation with a phase change temperature of 20.65, 23.05 and 24.10
268 °C, respectively.

269 The latent heat of PCM is another important criterion used for the selection of a proper PCM
270 in building application. The measured latent heats of fusion for resulting DESs are also listed
271 in Table 3. From the obtained results, it can be concluded that latent heat of DESs depends on
272 the mole fractions of its constituents (ChCl and CaCl₂.6H₂O). Moreover, all DESs have a
273 latent heat above 100 KJ.Kg⁻¹ except for DES1. The values of the latent heat of DES3, DES4
274 and DES5 revealed that they have a good potential for use as PCMs in building applications.
275 The DES1 as eutectic point was characterized by having a low density, high viscosity and
276 low freezing temperature as compared to other DESs. DSC analysis of DES1 showed no
277 melting peak, but a glass transition was observed instead. Such behavior is typical for DESs.
278 This is because the high viscosity of DES hinders nucleation and crystal growth.
279 Furthermore, the strength of hydrogen bonds and other intermolecular interactions between
280 ChCl and CaCl₂.6H₂O decrease the freezing temperature deeper and impress the trends in

281 phase transition temperature. From Table 3, it is clear that the ability of hydrogen bonding
282 and other forces in DESs increased with increasing mole fraction of ChCl. Accordingly, the
283 stability of the DESs was correlated with intensity of hydrogen bonds.

284 From above results, DES3 and DES4 were nominated as amendable PCMs and examined for
285 their supercooling behavior and thermal stability over 100 thermal cycles. Fig.3 shows the
286 cooling curves for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, DES3 and DES4 with a cooling rate of $0.95\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. It is
287 obvious from Fig.3 that they all subcooled heavily before freezing. The degree of
288 supercooling of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is about $18\text{ }^\circ\text{C}$ and the freezing temperature is $29\text{ }^\circ\text{C}$. The
289 reported value in literature [39] for the supercooling degree of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was about $20\text{ }^\circ\text{C}$
290 which is close to the value obtained in this work. The supercooling degree of DES3 and
291 DES4 was found even higher. The supercooling of the DESs is high and can prevent the heat
292 recovery in an application. Therefore, the DESs should be modified before using them as
293 PCMs.

294 To overcome this problem, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ as a nucleating agent was employed to provide
295 crystal nucleon in the DESs. The $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was added into DES3 and DES4 at different
296 concentrations (0.5, 1 and 2 wt%) to determine the effective nucleation rate. The
297 experimental results indicated that 2% by weight of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ had a very highly efficient
298 nucleation rate for DES3 and DES4. The degree of supercooling of DES3 and DES4 during
299 the 100 cooling processes was recorded and presented in Table 4. The maximum degree of
300 supercooling of DES3 and DES4 were found to be 2.54 and $2.33\text{ }^\circ\text{C}$, respectively, and the
301 average supercooling degree for DES3 was $1.47\text{ }^\circ\text{C}$ and for DES4 was $1.23\text{ }^\circ\text{C}$. The cooling
302 curves of DES3 and DES4 with 2 wt% of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ at first cooling cycle are shown in Fig.
303 4. As can be seen from Figs. 3 and 4, the subcooling was significantly reduced by the
304 nucleating agent used.

305 To investigate the stability of DES3 and DES4, they were melted and frozen 100 times. Phase
306 segregation was observed after 8 cycles for DES3 and 5 cycles for DES4. In addition, the
307 phase change temperature of the DESs increased as cycling was continued. Finally, the
308 freezing temperature reached $28\text{ }^\circ\text{C}$ after 20 cycles and then stayed constant for both DESs
309 for the remaining cycling test. It was expected that calcium chloride tetrahydrate is formed in
310 the DESs after few cycles since the chemical stability of studied DESs was influenced by
311 concentration of ChCl. One promising method to tackle this problem in hydrated salt PCMs
312 is to add a thickening agent. It has also been found that fumed silica and hydroxyethyl

313 cellulose can be used as a thickener in a PCM based $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to process long-term
314 stability [38, 39]. Thus, both fumed silica and hydroxyethyl cellulose were employed in this
315 work to examine their applicability as a thickening agent for the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ based-DESs.

