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Polymers in Molten Inorganic Salt Hydrates Phase Change Materials: Solubility and Gelation

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Abstract

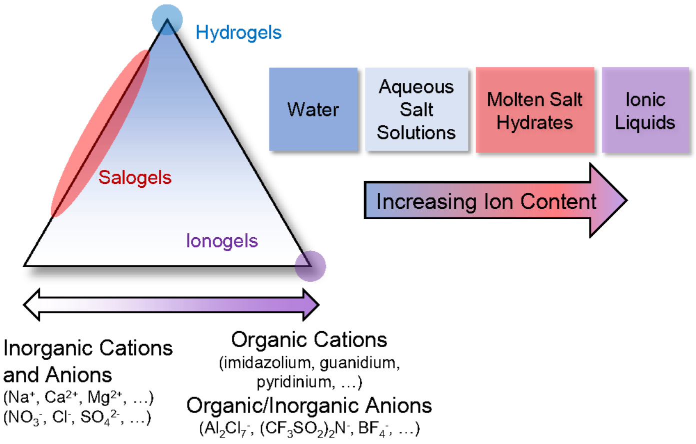
Inorganic salt hydrates are of interest as phase change materials (PCMs) for thermal energy storage because of their unique properties such as high latent heats of fusion, moderate melting temperatures, high volumetric energy storage density, and enhanced thermal conductivity compared to their organic counterparts. Because of the low viscosity of molten salt hydrates, leakage and settling of solids can easily occur during their application. Polymers are promising candidates for preventing these issues. In addition, non-flammability, non-volatility, and nontoxicity of many molten salt hydrates make them attractive as “green” solvents for polymers. However, solutions of polymers in molten salt hydrates are rarely studied and poorly understood. The highly ionic environment in these materials created by scarcity of hydration water for ions leads to strong ionic interactions which has ramifications for polymer solubility and chain expansion. This *Perspective* aims to focus on polymer solutions and gels in inorganic salt hydrates by comparing these with the existing knowledge on polymers in traditional ionic liquids and aqueous salt solutions. To provide insight on the state of ions and water in molten salt hydrates and the degree of hydration of polymers in these solvents, infrared spectroscopy experiments are performed, and the data are correlated with temperature-responsive gelation of poly(vinyl alcohol) -- one candidate currently used for shape stabilization of inorganic PCMs. Finally, the thermal properties of inorganic salt hydrates and ionic liquids are compared and strategies for shape stabilization of inorganic salt hydrates using polymers by forming physical gels are discussed.

1. Introduction

Inorganic salt hydrates are getting significant attention as phase change materials (PCMs) due to their high latent heats of solid-to-liquid transitions, moderate melting temperatures (often below 100 ˚C), and volumetric energy storage density of 200 to 450 MJ/m^3.[1-4] In addition, non-flammability and high thermal conductivity of approximately 0.5 W/m °C in the liquid phase, exceeding those for organic PCMs, such as paraffins,[4-7] make these materials advantageous for thermal energy storage applications.[8-10,11, 12] However, the low viscosity of inorganic salt hydrates in their molten state can result in leakage, separation of liquid PCMs from heat exchanger surfaces, and creation of internal void space, resulting in sub-optimal heat transfer.[13-16] Shape stabilization of salt hydrate PCMs using polymers is thus an important aspect for potential use in heat storage modules. [15-19] Furthermore, in the case of buoyancy-driven phase segregation from incongruently melting salt hydrates, shape stabilization has been used to partially mitigate the deterioration of thermophysical properties.[20] Therefore, an understanding of interactions between the polymer and the components of inorganic salt hydrate PCMs is necessary to develop robust shape stabilization strategies using polymers for thermal energy storage applications.

Recently, molten salt hydrates have been increasingly used as solvents for polymer or organic compounds and as part of deep eutectic solvents (DESs) -- aqueous salt hydrates.[21-25] This recent interest is largely due to the unique ability of molten inorganic salt hydrates to solubilize polymers based on cellulose, as well as non-volatility, non-flammability, and ease of recycling/separation achieved with these "green" solvents. These features along with the highly ionic environment resemble those found in traditional ionic liquid (ILs) -- ionically conductive, non-flammable, non-volatile, and thermally stable solvents with low melting points.[26-29] However, unlike molten inorganic salt hydrates, common ILs do not contain water and are composed entirely of ions.[23-25] The special features of molten salt hydrated as solvents stems from the fact that they contain high concentration of inorganic ions dissolved in water which is released from the crystalline structure of the salt upon melting. Such solvents represent a transition region between aqueous salt solutions and molten salts.[30, 31] Scarcity of water and incomplete hydration of ions in molten salt hydrates results in most of the water being coordinated at the cation, giving rise to low water activity, and increased viscosity compared to aqueous solutions of these salts.[30] Interactions between polymers and ions have been explored for traditional ILs, motivated by the applications in polymer thin-film transistors,[32] fuel cells,[33] and gas separation membranes,[34] or in aqueous salt solutions with abundant water.[35-40] In contrast, much less is known about polymers in molten salt hydrates.

This *Perspective* aims to focus on polymer solutions and gels in molten inorganic salt hydrates (molar water/salt ratio <7 for Li^+, Mg^{2+}, and Ca^{2+} salts).[30] This angle differentiates this work from several manuscripts focused on solubility and gelation of polymers in aqueous salt solutions (molar water/salt ratio >7),[35-38] polymer-free molten salt hydrates,[4, 7, 41-43] or polymer solutions in traditional ILs. [27, 44-46] To place this work in the context of the existing knowledge on solubility and gelation of polymers in related solvents, we compare the relevant literature on polymer solvation and gelation in traditional ILs and aqueous salt solutions (**Scheme 1**). We then discuss the unique features that the presence of both high concentration of salt ions



Scheme 1. Types of ionic solvents and corresponding polymer gels.

and scarcity of water molecules bring in for polymer chain solubilization in molten salt hydrate solvents, which results in competition for water for hydration of salt ions and polymer chains. We emphasize that molten salt hydrate solvents bring in distinctive behavior of dissolved polymer chains – such as physical gelation (i.e. the formation of salogels) of polymers which do not gel in aqueous solutions, and temperature responsiveness of the polymer salogels useful for applications of salt hydrates as PCMs.[19] A recent publication also demonstrated that a molten salt hydrate (such as lithium nitrate trihydrate, LNH) can be a better solvent than water for a neutral polar polymer, such as poly(vinyl alcohol), PVA.[47] This *Perspective* expands these studies to salt hydrate solvents other than LNH, and focuses on differences in solvation, expansion, and gelation of polymer chains in molten salt hydrates while comparing them with more common polymer solvents, such as traditional ILs or water. We believe that an improved understanding of solubility and gelation properties of polymers of diverse chemical nature in various molten salt hydrate solvents can facilitate their use as "green" solvents in their undiluted form or as a component of aqueous-salt-hydrate-based DESs, as well as enable wider applications of inorganic salt hydrates in thermal energy storage. To provide a contrast and comparison with well-studied polymer solution systems, the section below briefly discusses solubilization of polymer chains in traditional ILs and aqueous solutions prior to focusing on solutions of molten inorganic salt hydrates.

2. Polymers in ILs, aqueous solutions and molten salt hydrates

2.1. Polymers in traditional ILs

ILs are composed entirely of ions – often a bulky organic cation and a smaller organic or inorganic anion (such as $Al_2Cl_7^-$, $(CF_3SO_2)_2N^-$ or BF_4^-) (**Table S1**)– and are typically liquids at room temperature.[48] These chemically stable, non-volatile solvents have been used for polymer synthesis[49, 50] or for enhancing ionic transport in polymer electrolytes.[51, 52] Solubility of polymers in ILs is dependent on interactions of polymer chains with cationic or anionic constituents of IL solvents, which are determined by the chemical structure and Lewis acidity and basicity of IL cations and anions.[26, 53] The diversity of ILs provide different hydrophobic/polar properties, aromaticity, acidity/basicity of IL's ions yielding a wide range of binding modes with polymer chains, such as dispersive, π-π stacking and/or hydrogen bonding interactions.[54, 55] The occurrence of these interactions often leads to negative values of entropy of mixing, resulting in lower critical solution temperature (LCST) behavior.[56] Because of the low absolute values of entropy and enthalpy of mixing, phase behavior in polymer-IL systems can be easily tuned through chemical composition of IL solvents.[57]

One of the most explored polymer-IL systems is poly(ethylene oxide) (PEO) (or poly(ethylene glycol), PEG) in imidazolium-based ILs. In these systems, hydrogen bonding between hydrogen atoms on the C2 position of the imidazolium ring and oxygen atom of PEO/PEG leads to efficient solvation and solubilization of polymer chains.[58-66] The presence of hydrogen bonds between polymer chains and the imidazolium cations was recently shown using high-energy X-ray diffraction technique, and also demonstrated by molecular dynamics simulation.[66] As a result of solvation of PEO chains in imidazolium-based solvents, good solvent conditions, with chain expansion larger than in water, were predicted in computational studies [59, 61, 65] (**Fig. 1(a)**) and revealed by small-angle neutron scattering (SANS).[59]

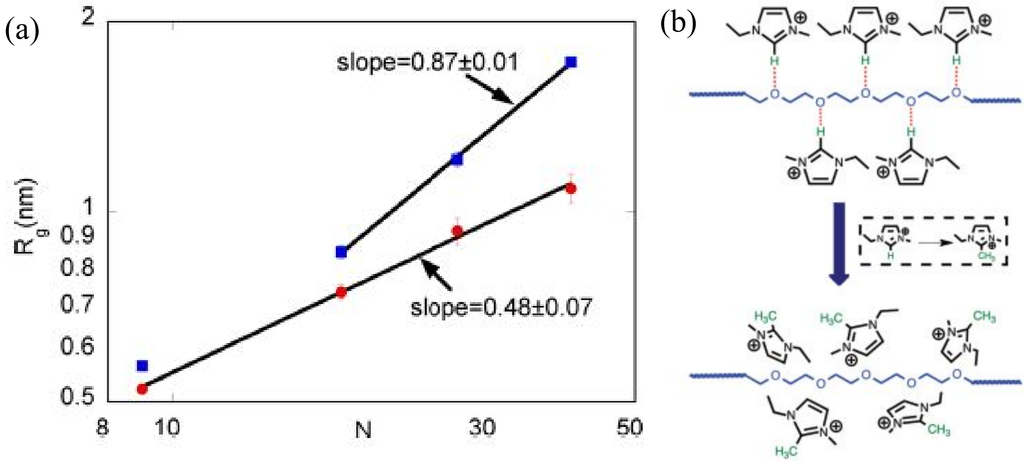


Fig. 1. (a) Simulation results for the variation of radius of gyration (R_g) of PEO with degree of polymerization N in water (red circles) and [BMIM][BF_4] (blue squares). Reproduced from ref. 65. (b) Effect of hydrogen bonding between the hydrogen atoms on the C2 position of imidazolium ring and oxygen of PEO. Reproduced from ref. 67.

