SUMMARY AND CONCLUSION
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Salt hydrates have been suggested as one of the most suitable materials for solar energy storage applications. This is due to their favourable properties such as high heats of fusion, low volumetric change, high thermal conductivity and relatively low cost. Their melting points are favourable for space heating/cooling and low grade heat storage applications. However, salt hydrates suffer from two major disadvantages i.e. supercooling and phase segregation. The supercooling in salt hydrates can be reduced to a great extent by the use of nucleating agents and cold finger techniques. Satisfactory solution of the phase segregation problem is yet to be found, inspite of considerable R and D efforts in this direction. Phase segregation in salt hydrates, occurs due to the formation of a lower salt hydrate or anhydrous salt during heating and cooling cycles. In a few cases, such as Na$_2$SO$_4$·10H$_2$O and Na$_2$CO$_3$·10H$_2$O, phase segregation is due to decrease in the solubility of anhydrous salt with rise in temperature above the transition temperature. The loss of water of crystallization during heating/cooling cycles may also contribute towards phase segregation of salt hydrates. When a salt hydrate is heated, its water of crystallization comes out from its lattice and the basic salt dissolves in this water of
crystallization resulting in the melt formation. Vapour pressure of water increases with temperature and some water of crystallization change into vapour with the increase in temperature of the melt. These vapours fill the space above the melt. An equivalent amount of anhydrous salt settles to the bottom. The condensed vapours do not diffuse completely to the lower layers of the anhydrous salt resulting in the formation of lower salt hydrate or anhydrous salt. The amount of anhydrous salt formed increases with each successive cycle. Various methods suggested by research workers for prevention of phase segregation are the use of thixotropic thickening agent, rotating mechanism and extra water principle.

In the present investigation, an effort has been made to study the behaviour of salt hydrates on heating, in order to study the mechanism of loss of water of crystallization. It further aims to establish a criterion to determine the thermal stability of salt hydrates. The selection of salt hydrates was based on the criteria of high heats of fusion, appropriate melting points for low grade heat storage, low volume change, high thermal conductivity, easy availability in large quantities at low cost. In the selection, care has also been taken to include salt hydrates belonging to
different groups such as congruent, semi-congruent and incongruent melting. On the basis of the above criterion, the salt hydrates, namely NaOH·H₂O, NaCH₂COO·3H₂O, Na₂CO₃·10H₂O, Na₂SO₄·10H₂O and Na₂HPO₄·12H₂O were selected.

Differential thermal analysis technique combined with thermogravimetry has been used to study the kinetics of dehydration of salt hydrates on heating. Kinetic parameters such as mechanism and energy of activation of these salts have been determined and discussed in chapter V. Some of the thermophysical properties such as heat of fusion, density and viscosity, which have profound effect on storage density and crystallization behaviour have been determined and discussed in chapter IV&V. Generalized correlation for viscosity and density as function of temperature have been reported in chapter V.

The evaluation of thermal analysis results given in chapter V show that these salt hydrates lose appreciable amount of water of crystallization when heated above their melting points. In the case of NaCH₂COO·3H₂O, nearly 13 percent loss of water of crystallization has been observed with a temperature swing of 25°C above its melting point. Na₂SO₄·10H₂O, Na₂CO₃·10H₂O, Na₂SO₄·5H₂O and Na₂HPO₄·12H₂O loses water
to the extent of 5, 3.5, 4 and 4.5 percent respectively. However, in the case of NaOH$_2$O, no loss of water has been observed up to a temperature swing of 25°C above its melting point. These observations indicate that a considerable loss of water of crystallization at small temperature swings above the melting point could be responsible for the degradation of salt hydrates. This problem becomes severe when salt hydrates are subjected to large number of heating and cooling cycles. This observation also leads to the conclusion that in the thermal energy storage systems using salt hydrate, charging temperature should not exceed beyond 10 to 15°C above the melting temperature. The sensible heat storage component of the salt hydrate should be kept low. However, in the case of NaOH$_2$O this range can be extended due to the better stability of this material even at temperature swing of 25°C above its melting point. The thermogram of these salt hydrates show that dehydration of salt hydrates takes place in more than one stage. For example in the case of Na$_2$SO$_4$.5H$_2$O, Na$_2$CO$_3$.10H$_2$O and Na$_2$HPO$_4$.12H$_2$O, the dehydration occurs in two stages with the formation of intermediate salt hydrates. However, in the case of NaOH$_2$O, NaCH$_2$COO.3H$_2$O and Na$_2$SO$_4$.10H$_2$O the dehydration of salt hydrate gets completed in one stage only.
The kinetics of dehydration of these salts has been evaluated by using integral methods suggested by Coats & Redfern and Zsako. Different mechanisms have been tested to arrive at the best possible mechanism which can explain a specific dehydration mechanism. The mechanisms based on phase boundary movement, diffusion and random nucleation and growth of the decomposition of solids have been considered in the present investigation. The results obtained by the use of these integral techniques show that it is not possible to isolate a single mechanism for explaining the process of dehydration, because more than one mechanisms fit the experimental data. This necessitates the need for establishing another criterion, which could help in deciding the controlling mechanism of the dehydration process, for the salt hydrates under investigation.