316 The hydroxyethyl cellulose was mixed with DES3 and DES4 at different concentrations (0.5,
317 1 and 2 wt%) to reveal the optimum condition. The cycling test showed that the hydroxyethyl
318 cellulose at selected concentrations could not prevent phase segregation in DES3 and DES4
319 over 100 cycles, and tetrahydrate formation was observed after 10 cycles. On the other hand,
320 the fumed silica was also added to DES3 and DES4 at different weight percentages (0.5, 1
321 and 2 wt%). The phase change temperatures of DES3 and DES4 with fumed silica for the 100
322 cycles were presented in Figs. 5 and 6, respectively. The additions of 0.5 and 1wt% of this
323 thickener were not able to stabilize the DES3 and DES4 through the 100 cycles, and the
324 phase change temperature of the DESs gradually increased to 27.8 °C. However, it can be
325 noted that there is a noticeable improvement in the stability of DES3 and DES4 by adding 2
326 wt% of fumed silica as thickener. The freezing point of both DES3 and DES4 remained
327 unchanged during cycling indicating excellent stability.

328 The DSC results of DES3 and DES4 before and after 100 cycles are shown in Fig. 7 and 8,
329 respectively. The latent heat of DES3 was reduced from 123.02 to 112.69 KJ.Kg^{-1} after 100
330 cycles. The deviation of latent heat for DES4 was also found to be 7.8% after 100 cycles (Fig.
331 8). From the obtained results, it can be concluded that $\text{ChCl} : \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ DESs in the molar
332 ratios of 1:6 (DES3) and 1:8 (DES4) have the potential to be utilized as PCMs in building
333 applications with large latent heat (127.2-135.2 KJ.Kg^{-1}), proper phase change temperature
334 (20.65-23.05 °C), and low-cost. **Based on rough estimates of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (0.25 USD/Kg) and**
335 **ChCl (1 USD/Kg), the cost of DES3 and DES4 is about 0.35 USD/Kg.** Although, the DES3
336 and DES4 suffered from the supercooling and phase segregation, the use of 2 wt% of
337 $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and fumed silica were successful to mend these problems. **It should be also noted**
338 **that these new PCMs can be macro-encapsulated and be used in other applications, since**
339 **micro-encapsulation of hydrated salts was proven to be still difficult [28].**

340 **4. Conclusion**

341 In this work, five new type III DESs were prepared using ChCl as the quaternary ammonium
342 salt and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ as the hydrated salt and their important physico-chemical properties
343 were also measured. It was found that the mole fraction of ChCl has noticeable effects on the

344 freezing temperature, latent heat, density, viscosity and chemical stability of the synthesized
345 DESs (DES1 to DES5). Besides, the potential of using DESs as PCMs in building application
346 were investigated. DES3 and DES4 with a large latent heat of 127.2 and 135.2 KJ.Kg^{-1} , and
347 also a proper phase change temperature of 20.65 and 23.05 $^{\circ}\text{C}$, respectively, were selected for
348 thermal cycling test. The cycling results showed that the supercooling degrees of both DESs
349 were huge and phase segregation occurred after few cycles. Hence, both DESs were required
350 to be modified by using nucleating and thickening agents before utilizing them as PCMs. The
351 experimental results specified that adding 2 wt% of $\text{SrCl}_2.6\text{H}_2\text{O}$ as a nucleating agent reduced
352 the degree of supercooling with an average supercooling degree of 1.47 $^{\circ}\text{C}$ for DES3 and
353 1.23 $^{\circ}\text{C}$ for DES4 over 100 cooling cycles. In addition, the hydroxyethyl cellulose and fumed
354 silica were employed as thickening agents to tackle the phase segregation problem. The
355 hydroxyethyl cellulose was not able to prevent tetrahydrate formation with the different
356 concentrations (0.5, 1 and 2 wt%) investigated. On the contrary, when 2 wt% of fumed silica
357 was used, the cycling results indicated an excellent stability for both DES3 and DES4. These
358 results successfully present the newly prepared DESs as potential PCMs for building
359 applications.