Changes in basicity of anion and alkyl length of a cation in imidazolium-based ILs were demonstrated to have a significant effect on the phase behavior (i.e., the solubility and LCST transition temperature) of polymers in ILs.[62] Replacing the acidic proton in the imidazolium ring with a methyl group lowers its hydrogen bond forming capability with PEO chains, leading to a decreased miscibility between IL and PEO (**Fig. 1(b)**) and lowering of LCST transition temperatures.[67] Furthermore, varying the alkyl chain length of 1-alkyl-3-methylinimidazolium cations in ILs enabled tuning of the transition temperature by more than 100 °C.[64, 68, 69]

The chemical structure of polymers also has a dramatic effect on the phase behavior of polymer-IL systems. In the case of polymers with alkyl side groups, such as poly(n-butylmethacrylate) (PnBMA), lengthening of the alkyl chain of IL cations can strengthen inter-IL and/or polymer/IL interactions, increasing enthalpy of mixing and raising LCST transition temperature.[70] Additionally, LCST behavior can be induced by interactions of aromatic moieties in polymer chains with salt ions of ILs.[71-73] For example, in solutions of poly(benzyl methacrylate) in imidazolium-based ILs, cation−π interactions between aromatic rings of the polymer and IL cations create a structurally ordered solvation layer, leading to reduction of entropy of mixing and the resultant LCST behavior.[74-77] The phase transition temperature in these systems was also dependent not only on the alkyl length of the cation, but also on the anion type.[74]

In addition to LCST, ILs can also enable upper critical solution temperature (UCST) behavior in polymer solutions. For example, a temperature-responsive polymer – poly(N-isopropylacrylamide), PNIPAM – which exhibits a well-known LCST behavior in aqueous solutions, switches to enthalpy-driven UCST behavior of PNIPAM in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide, [EMIM][TFSI].[78] The emergence of UCST behavior was explained on the basis of weak Lewis acid/base interactions between PNIPAM and [EMIM][TFSI] resulting in lower solubility due to existence of hydrogen bonding between PNIPAM units at lower temperatures. Later in this manuscript, we will discuss an analogy of such a behavior with that observed in solutions of a different polar polymer in molten salt hydrates.

2.2. Polymers in aqueous solution

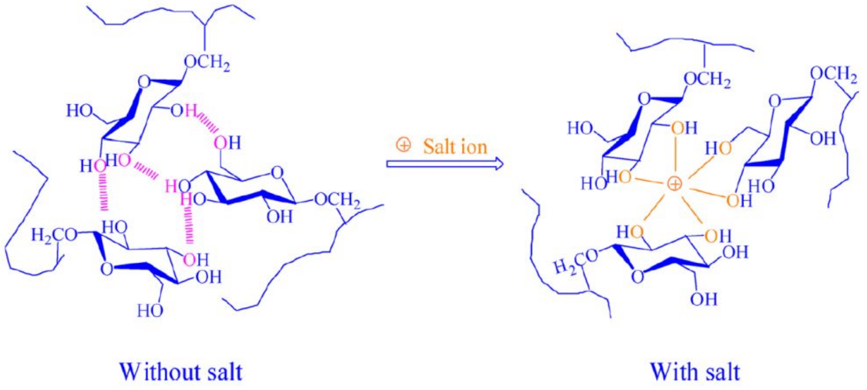
In contrast to traditional ILs, where the polymer-ion interactions are solely responsible for polymer solubility, aqueous salt solutions contain abundant water in addition to the salt ions. In this scenario there are additional interactions which need to be considered, namely water/ion, polymer/ion, and water/polymer interactions. These interactions compete with polymer/polymer interactions and, depending on the specific salt species, can either increase polymer solubility or can result in precipitation. The effect of salt on polymer solubility is often described by the

Hofmeister series,[35-38] with a typical order of anions ranging from kosmotropes which "make" water structure (left) to chaotropes which "break" such a structure (right):

$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^{-} > F^{-} > Cl^{-} > Br^{-} \approx NO_3^{-} > I^{-} > ClO_4^{-} > SCN^{-}$

Kosmotropes were demonstrated to weaken hydrogen bond interactions between polymer and water molecules for LCST polymer PNIPAM, resulting in a decrease in LCST transition by the salting-out mechanism. In contrast, chaotropes directly interact with polymer chains and increase their solubility through the salting-in path.[39, 79-81] The effects of salt ions on phase separation of PNIPAM was explained via three types of interactions: (a) anion-induced polarization of hydrogen-bonded water molecules at the amide group; (b) modulation of the surface tension associated with the hydrophobic hydration of the polymer by salt, and (c) direct interaction of the amide group with the anions.[39] In the case of kosmotropic ions, polarization of water by the anion weakens hydrogen bonding between water and amide groups, leading to dehydration of amide and a decrease of LCST. Chaotropes increase surface tension of the water/hydrophobic interface and bind strongly to the amide group compared to kosmotropes, leading to an increase of LCST. The opposite, UCST transitions are much more rare in aqueous solutions, thus there are only fewer studies focusing on the salt effect.[82-85] In one example, UCST transition temperature increased in branched polyethylenimine solutions after addition of halide salts as a result of protonation of the amine groups and the salting-out effect in the presence of high salt concentrations.[84]

Understanding of ions and polymer solvation, and interaction between ions and polymer in the presence of water are crucial for a range of applications that involve aqueous environment, including water purification, ion-separating membranes, and biological applications such as drug delivery and anti-bacterial applications of polymer-metal ion complexes.[40, 86] Yet another application where understanding of polymer-ion interactions are essential involves the use of associative polymers in fracking.[87, 88] Polyacrylamide (PAM) and its copolymers containing vinyl glucoside,[88] sulfonate,[89, 90] sulfonic acid,[91] and ammonium[92] functional groups are typically used in this application. For PAM modified with vinyl glucoside salt induced thickening in the presence of NaCl, Ca(Cl)$_2$, and Mg(Cl)$_2$ salts was attributed to the interaction between cations and hydroxyl moieties on the glucose backbone (**Fig. 2**).[88, 93] Cation-hydroxyl interactions have been demonstrated for other salt-polymer combinations as well.[19, 94, 95] In addition, cations (Na$^+$ and Ca^{2+}) were also shown to interact with oxygen in C-O bond of PEO side chains of sulfonate-modified PAM copolymer. Such ion binding, along with hydrophobic interactions between polymer units were demonstrated to be responsible for salt induced thickening of this copolymer.[90]



Without salt

With salt

Fig. 2. Schematic showing interaction between cations and hydroxyl groups on glucose as the proposed mechanism for viscosity increase in a PAM-vinyl glucoside copolymer. Reproduced from Ref. 87.

While the studies described in this section comprise a useful foundation for an understanding of interactions of salt ions with polymers in the presence of water, most experiments conducted in aqueous salt solutions were performed at salt concentrations much lower than those found in molten salt hydrates (see Table 1) and thus do not incorporate the case of the most interest for this *Perspective*, *i.e.* interactions of polymers with solvent ions when the latter are not fully hydrated.

2.3. Molten salt hydrates as polymer solvents

In contrast to typical ILs or typical aqueous salt solutions, solubility, and phase behavior of polymers in molten inorganic salt hydrates are poorly studied. Most of the earlier experimental data are related to the use of polymers as thickeners for inorganic salt hydrates during their exploitation as PCMs.[9, 96-101] These studies focused on preventing phase separation of inorganic salt hydrate PCMs during thermal cycling using a superabsorbent polymer[9, 97] made from polyacrylic acid copolymer,[9] starch,[9, 96] bentonite,[96] cellulose,[96, 98-100] and xanthan gum[101] along with nucleation additives to reduce supercooling. However, an understanding of the main factors governing behavior of polymer chains in molten salt hydrates has not yet emerged.