It has been proposed that enthalpy of dehydration of salt hydrates could be used as an added parameter for deciding the controlling mechanisms. This is based on the assumption that dehydration of salt hydrates is similar to that of vapourization of water from a liquid pool. This in turn suggests that the enthalpy of dehydration of salt hydrate should be greater than the latent heat of vaporization of water. The enthalphy of dehydration (\(\Delta H\)) of these salt hydrates have been determined by using the modified Vanthoff's equation.
proposed by Stepin et al. On the basis of the
criterion, proposed, $E_{act} = \Delta H$, the mechanism and the
energy of activation ($E_{act}$) values of the various
reactions of salt hydrates were determined and are
reported in table (5.24) of chapter V. These results show
that energy of activation is lowest in the case of
$\text{NaCHCOO}_3\text{H}_2\text{O}$ and highest for $\text{NaSO}_4\cdot 5\text{H}_2\text{O}$. On the
basis of the energy of activation values, the thermo-
kinetic stability of the salt hydrates studied was
proposed as:

$$
\text{NaCHCOO}_3\text{H}_2\text{O} < \text{NaOH}_2\text{H}_2\text{O} < \text{NaSO}_4\cdot 10\text{H}_2\text{O} < \\
\text{NaSO}_4\cdot 5\text{H}_2\text{O} < \text{NaCO}_3\cdot 10\text{H}_2\text{O} < \text{NaHPO}_4\cdot 12\text{H}_2\text{O}. \quad \text{(Scheme A)}
$$

However, on the basis of the water loss, the
thermal stability of the salt hydrates was proposed in
the following order:

$$
\text{NaCHCOO}_3\text{H}_2\text{O} < \text{NaSO}_4\cdot 10\text{H}_2\text{O} < \text{NaHPO}_4\cdot 12\text{H}_2\text{O} < \\
\text{NaSO}_4\cdot 5\text{H}_2\text{O} < \text{NaCO}_3\cdot 10\text{H}_2\text{O} < \text{NaOH}_2\text{H}_2\text{O}. \quad \text{(Scheme B)}
$$

Comparing the sequence shown in Scheme A and B it
is observed that there is some conflict about the
position of the salt hydrate. In view of this anomaly,
it was found that the ratio of percent water loss to the
energy of activation could be a more suitable criterion.
The ratios of percent water loss to the energy of
activation of the salt hydrates investigated, in the present work, are reported in table (5.25). Higher values of this ratio mean low thermal stability and the lower values indicate high thermal stability. This ratio is the highest in case of NaCH CO0.3H 0 and lowest in case of NaOH H 0. Other salt hydrates have values in between these two. On the basis of the above criterion, the thermal stability of the salt hydrates has been proposed as under:

NaCH CO0.3H 0 < Na SO.10H 0 < Na HPO.12H 0 < Na CO.10H 0 < Na S0.5H 0 < NaOH H 0.