360

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495 **Figures captions:**

496

497 **Fig. 1.** Density of calcium chloride hexahydrate-based DESs as a function of temperature.

498 **Fig. 2.** Viscosity of calcium chloride hexahydrate-based DESs as a function of temperature
499 (1/T).

500 **Fig. 3.** Cooling curves of calcium chloride hexahydrate, DES3 and DES4 (with cooling rate
501 of 0.95 °C.min⁻¹).

502 **Fig. 4.** Cooling curves of DES3 and DES4 with 2 wt% nucleating agent (with cooling rate of
503 0.6 °C.min⁻¹).

504 **Fig. 5.** Phase change Temperature of DES3 with thickening agent during 100 cycles.

505 **Fig. 6.** Phase change Temperature of DES4 with thickening agent during 100 cycles.

506 **Fig. 7.** DSC melting curves for DES3, DES3 with thickening agent and DES3 with
507 thickening agent after 100 cycles.

508 **Fig. 8.** DSC melting curves for DES4 and DES4 with thickening agent after 100 cycles.

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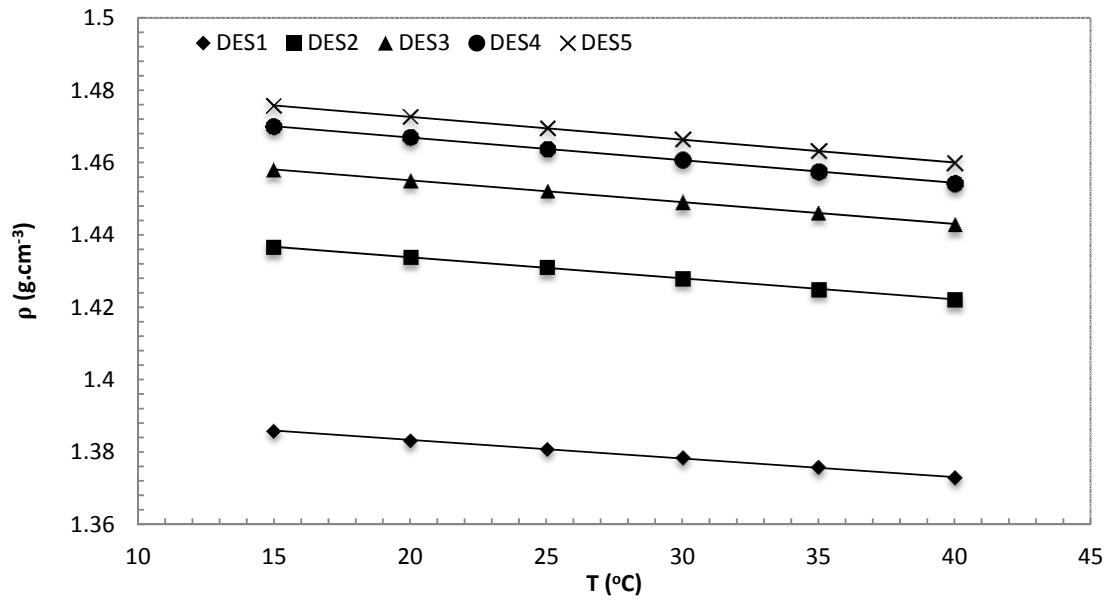
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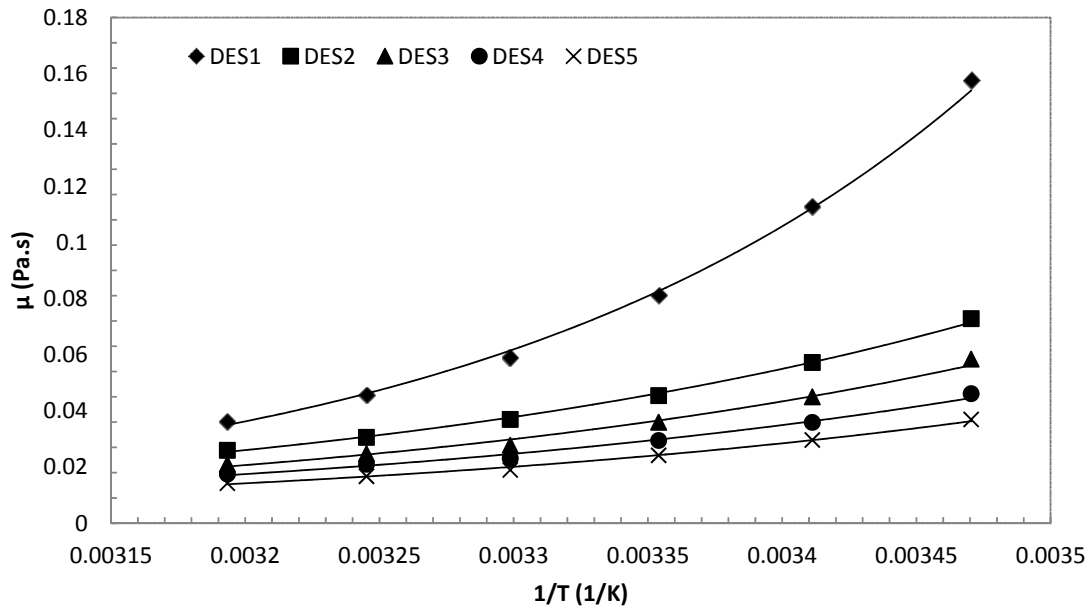
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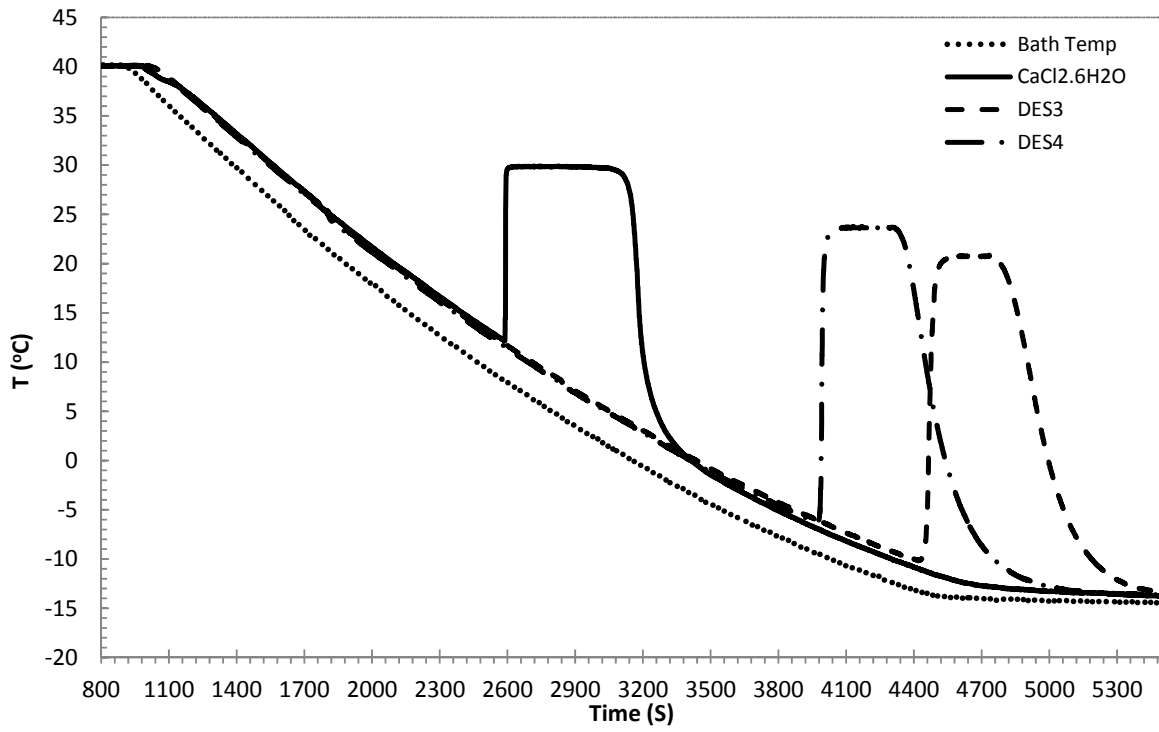
Fig. 1