2.3.1. Contact pairing vs. ion hydration in concentrated salt solutions

In comparison with traditional ILs, salt hydrates are composed of much smaller inorganic ions, and additionally contain water as part of the structure. Stoichiometric salt hydrates are generally shown as $AB\cdot n(H_2O)$, where AB are the salt ions and n is the number of water molecules per salt molecule, the amount of which is controlled by the size and charge of ions.[102] Melting of a crystalline salt hydrate, which contains ions coordinated by water molecules in a crystalline structure, results in a highly concentrated liquid brine, where water molecules primarily occur within the hydration shells of dissolved cations.[30, 31] The differences in the state of water in molten salt hydrates as compared to bulk salt-free water solutions can be clearly observed by vibrational spectroscopy.[19] In our recent work, we observed different states of bound water within solvation shells of ions in deuterated lithium nitrate tri-hydrate (LND), in comparison with bulk water using ATR-FTIR spectroscopy.[19] The use of deuterated rather than hydrogenated molten salt hydrates was pursued keeping in mind that vibrational features of the solvent should be separated from those of hydrogenated polymers during studies of polymer solutions and gels. Hydrogen bonding between water molecules can be studied but the analysis of -OD stretching modes associated with different strength and size of hydrogen-bonded water clusters. **Fig. 3** illustrated the drastic difference in the -OD stretching vibrational modes for the polymer-free bulk water, molten LND and deuterated calcium nitrate tetrahydrate (CND). Deconvolution of -OD peak of D_2O performed based on Sun's sub-bands theory showed that at room temperature the hydrogen bonding network of water consists of five bands.[103] These clusters can be classified as strongly and weakly hydrogen bonded and include the following modes shown in **Fig 3(a)**: single donor double acceptor (DAA, strong, 2300 cm^{-1}), double donor double acceptor (DDAA, strong, 2385 cm^{-1}), single donor single acceptor (DA, weak, 2479 cm^{-1}), double donor single acceptor (DDA, weak, 2574 cm^{-1}), and free -OD (2668 cm^{-1}) vibrational modes.[103] The stronger hydrogen bonding modes are believed to result in larger hydrogen bonding network clusters due to maximization of the number of hydrogen bonds that a water molecule can form while forming a stable structure.[104, 105] This results in a red shift in the -OH stretching modes as strong hydrogen bonds result in shorter intermolecular distances as has been predicted using ab initio calculations.[104] As seen in **Fig. 3,** the fractional area of DDAA band characteristic of strong hydrogen bonding and most abundant in bulk water was drastically reduced in salt hydrates. **Fig. S1** presents quantification of the hydrogen bonding -

OD modes in LND and CND upon dilution with D_2O. As salt concentration increased from pure D_2O to LND/CND, the larger hydrogen bonding networks (DDAA and DAA) were broken and formed smaller networks (DA and DDA). This result emphasizes that the ions' first hydration shell does not contain enough water for complete hydration in LND/CND. In addition, the blue shift observed for all the bands in molten LND and all but one in CND indicated weakening of the water-water hydrogen bonding due to increased interaction with ions in molten salt hydrates (**Table S2**). Taken together, the ATR-FTIR analysis of -OD vibrational range reveals that the hydrogen bonding of water in molten salt hydrates is dramatically different from that in dilute aqueous salt solutions.

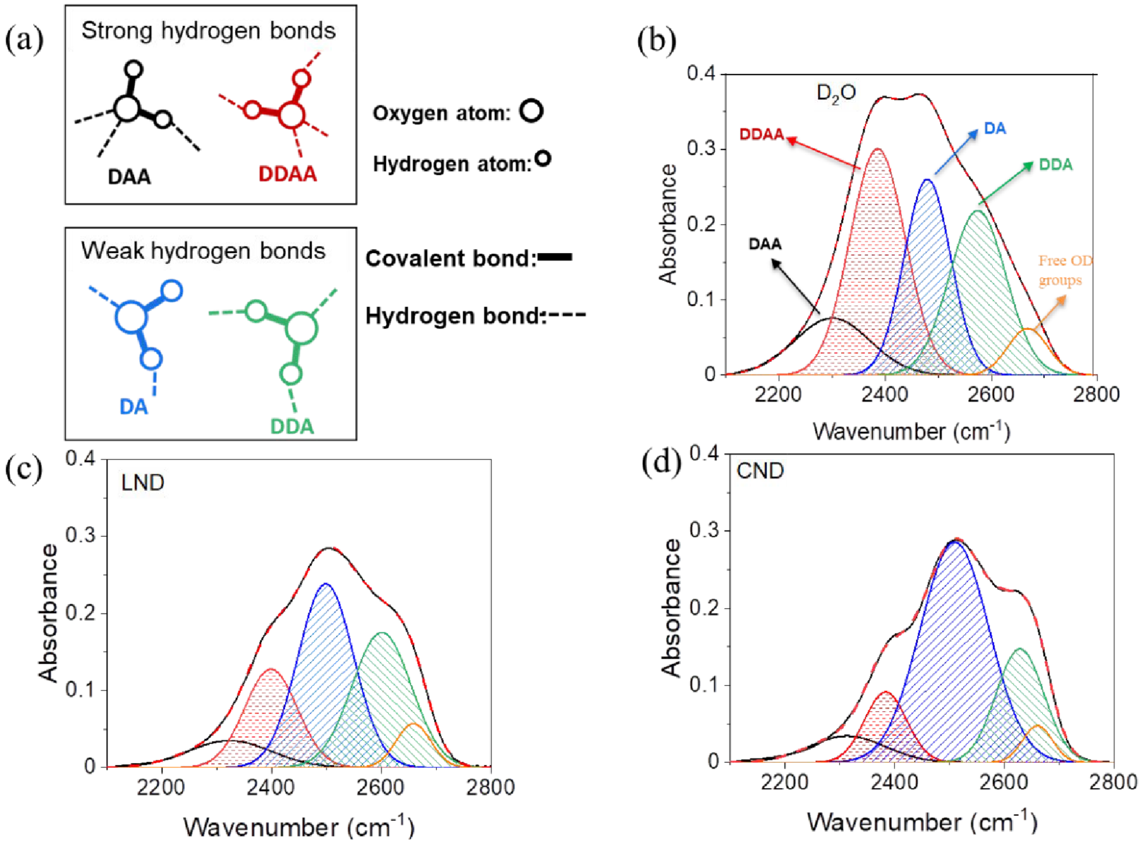


Fig. 3. (a) Schematic showing weak and strong hydrogen bonding structures in D_2O. FTIR analysis of 2100-2800 cm^{-1} –OD vibrational region in (b) D_2O, (c) LND, and (d) CND.

Table 1 summarizes melting temperature (T_m), viscosity (η), hydration states and ionic concentrations in select nitrate salt hydrates which are relevant for thermal storage and "green" solvent applications. Importantly, the amount of water released during melting of solid salt hydrates is generally not sufficient for saturating the hydration shells of the cations. The degree of saturation (DS) calculated as the ratio of moles of water in the hydrated salt to the sum of coordination numbers of cations and anions (CN_{cat}, CN_{an}), varies for different molten salt hydrates, but does not exceed 50% for the nitrate-based molten salt hydrates shown in the table. The nitrate ion can accommodate six water molecules to saturate its first hydration shell (CN_{an} = 6).[106] However, the water available as part of the salt hydrate structure preferentially coordinates with the cation.[30, 31] For the case of molten LNH, number of water molecules per ion is even lower than the hydration number of Li^+ ions in aqueous solutions (CN_{cat} = 4 or even 6, depending on salt concentration),[107] and water does not saturate the hydration shell of the cation.[108] Calcium ions (CN_{cat} = 6) in $Ca(NO_3)_2$ (CNH) shows incomplete hydration similar to LNH, whereas the magnesium ions (CN_{cat} = 6), which have a strong propensity for binding with water[109, 110] have the highest degree of saturation among the nitrate molten salt hydrates compared here.

Table 1. Melting temperature (T_m), Viscosity (η), Hydration States and Concentrations of Ions in Select Molten Salt Hydrates

Salt Hydrate	Number of water molecules per cation	The average degree of saturation of the ionic hydration shell, DS	Ionic strength
$LiNO_3.3H_2O$, LNH (T_m= 303 K, η = 5.34 mPa.s at 308K)[111]	3	$\frac{3}{4+6} = 30\%$	18 M
$Ca(NO_3)_2.4H_2O$, CNH	4	$\frac{4}{6+6} = 33.33\%$	13 M

(T_m= 315 K, η = 67 mPa.s at 323 K)[112]			
$Mg(NO_3)_2.6H_2O$, MgNH (T_m= 362 K, η = 0.18 mPa.s at 368 K)[113]	6	$\frac{6}{6+6} = 50\%$	9 M

A picture of molten salt hydrate solvents as highly inhomogeneous at the molecular level and involving ionic pairing is reminiscent of ion clustering found in conventional ILs.[114] In the case of molten salt hydrates, however, an additional factor to consider is the state of ion-hydrating water and competition of ions (and polymers) for binding with water molecules in the water-scarce molten salt hydrate environment. While the state of the water in molten salt hydrates can be analyzed using -OD or -OH stretching vibrational region shown above in **Fig. 3**, vibrational features of nitrate salts are sensitive to ionic pairing in these solvents. Among the four bands observed by Raman and FTIR techniques for the nitrate ion (symmetric stretch (SS), out-of-plane deformation (OPD), asymmetric stretch (AS), and in-plane deformation (IPD)), [115-122] the IPD and AS bands are in particular a good indicator of contact ion pairing. Specifically, splitting of the nitrate IPD (~740 cm^{-1}) [117, 118, 123, 124] and AS (at ~1380 cm^{-1}) [119, 123-127] vibrational bands is often used as an indicator for contact ion pairing in concentrated aqueous nitrate salt solutions (**Fig. 4**).[128] The formation of direct contact pairs is associated with changes in the vibrational features of NO_3^- ions as they enter the coordination sphere of cations in the dehydrated environment in molten salt hydrates. Overall, the tendency for band splitting and contact ion pair formation depends on cation type and decreases with decreasing cation size and increasing of its charge density. Nitrate salts of a variety of cations, such as lithium,[118, 129] sodium,[118] cadmium,[129] calcium,[117, 119-121, 127,