This, further concludes that NaOH H 0 and Na S0.5H 0 are more suitable salt hydrates for thermal storage applications. The above information may also be useful for judging the demand of extra water, qualitatively, to be added to the storage system. The extra water requirement will be more in the case where the ratio of water loss to energy of activation is high and the demand of extra water will be less where this ratio is low.

The heat of fusion, densities and viscosities of these salt hydrates were also determined. The experimental values of heats of fusion are reported in table (4.8) and are comparable to the values reported
Densities of the molten salt hydrates, at different temperatures determined in the present investigation, are reported in Table (A.9) and show that density decreases with increase in temperature. The variation of density with temperature is linear, as is obvious from the Figs. (5.42) and (5.43). The linear relationship of density with temperature can be written as

\[
P = a - bT
\]

(5.10)

where \(a\) and \(b\) are the salt specific coefficient and \(T\) is the temperature in \(^\circ\)C.

A generalized correlation for determining the density of salt hydrates at different temperatures above their melting points has been proposed. This correlation can be represented by the equation:

\[
\frac{P}{P_M} = 1 + \beta \left( \frac{T}{T_M} - 1 \right)
\]

(5.11)

This correlation was tested with the data available in literature for the salt hydrates other than salt hydrates considered in the present work. The result reported in Table (5.32) shows that the density values of the salt hydrates obtained from this correlation are accurate within \(\pm\) 0.5 percent in the temperature range of 40 to 50 \(^\circ\)C above the melting point. At higher temperature, deviations in the density values increase. This can be attributed to the fact that the salt
hydrates lose considerable amount of water of crystallization at higher temperatures.

Viscosity of these salt hydrates was also measured as a function of temperature. The temperature range was limited to 40 above the melting point of the individual salt, because salt hydrates have a tendency to lose water at higher temperatures. The results show that like liquids, the viscosities of molten salt hydrates decrease non-linearly with increase in temperature. However, the plot of \( \log \eta \) vs \( 1/T \) is linear. This linear relationship is consistent with the equation published by Andrade [5] to express the change of viscosity of a liquid with temperature and is analogous to the equation proposed by Arrhenius. The Arrhenius relation between viscosity and temperature can be expressed by the equation

\[
\eta = Z' \exp \left( \frac{E_{\text{vis}}}{RT} \right)
\]

The slope of the plot between \( \ln \eta \) vs \( 1/T \) gives the value of energy of activation of viscous flow \( E_{\text{vis}} \). The values of \( E_{\text{vis}} \) for the salt hydrates studied in the present investigation are given in Table (5.2).

In the present work, an attempt has been made to develop a generalized correlation between viscosity of the salt hydrates and temperature, so as to develop a unified relationship between temperature and viscosity.
for a group of salt hydrates rather than salt specific equations. The proposed correlation is:

\[ \frac{\eta}{\eta_m} = 0.09797 \exp\left[-10.95(\Delta T/T)\right] \] (5.9)

where \( \eta \) is the viscosity of salt hydrate at its melting point \( T \) and \( \Delta T \) is \( (T - T_m) \) i.e. departure from melting point. \( T_m \) is the temperature at which viscosity is to be measured. The results reported in table (5.28), show that the above correlation predicts viscosity within an accuracy of \( \pm 5 \) percent. The deviation increases with increase in temperature. This may be attributed to the loss of water of crystallization at higher temperatures. This correlation was also tested with the literature values of salt hydrates other than those studied on the present work. The results were predicted with 5 percent of the experimental values. Hence the generalised correlation of viscosity, as stated above, can be used to determine viscosities of salt hydrates at temperatures up to 40°C above their melting points.

The present work has thus filled the gap in the availability of physicochemical properties of salt hydrates. The generalised correlations developed will help in the generation of reliable density and viscosity data without rigorous and time-consuming experimentation.
Finally, it can be concluded that the new criterion proposed, may prove to be an important landmark in the methodology for the selection of salt hydrates in thermal storage applications. The present study provides a deeper insight into the kinetics of dehydration of salt hydrates. It has reduced, to a large extent, the controversies associated with the selection of mechanism for the dehydration reactions. The mechanism proposed by the new model fit the experimental data more closely than those predicted by earlier models.