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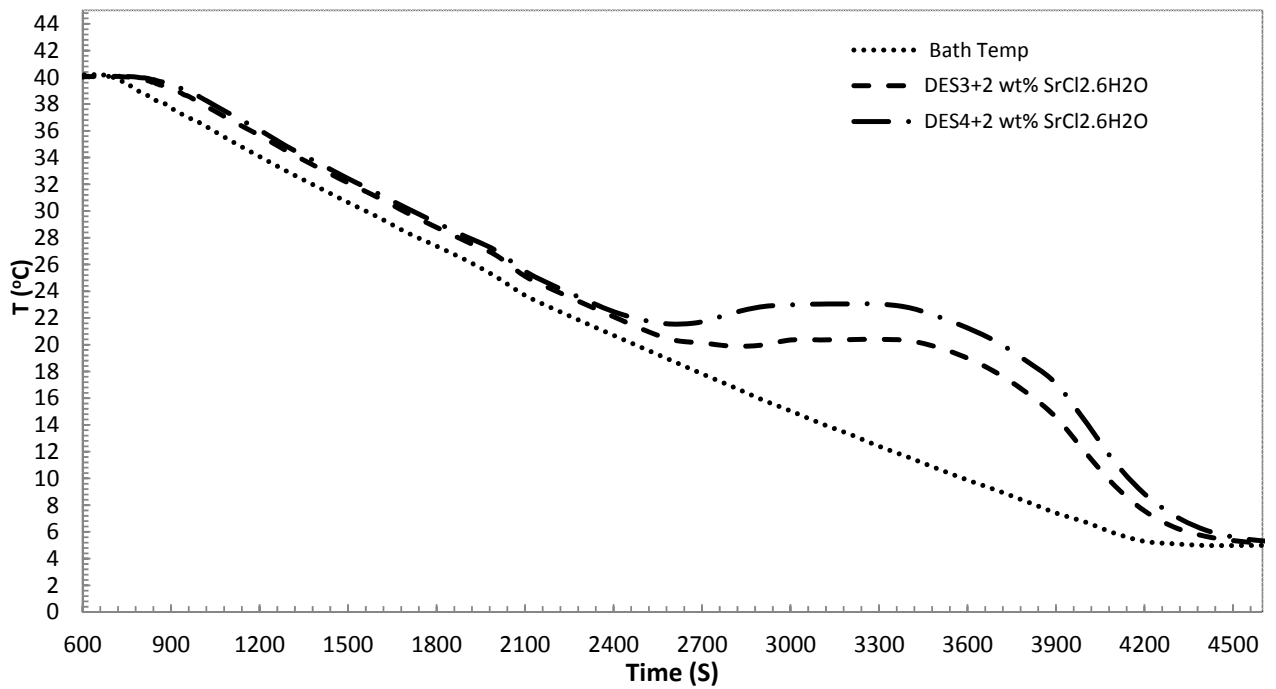
Fig. 2