[130] strontium,[117, 128] lead,[128] and zinc[120, 122, 124, 131] demonstrated such peak splitting and enhanced direct contact ion pairing at high salt concentrations. On the other hand, **Fig. 4** shows that the bulky ammonium ion does not show significant band splitting,[128] likely due to the similar strength of interactions of ammonium ions and water molecules with nitrate ions.[128, 132-136] At the same time, peak splitting is also minimal for the salt of the strongly hydrated Mg^{2+} ion, in which the hydrating water molecules reduce the cation perturbation on the IPD mode of the nitrate ions.[116, 117, 123, 128, 137] As illustrated in **Fig. 5** by results from molecular dynamics (MD) simulations, larger and less hydrated ions, such as Ca^{2+}, tend to form direct contact ion pairs with nitrate salts (with the third from left configuration in **Fig. 5(a)** corresponding to the minimum energy), while the smaller Mg^{2+} ion forms the solvent-shared and solvent-separated ion pairs (the second and third from left configurations in **Fig. 5(b)**, respectively). [120]

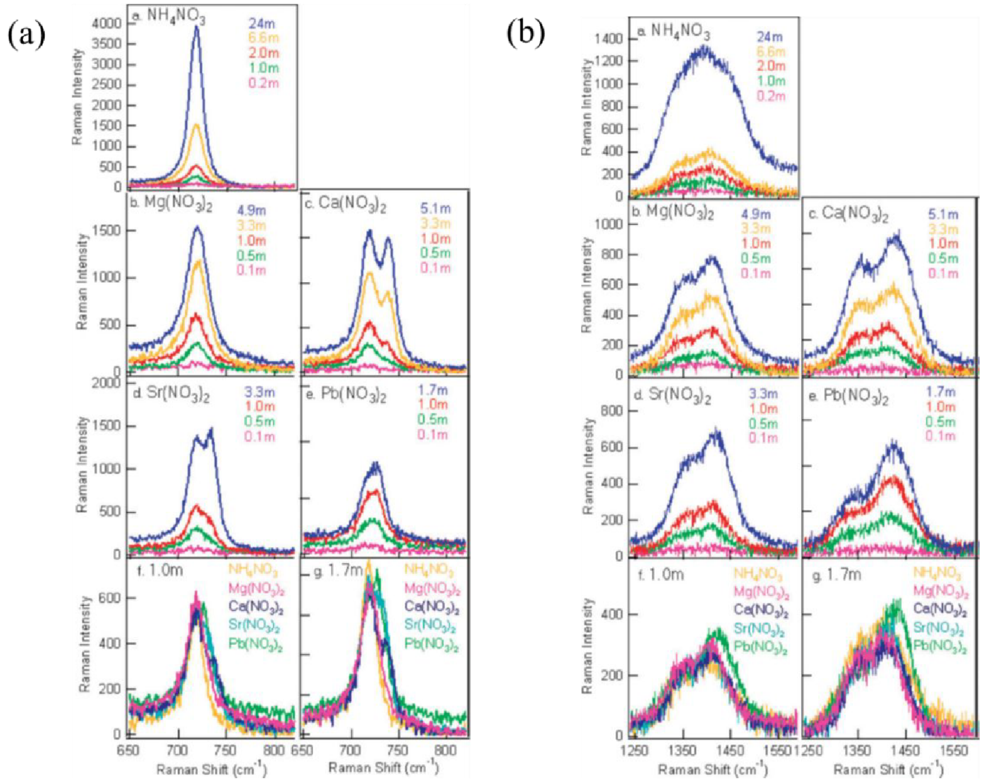


Fig. 4. Raman spectra of various nitrate salts showing (a) in-plane deformation (IPD) and (b) asymmetric stretching (AS) bands for the nitrate ions at different concentrations. Reproduced from Ref. 128.

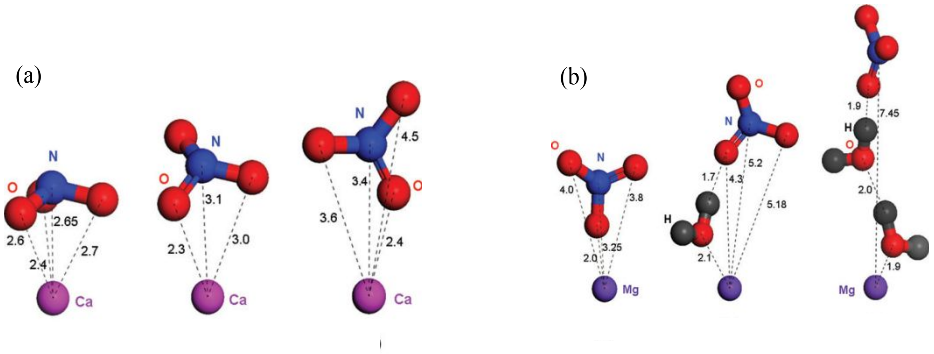


Fig. 5. Molecular dynamics simulations showing (a) contact ion pairing in calcium nitrate and (b) absence of contact ion pairing in magnesium nitrate aqueous solutions. Reproduced from Ref. 128.

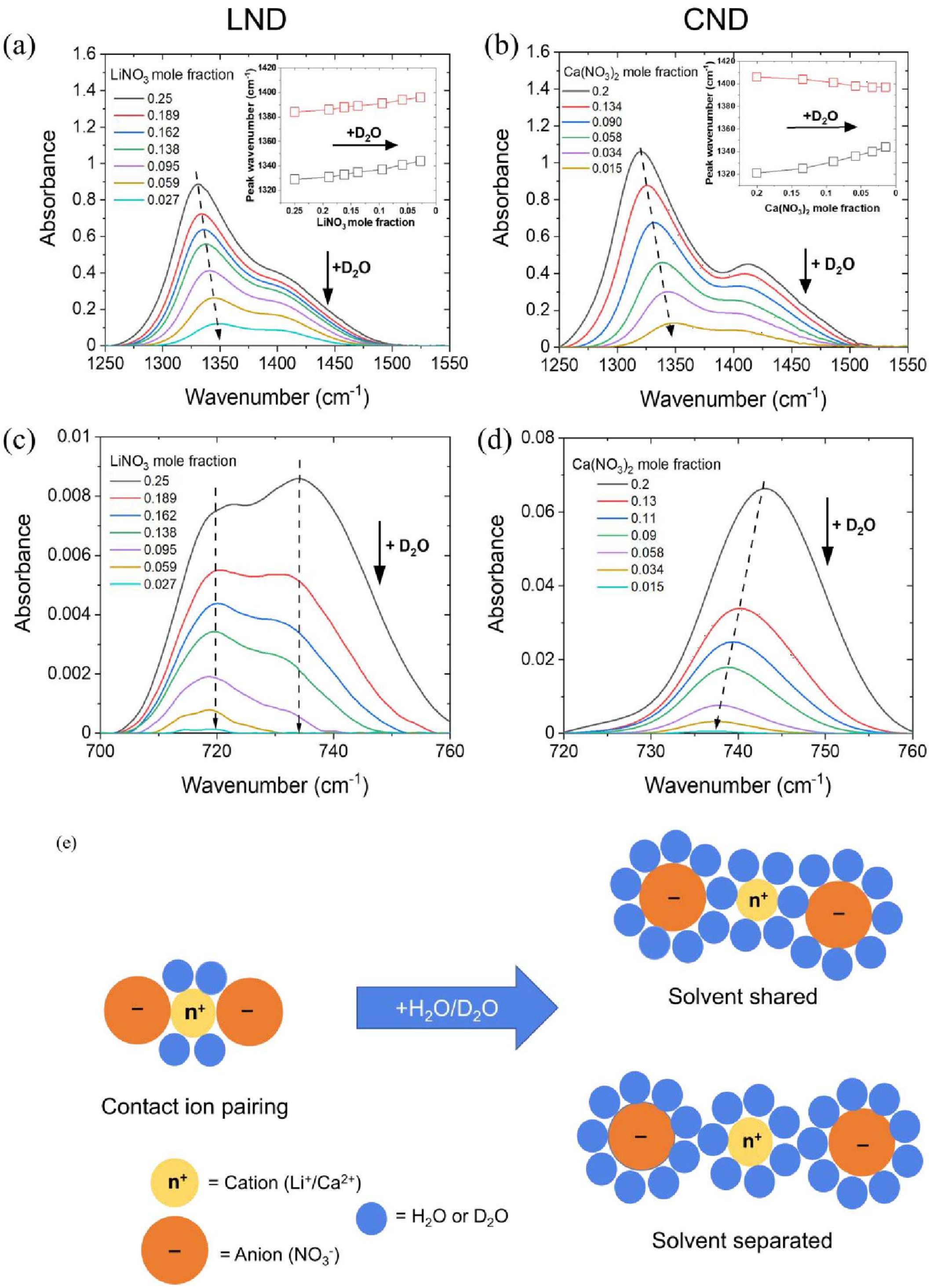


Fig. 6. Nitrate AS stretch ((a), (b)) and IPD peaks ((c), (d)) of nitrate ions obtained from ATR-FTIR for dilution with D_2O for LND ((a), (c)) and CND ((b), (d)). Insets in (a) and (b) show the magnitude of split of the AS peaks as function of $LiNO_3$ and $Ca(NO_3)_2$ mole fraction. (e) Schematic representation of changes in the ion pairing structures upon increased hydration.

Fig. 6 compares spectroscopically observed changes in ionic paring in two deuterated molten salt hydrates (LND and CND) upon their dilution with heavy water. The nitrate AS bands for neat LND and CND showed a split (**Fig. 6(a), (b)**), indicating the presence of contact ion pairs similar to what was observed by others in concentrated aqueous salt solutions.[118-121, 127, 130] The larger magnitude of the AS peak split for CND vs. LND (85 cm^{-1} and 55 cm^{-1}, respectively, inset **Fig. 6(a)** and **(b)**) suggests stronger contact ion pairing in CND compared to LND. Dilution with D_2O decreases the magnitude of the split in AS nitrate peaks (insets in **Fig. 6(a),(b)**), indicating the formation of solvent shared or solvent separated ionic pairs. In the case of IPD band, splitting was observed for neat LND, but not for CND (**Fig. 6(c)**, **(d)**), in agreement with prior reports on splitting of IPD band detected by FTIR and Raman spectroscopies. [117, 119-121, 127, 130] The 740 cm^{-1} peak, which is attributed to formation of direct contact ion pairs, [117, 118, 123, 124] systematically decreased or showed a systematic red shift upon dilution of LND and CND, respectively, also reflecting increased hydration and separation of direct contact ionic pairs upon dilution with D_2O (**Fig. 6 (e)**).

2.3.2. Molten salt hydrates vs water as polymer solvents: implications for polymer solvation and gelation

When polymers are added to molten salt hydrates, spectroscopic changes can reveal interaction of polymers with components of the solvent. Because PVA previously demonstrated promising properties for shape stabilization of molten salt hydrates in their applications as PCMs,[19, 138] this polymer was originally targeted for these studies. However, because of the limited solubility of PVA in molten salt hydrates at concentrations exceeding 10%, the intensity of the band associated with stretching vibrations of the hydroxyl group was not strong enough for analysis by ATR-FTIR. Therefore, glycerol – a structurally similar low-molecular analogue of

PVA, but miscible with molten salt hydrates at all proportions – was used to study the interactions of the hydroxyl groups of PVA with molten salt hydrates. We also used deuterated molten salt hydrates (LND and CND) to separate the -OD stretching vibrational band in the solvent (2100-2800 cm^{-1}) from -OH stretching vibrations (3200-3550 cm^{-1}) associated with PVA or glycerol. At the same time, the state of nitrate ions in molten salt hydrates upon addition of a polymer-mimicking glycerol was tracked via changes in AS (1250-1550 cm^{-1}) and IPD (700-760 cm^{-1}) vibrational modes.

Studies of mixtures of deuterated molten salt hydrates with glycerol revealed the important clues on interactions between the solvent (molten LND or CND) and hydroxyl groups of glycerol. Specifically informative was analysis of the -OH stretching vibrational region of glycerol (3000-3800 cm^{-1}) as composition of the mixtures was systematically changed from neat molten salt hydrates to neat glycerol. In its undiluted state, glycerol molecules are extensively hydrogen bonded through intermolecular bonding of -OH groups, which give rise to a vibrational band at 3264 cm^{-1}. **Fig. 7** (corresponding spectra shown in **Fig. S2**) shows that as glycerol was mixed with molten salt hydrates, a large blue shift in its -OH vibrational band occurred, indicating weakening

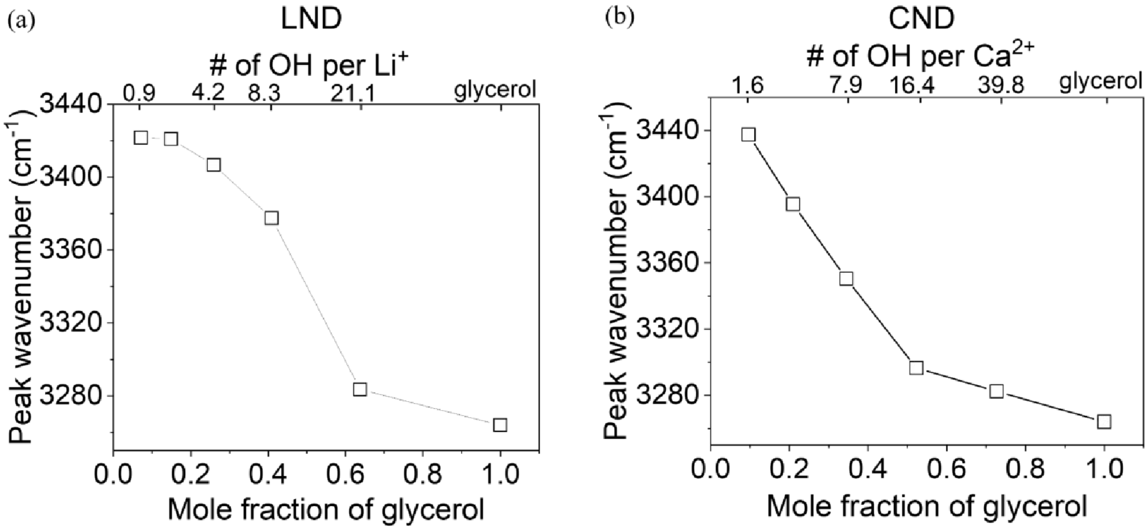


Fig. 7. Analysis of -OH peaks of glycerol in mixtures with (a) LND and (b) CND obtained from ATR-FTIR.

of hydrogen bonds between glycerol molecules due to increased hydration by water molecules provided by the solvent. **Fig. S3** shows changes in hydrogen bonding modes of heavy water in LND and CND upon an increase in glycerol content. The most pronounced trend for both molten salt hydrates is the disappearance of DDA band and an increased contribution of weak hydrogen bonding (DA) band, suggesting enhanced competition for water molecules upon addition of glycerol. Finally, an increase in glycerol concentration also affected the IPD nitrate vibrational bands of LND and CND (**Fig. S4 (a), (b)**), with more pronounced spectral changes occurring for CND. This data suggests that interactions between polymer chains and nitrate ions can occur directly or indirectly by binding through Ca^{2+} (**Fig. 2**)[88].

The unique picture thus emerges of the state of polymers (such as PVA) dissolved in molten salt hydrates. The competition between the ions and the polymer for water molecules results in a dehydration of the polymer chain, while interaction with ions in the solvent can significantly affect solubility and expansion of polymer chains. Dehydration of PVA in LND solutions as compared to D_2O solutions was demonstrated in our earlier publication (**Fig. 8**).[19] With a gradual increase of LND concentration, the –OH stretching peak of PVA showed a large blue shift from 3390 cm^{-1} to 3430 cm^{-1}, indicating disruption of hydrogen bonding between –OH band of PVA and water, *i.e.* significant dehydration of PVA chains in LND. At the same time, direct binding of Li^+ ions with PVA in PVA/LNH solutions was demonstrated using ^7Li NMR spectroscopy (**Fig. 9(a)**).[47] PVA-bound Li^+ ions had significantly altered polymer chain conformation and diffusion. In particular, the studies of the molecular weight dependence of diffusion coefficients by fluorescent correlation spectroscopy (FCS) yielded the Flory exponent of ~0.6 for PVA in LNH, which was higher than that for PVA in aqueous solutions (**Fig. 9(b)**), suggesting good solvent conditions for the polymer chains. Viscosity measurements of the overlap concentrations of polymer chains in two solvents – LNH and water – further confirmed expansion of polymer chains in LNH.

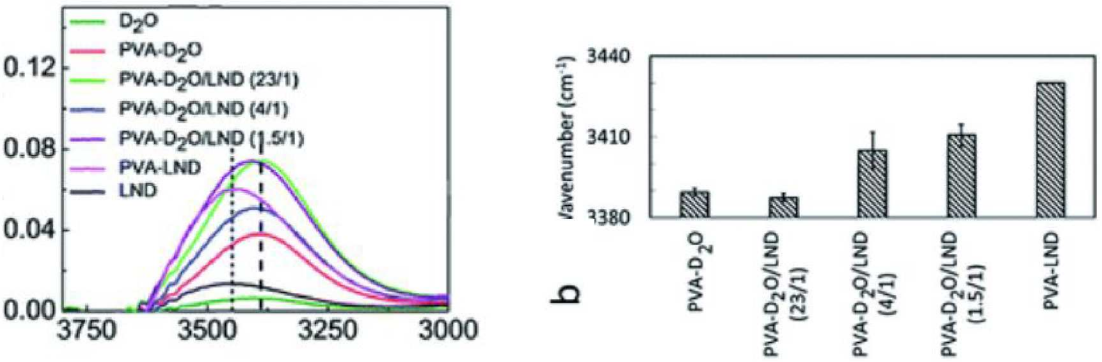


Fig. 9. Blue shift of the –OH stretching band of PVA in mixed D_2O/LND solvents as a function of an increased content of LND. Reproduced from ref. 19.