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Fig. 3

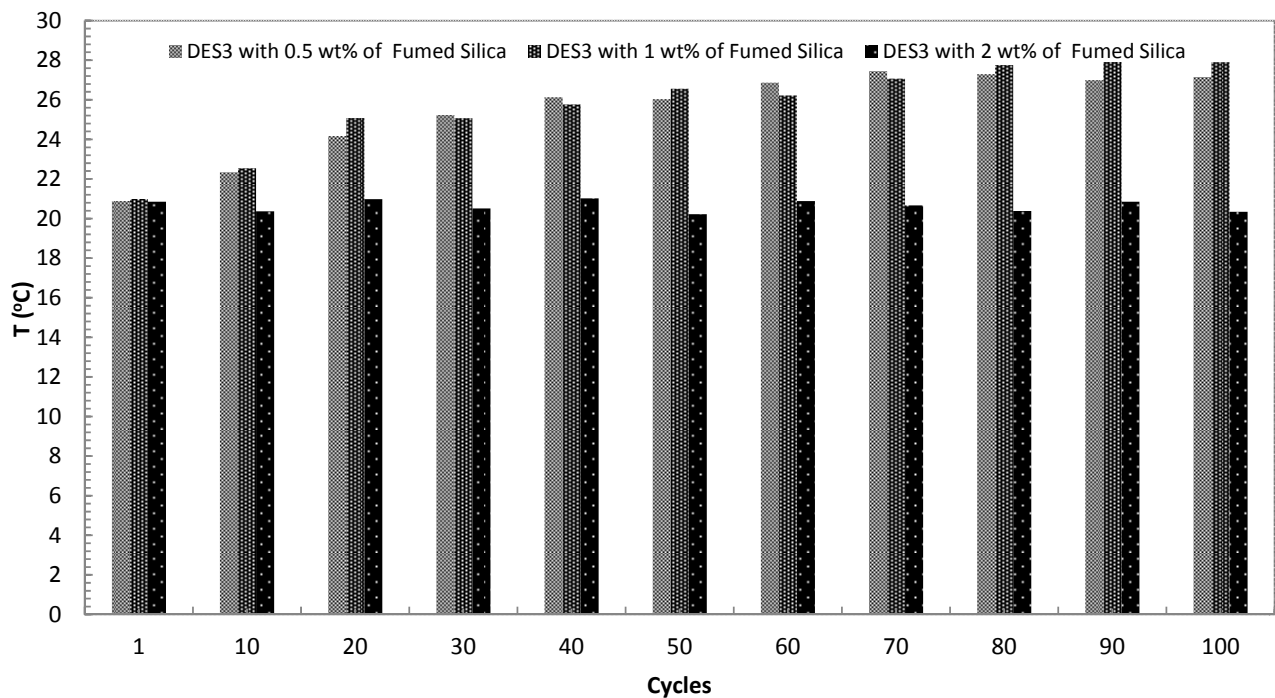


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