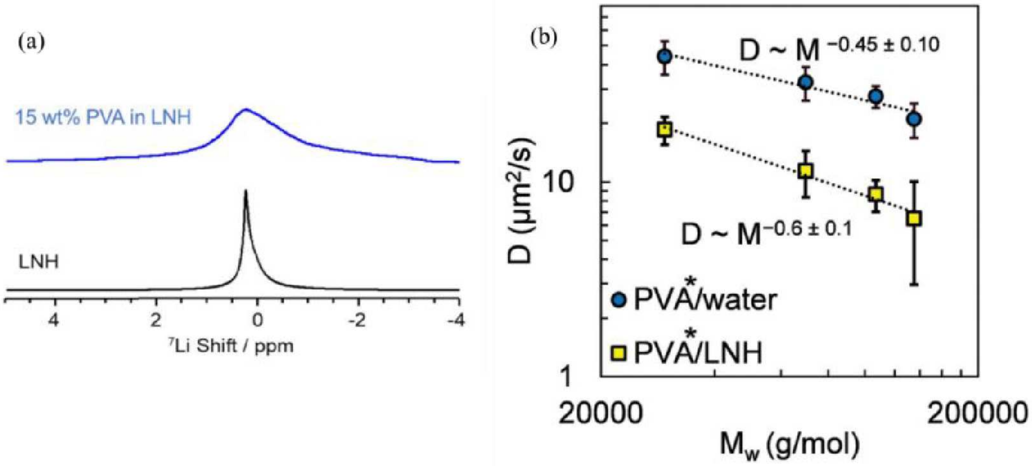
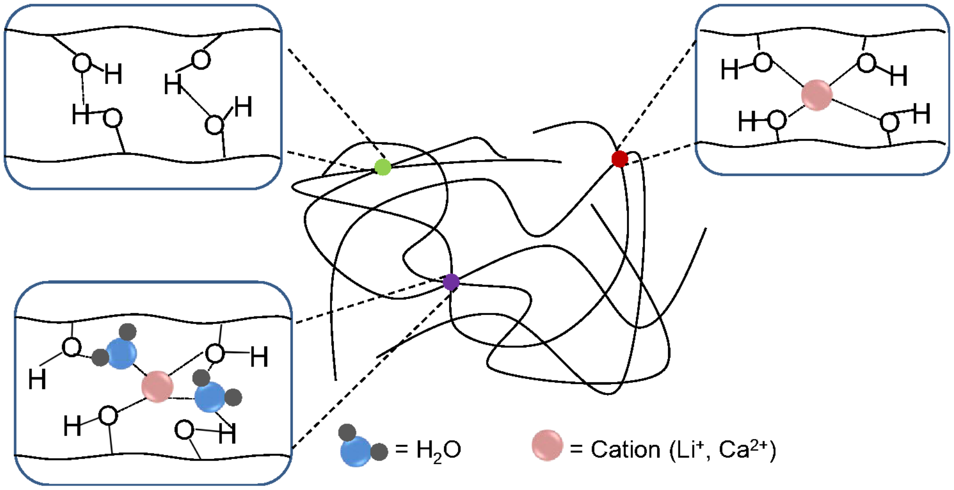


Fig. 8. (a) ^{7}Li NMR spectra of LNH and 15% PVA in LNH. (b) Molecular weight dependences of FCS diffusion of fluorescently labeled PVA, PVA*, measured in 10^{-4} mg/ml aqueous or LNH solutions at 22 °C. Reproduced from ref. 47.



Scheme 2. Suggested interactions acting between PVA chains in salogels.

While the distinct solvation features of PVA in molten salt hydrates leads to expansion of individual polymer chains in dilute solutions, the same features support formation of salogels at increased polymer concentrations.[19] **Scheme 2** summarizes the type of interactions (polymer-polymer, polymer-ion, and polymer-water) involved in the physical crosslinking of PVA in salogels. A significant role of dehydration of polymer chain can be evidence in the lack of PVA gelation in purely aqueous environment even at high polymer concentrations. At the same time, an effect of binding of ions from the molten salt hydrates with polymer chain on gelation manifests itself through easier gelation of PVA in the calcium salt as compared to the lithium salt solvent (**Fig. S5**). Understanding of the molecular mechanism of polymer gelation in molten salt hydrates can enable rational development of polymer salogels for thermal storage applications. The next section will first discuss key features of molten salt hydrates as energy storage materials, and then focus on the emerging area of shape stabilization of molten salt hydrates using temperature-reversible salogels. In both cases, a comparison with traditional ILs will be made.

3. Molten Salt Hydrates *vs*. Traditional ILs as Phase Change Materials

3.1. Thermo-physical properties of IL and molten salt hydrate PCMs

Inorganic salt hydrates and to a lesser extent ILs have been proposed for use as phase change materials (PCMs), due to their ability to store thermal energy associated with the latent heat of fusion.[2-4, 7, 139-143] Among these, congruently melting stoichiometric salt hydrates tend to be utilized, due to phase segregation problems associated with incongruently melting compounds. **Fig. 10** compares heats of fusions and melting temperatures of several ILs and stoichiometric inorganic salt hydrates. In practice, the selection of a PCM for a particular application requires 1) the PCM to melt at a specific temperature required for the application, and 2) desirable thermophysical properties in the PCM – chief among these are the specific or volumetric energy density of the material. Within the inorganic salt hydrates, different anionic families (e.g., chlorides, nitrates, sulfates, etc.) melt over a comparable range of temperatures (25 to 100 °C; **Fig. 10**). Within this range, the dependence of melting temperature on composition is rather complicated, as it results from the relative stability of different salt hydrate phases compared to a liquid phase, where the activity of water in the liquid phase can vary greatly. Across this temperature range, inorganic salt hydrates tend to have larger specific and volumetric (not shown here) heats of fusion than ILs because of 1) the large molar entropy of fusion of salt hydrate phases, and 2) the low molecular weight of salt hydrate complexes which consist of water, and monatomic, or simple polyatomic ionic species. While the molecular weight of compounds is straightforward to calculate, the molar entropy of fusion also behaves fairly systematically, and can be approximated to a reasonable degree, if the melting temperature is a known quantity.

The molar enthalpy of fusion is proportional to both entropy of fusion of the substance, and the equilibrium melting point of the compound, as $\Delta H_{\text{fus}} = T\Delta S_{\text{fus}}$. In general, the entropy of fusion of simple substances accounts for the increases in translational and rotational degrees of freedom caused by the melting of a substance, as well as the increase in disorder associated with the disruption of the crystalline lattice[144] and any associated volume expansion.[145] In simple substances (e.g., monatomic substances or binary salts), the molar entropy of fusion of a compound scales with the total number of individual atoms and molecules that exist after melting as each molecule adds to the total degrees of freedom of the system.[144] This trend holds fairly well for inorganic salt hydrates as well (**Fig. 11(a)**). The molar entropy of fusion of salt hydrates is also strongly correlated with the number of water molecules in the structure,[146] resulting in part from the anomalously large molar entropy of fusion of water. In contrast, traditional ILs melt through dissociation of weakly associated ionic pairs and often yield below ambient melting temperatures.[139, 147] Melting of ILs containing long saturated carbon chains (e.g., alkanes) is primarily influenced by the total number of carbon atoms in the backbone, as each C-C bond can add additional rotational degrees of freedom to the molecule. This trend is observed in all of the ionic liquids with reported specific enthalpy of fusion >100 J/g, indicating that the primary contribution to the large entropy of fusion in these compounds are rotations along the C-C backbone (**Fig. 11(b)**). The large size of ions, high ionic volume, and weak coordination between the ions result in low enthalpy and low melting points which have been predicted using DFT calculations and found to be in agreement with experimental values.[148] Furthermore, specific heat of fusion (37.5 to 150 J/g) of ILs is depressed due to the relatively high molecular weight of the salts involved (**Table S3**).[139, 140, 142, 143, 149, 150] In contrast, stoichiometric inorganic salt hydrates have relatively high specific heats of fusion (100 to 300 J/g), as well as higher thermal conductivities than traditional ILs, a result of the strong hydrogen bonding in the water system, making these materials highly suitable for their use as PCMs in thermal storage applications.[5, 30, 82, 146, 151-159]

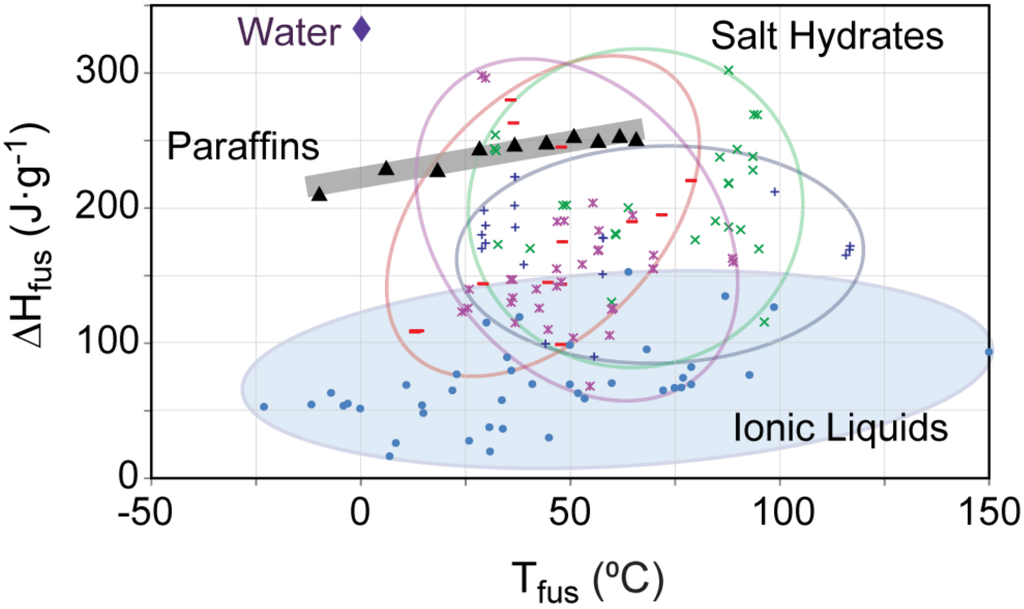


Fig. 10. Enthalpy of fusion (ΔH_{fus}) and melting temperatures (T_{fus}) of different classes of salt hydrates (sulfate hydrates, green x; phosphate hydrates, red -; chloride hydrates, blue +; nitrate hydrates, purple *,[5, 30, 82, 146, 151-155] where the cations are monatomic, such as Ca^{2+}, Na^{+}, K+, Mg^{2+}, Zn^{2+}, etc.), and ionic liquids (blue points),[156] as well as some common near-room temperature PCMs, for reference (even-numbered paraffins, [157, 158] water [159]).