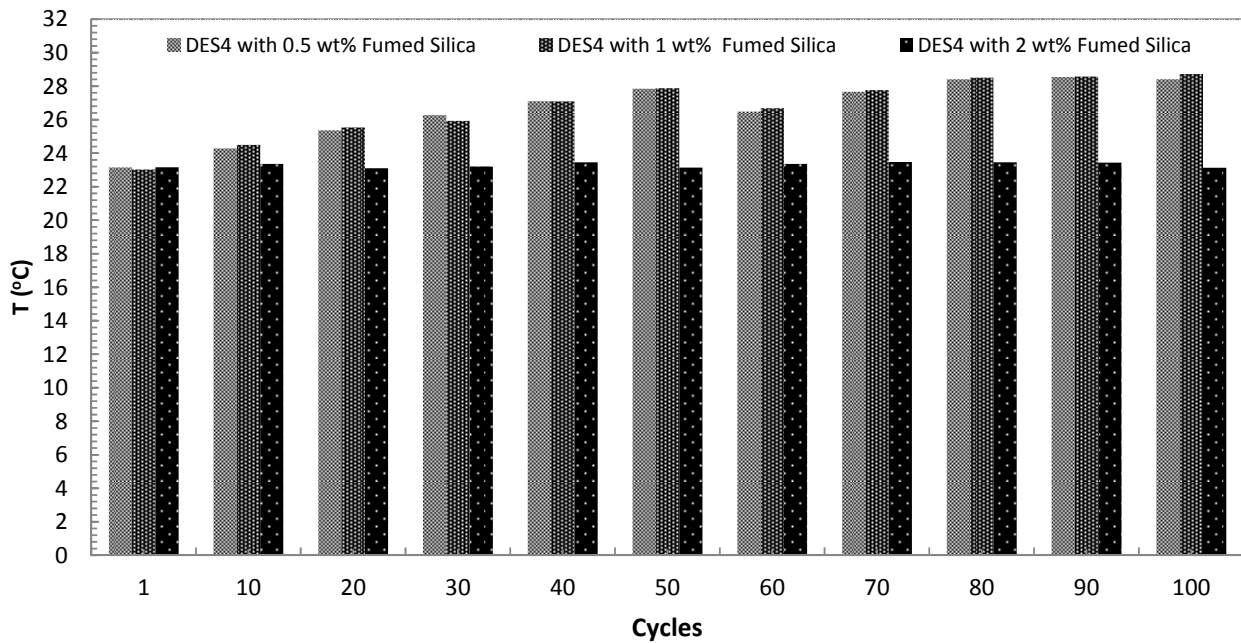
Fig. 4



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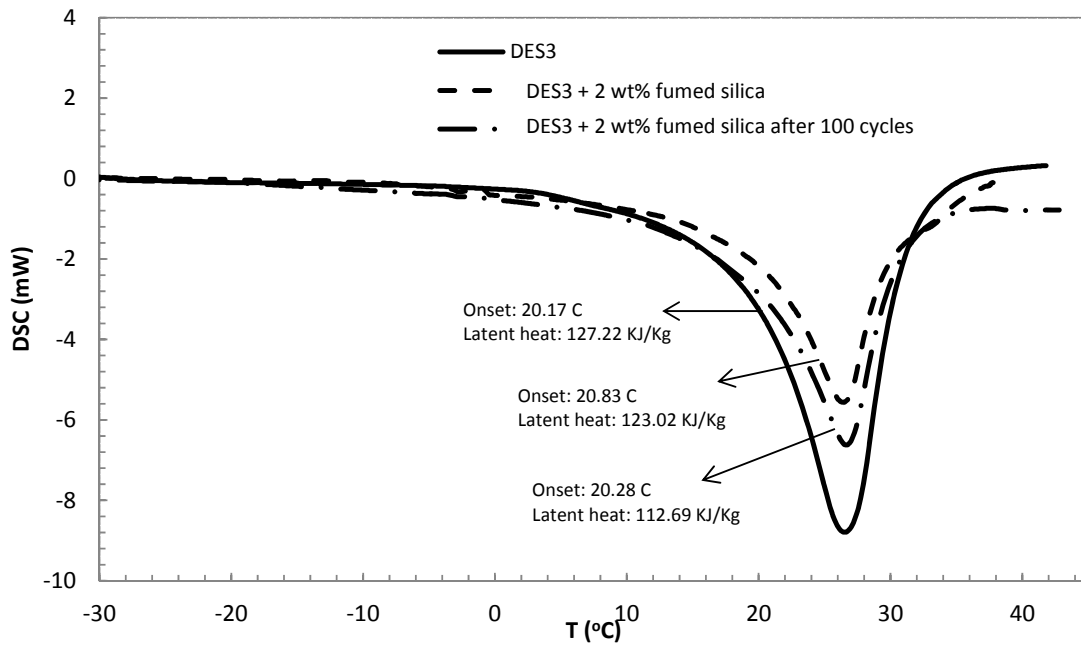
Fig. 5