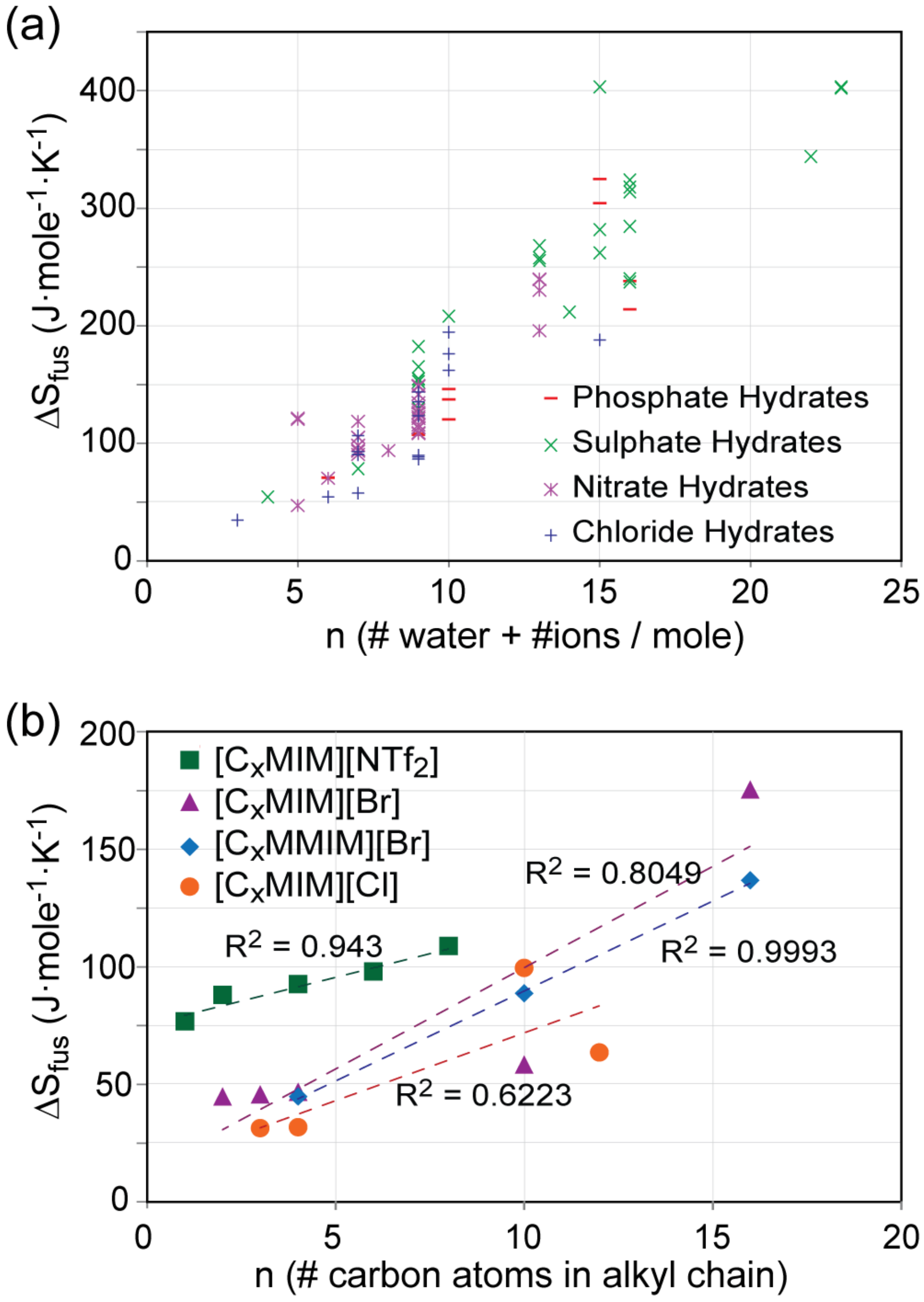


Fig. 11. a) Molar entropy of fusion of stoichiometric salt hydrate compounds (sulfate hydrates, green x; phosphate hydrates, red -; chloride hydrates, blue +; nitrate hydrates, purple *)[5, 30, 82, 146, 151-155] as a function of the total number of cations, anions, and water molecules in a mole of the stoichiometric salt hydrate. b) Molar entropy of fusion of select long-chain ionic liquids,[156] as a function of the number of carbon atoms in the chain.

Yet the use of both ILs and inorganic salt hydrates for thermal storage applications is associated with significant challenges. First, while both ILs and Inorganic salt hydrates are often considered 'green' because of their low vapor pressure and nonflammability, [21-23, 140, 142, 143] ILs, such as imidazolium-based ILs, are highly toxic. Supercooling, resulting in nucleation of solid phase occurring at a much lower temperature (2-30 °C lower)[2] than expected for a particular PCM, poses challenges for practical application such as long nucleation and cycling times for both salt hydrates[9, 160] and ILs.[161-163] The use of nucleation agents, and other techniques such as seeding (using same material as the PCM or another surface), electrical and mechanical shock, ultrasound, and mechanical agitation have been proposed to induce crystallization of solid PCM.[2, 9, 96, 164] The hygroscopic nature of inorganic salt hydrates reduces reliability during thermal cycling due to changes in melting temperature and reduced heat storage capability from water evaporation and absorption which changes the salt hydrate composition.[3, 111] Furthermore, because of the high salt content, both salt hydrates[165-167] and ILs[168-170] are corrosive, although, the chemical species of the anion plays a dominant role in dictating the degree of corrosivity associated with a particular compound. As an example, chloride salt hydrates are, generally speaking, more aggressive than nitrate salt hydrates.[171] This can be especially problematic, as one way to overcome the low rates of heat transfer into a PCM is through the inclusion of thermally conductive metallic fins, wires, or particles.[172-174] Thus, long-term stability of systems combining either ILs or inorganic salt hydrates and metallic conductivity enhancements usually requires some form of surface passivation or protective barrier coating.

In addition to these widely reported and investigated challenges, the low viscosity of molten inorganic salt hydrates (4.32 cP (at 298 K) for potassium fluoride tetrahydrate,[175] 5.34 for lithium nitrate trihydrate (at 308 K),[111] ~ 3-5 cP for water at room temperature, and <10 to >1000 cP at room temperature for typical ILs,[176]) can introduce a number of reliability issues associated with robust energy storage over 10^3 to 10^4 cycles. These include: 1) the tendency for solids to gravitationally settle, and then expand during melting, which can introduce internal stresses and cause a PCM containment vessel to fail, 2) the lack of shape-stability, which limits the use of thin lightweight pliable containment vesicles that are designed with a particular shape to maximize heat transfer, 3) the tendency for solid nucleation agents to settle out of suspension and potentially segregate to a region where they are less effective (i.e., away from an actively cooled surface), and 4) the tendency for incongruently melting compounds to gravitationally segregate, resulting in chemical stratification and irreproducible melting behavior. Of these concerns, the last point has achieved the most recognition,[20] although incongruent melting behavior and accompanying phase segregation is not exhibited in all salt hydrates. For these reasons, there is a demonstrated need to develop polymer systems that can act as a stabilizing matrix and prevent flow and settling generally observed in a molten PCM.

3.2. Polymers for shape stabilization of ILs and molten salt hydrates

Polymers were first used for shape stabilization of traditional ILs, which also suffer from leakage.[177-179] Shape stabilization for immobilization of ILs is essential for applications such as fuel cells, separation membranes, actuators, and electronics applications like supercapacitors, sensors, ion batteries and flexible displays to prevent leakage.[178, 179] A strategy of forming ionogels, which are defined as hybrids of ILs with polymers or composites of polymers and inorganic fillers or with inorganic gelators such as silicon alkoxides, has been widely applied to provide mechanical integrity to ILs while retaining high ionic conductivity.[177-182] Formation of polymeric ionogels can involve physical or chemical gelation of polymers such as poly(methyl methacrylate), poly(ethylene oxide), and copolymers such as Nafion or poly(vinylidene fluoride-co-hexafluoropropylene), in ILs. Temperature-responsive polymer ionogels were also developed. In particular, ionogels with UCST behavior were constructed based on triblock copolymers,[180] whereas LCST behavior in ILs has been demonstrated in hydrophobic ILs using poly(benzyl methacrylate) and its copolymers with methyl methacrylate and styrene.[183] In the UCST ionogel, the microphase-separated physical crosslinks were designed to dissociate above a certain gelation temperature, and tunable gelation temperature, mechanical properties, and ion conductivity were achieved through varying the chemical identity and molecular weight of block copolymers, as well as polymer concentration.[179, 180] In the LCST ionogel, transition temperature could be tuned by changing the copolymer composition (methyl methacrylate or styrene) and also by controlling the alkyl chain length of the imidazolium cation in the IL.[183] In addition, tuning of viscoelastic and thermal properties of gelatin-based ionogels in imidazolium ILs has also been demonstrated by manipulating the hydrophobicity or the composition of IL mixtures.[184]

Polymer gelation is less explored in inorganic salt hydrates as compared to ILs. However, shape stabilization is probably more important for inorganic salt hydrates because of their low viscosity and propensity to gravitational settling of solids.[4, 13-16, 19] Several approaches to shape stabilization of salt hydrates have been explored.[42] These include impregnation into porous materials using capillary forces and surface tension to prevent flow,[185-190] encapsulation within core-shell structured materials,[185, 191-195] and the use of polymers [196-198] or polymer-inorganic composites to form three-dimensional networks.[96] The use of porous materials and microencapsulation techniques are the most explored, and many strategies involving polymers are based on application of composite rather than purely polymer materials, such as bentonite/starch[94,] and graphite/polymer hybrids[199] to provide mechanical stabilization, or a combination of polymers with expanded graphite, graphene flakes, or graphene oxide to increase the thermal conductivity.[4,]

[17, 198, 200, 201] Applications of neat polymers for shape stabilization of inorganic salt hydrates are less explored, but the use of polyacrylamide its co-polymers,[17,202] or salts of polyacrylic acid, or curing acrylic resins,[200, 201] was reported. These approaches usually require the use of high polymer concentrations, often lead to the formation of viscoelastic slurries rather than robust gels,[203] and are focused on the practical aspects of the effect of the addition of polymers on thermo-physical properties of the PCM, such as heat of fusion[196-198, 200, 202] and the melting temperatures of the PCMs.[174, 183, 184, 186] Fundamental aspects of interactions of polymers and salt hydrates have not been well understood, however. This hindered rational design of polymer networks with controlled mechanical and salt-retention properties.