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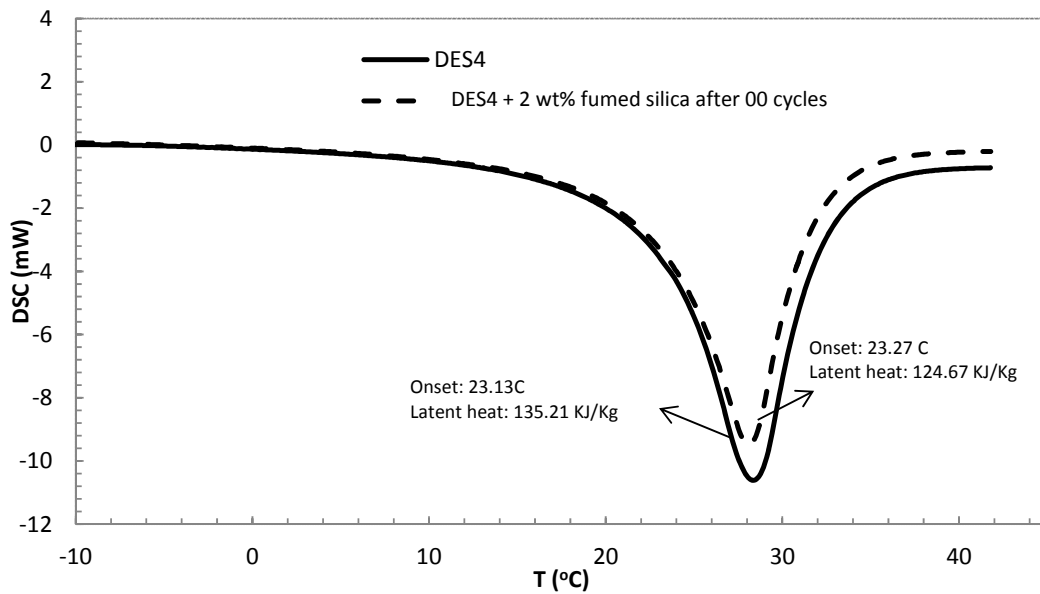
Fig. 6



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Fig. 7



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Fig. 8

546 **Table 1**
 547 Compositions and abbreviations of synthesized DESs.

QAS	Hydrated salt	x_{QAS}	$x_{Hydrated\ salt}$	Abbreviation
		0.34	0.66	DES1
		0.20	0.80	DES2
Choline chloride	Calcium chloride hexahydrate	0.14	0.86	DES3
		0.11	0.89	DES4
		0.09	0.91	DES5

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551 **Table 2**
 552 Values of fitting constants for density and viscosity.

DES	a	b	$\mu_o (Pa.s)$	$E_o (Pa\ m^3\ mol^{-1})$
1	-5×10^{-4}	1.3936	1×10^{-9}	5349.10
2	-6×10^{-4}	1.4454	2×10^{-7}	3736.20
3	-6×10^{-4}	1.4672	1×10^{-7}	3700.00
4	-6×10^{-4}	1.4797	3×10^{-7}	3458.10
5	-6×10^{-4}	1.4853	2×10^{-7}	3471.10

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556 **Table 3**
 557 Freezing temperatures and latent heat of fusion for the synthesized DESs

DES	Freezing Temperature ($^{\circ}C$)	Latent heat (kJ/kg)
DES1	2.70	-
DES2	16.80	100.05
DES3	20.65	127.22
DES4	23.05	135.21
DES5	24.10	146.57

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562 **Table 4**
563 Degree of supercooling of DES3 and DES4 with 2 wt% nucleating agent through the 100
564 cycles.

No. of cycles	Supercooling (°C)	
	DES3	DES4
1	1.23	0.57
10	0.88	0.89
20	0.94	1.04
30	1.22	1.69
40	1.80	1.00
50	0.40	1.49
60	2.12	1.47
70	2.54	2.33
80	1.64	0.75
90	1.71	1.03
100	1.77	1.33

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