Our group has recently introduced a new feature in shape stabilization of inorganic PCM using temperature-reversible polymer gelation in molten inorganic salt hydrates. Specifically, we reported salogels of PVA in LNH which reversibly disassembled at elevated temperatures above a PCM transitions temperature, thus enabling easy replacement of the used thermal storage material.[19] The salogels demonstrated a gel-to-sol transition temperature of 20 ± 1 °C (**Fig. 12(a)**). In contrast, as also discussed in section 2.3.2, PVA did not form a gel and remained molecularly dissolved when water was used as a solvent (**Fig. 12(b)**), illustrating the critical role of solvation of polymer chains on gelation in these two cases. The data presented in prior publications[19, 47, 138] and presented in this manuscript in section 2.3.2 reveal that in the salt hydrate environment, polymer-polymer and polymer-ion contacts are more readily formed, supporting polymer gelation versus dissolution.

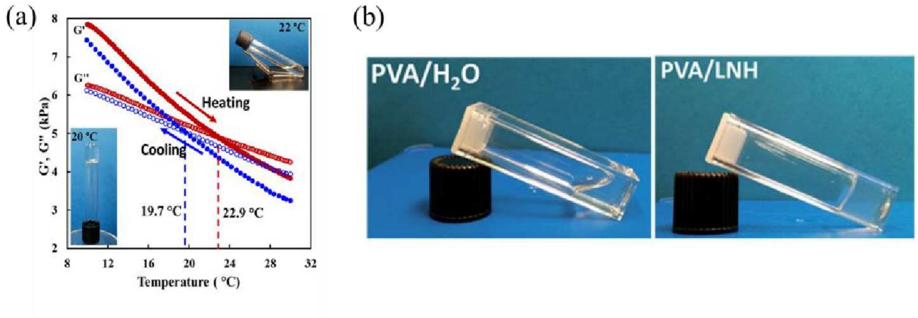


Fig. 12. (a) Temperature-dependent *G′* and *G”* of PVA/LNH gel measured at an angular frequency of 10 rad/s, γ_L= 10%. Images show PVA/LNH system above and below the gel transition temperature. (b) 15% PVA solutions in water and LNH at ambient temperature. Reproduced from ref. 19.

Despite the tendency to gelation in molten salt hydrates, PVA salogels were mechanically weak.[19] To improve mechanical strength of the salogels and enable control of their gelation temperature, we used amine-terminated dendrimers as physical crosslinkers.[138] Formation of multiple hydrogen bonds between *–OH* groups of PVA and amino groups of the crosslinker resulted in the formation of strong salogels. The crosslinker geometry (linear vs. branched) could be also used to control the salogel gelation temperature, with branched crosslinkers being more efficient gelators due to their higher functionality.[138]

The dynamic nature of physical crosslinks in the salogels provides the additional advantageous properties of these materials. This was demonstrated via self-healing of dendrimer-crosslinked salogels (**Fig. 13a**), that occurred despite a relatively high elastic modulus of the material (~700 MPa). **Fig. 13b** quantitatively confirmed recovery of the storage and loss moduli of the salogels after several cycles of network deformation. At the same time, salogels showed good retention properties of molten LNH (**Fig. 13f**).[138]

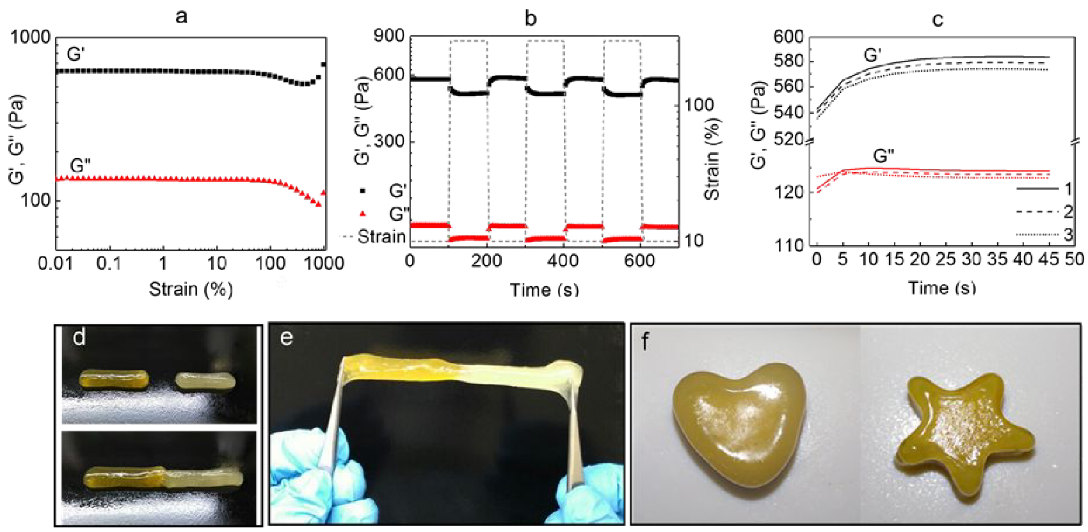


Fig. 103. Self-healing and shapeability of PVA/G3/LNH salogels: (a, b) strain amplitude sweep (ω =10 rad s^{-1}) and step-strain measurements; (c) the recovery rate of G' and G'' over three cycles of braking and recovery; (d-f) illustration of self-healing and shapeability of the salogels at ambient temperature. Reproduced from ref. 138.

4. Conclusion and Outlook

This *Perspective* discussed the unique properties of molten salt hydrates as polymer solvents. The use of inorganic salt hydrates for thermal energy storage is an actively developing field, which would benefit immensely from further investigation of the interactions between polymers and molten inorganic salt hydrates. Of special importance, we note two key opportunities. 1) Inorganic salt hydrates are subject to an ongoing search for binary, ternary, and higher order eutectic systems with repeatable melting behavior at lower temperatures (particularly between 0 and 25 °C). Binary or ternary eutectics offer a potential approach to develop PCMs for thermal energy storage that have the favorable intrinsic properties associated with salt hydrates but can be developed with a very specific melting temperature which is depressed below the melting temperature of the end-member salt hydrates. However, the behavior of polymers in inorganic salt hydrate systems with multiple cations present, each of which may be coordinated by the available water molecules, remains largely unknown. 2) Undercooling in inorganic salt hydrates remains a key limitation and is often addressed by introducing insoluble solid particles which serve as phase-specific nucleation agents. However, nucleation rates in gel systems in both the absence and presence of additional nucleation agents have not been reported. Salogels limit the mobility of ionic species within the system, and partially coordinate the available water molecules, which may serve to decrease nucleation rates. However, salogels also introduce internal discontinuities and interfaces at the molecular length scale, which may have the opposite impact. In both of these cases, advancing the understanding of polymer – inorganic salt hydrate interactions is key to improving the performance of PCMs based on inorganic salt hydrates.

Overall, studies of polymer solubility and gelation in molten inorganic salt hydrates are still in their infancy, and much less explored than polymers in aqueous solutions or in ILs. The key is that the molecular interactions between the solvent components and the polymer, are vastly different between these solvents. This *Perspective* considers molten salt hydrates as a case intermediate between the environment created for the polymer chains in water and in traditional ILs. In water as a solvent, the only interactions are between polymer chains and water molecules, whereas polymer-ion or polymer-water interactions co-exist in aqueous salt solutions and one can be more dominant than the other depending on ionic concentration. On the other hand, polymer-ion interactions exist solely in ILs. Thus, inorganic salt hydrates are distinctive as solvents and share some common features with water, aqueous salt solutions, and ILs since polymer-water and polymer-ion interactions both exist. Yet polymer-ion interactions dominate in the molten salts due to scarcity of water (molar water/salt ratio <7 for Li^+, Mg^{2+}, and Ca^{2+} salts).[31] However, the polymer-ion interactions in salt hydrates are significantly different compared to those in ILs due to difference in structure of the cations and anions in the two solvents.

As a result of the unique environment in the molten salt hydrates, polymer chains are much less hydrated as compared to aqueous solutions, and at the same time are interacting with abundant ions. Consequences of these interactions include facilitated polymer-polymer and polymer-ion binding which can cause expansion of polymer chains and facilitate gelation in these solvents. The ease of gelation of neutral polar polymers in molten salt hydrates opens an important opportunity in both fundamental studies and applications of the polymer salogels for thermal energy storage. Recent studies have demonstrated the promising features of temperature responsive salogels for shape stabilization of inorganic salt hydrates,[19] tunability of gelation temperature using a hydrogen bonding crosslinker,[138] and explored the gelation mechanism using NMR[47] and spectroscopic techniques.[138] While these studies are providing insight on the state of water, salt ions, and polymer solvation in inorganic molten salt hydrates, these explorations are still limited to one type of salt hydrates (nitrates) and a single polymer (PVA). Therefore, there exist rich opportunities for exploring both fundamentals and applications of salogel systems formed with different polymer and salt hydrate (chlorides, sulfates, etc. and their eutectic mixtures) combinations. Therefore, progress in this area can greatly facilitate rational development of polymer/molten salt hydrate systems for a variety of applications, ranging from synthesis and separation to thermal energy storage.

Author contributions

K. K. R. contributed with manuscript writing, making figures and tables, furnishing references, experiment planning and execution. P. K. did initial planning and writing of the manuscript. X. Z.

performed FTIR experiments and analyzed the data. P.S. did significant writing of section 3.1 and reviewed and edited the overall manuscript. S.A.S. performed initial planning and outlining, and led reviewing and editing of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

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