Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

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

K. Rajagopalan, Dr. P. Karimineghlani, X. Zhu, Prof. P. Shamberger, Prof. S.A. Sukhishvili,

Department of Materials Science & Engineering, Texas A&M University,

College Station, TX 77843, USA

E-mail: svetlana@tamu.edu

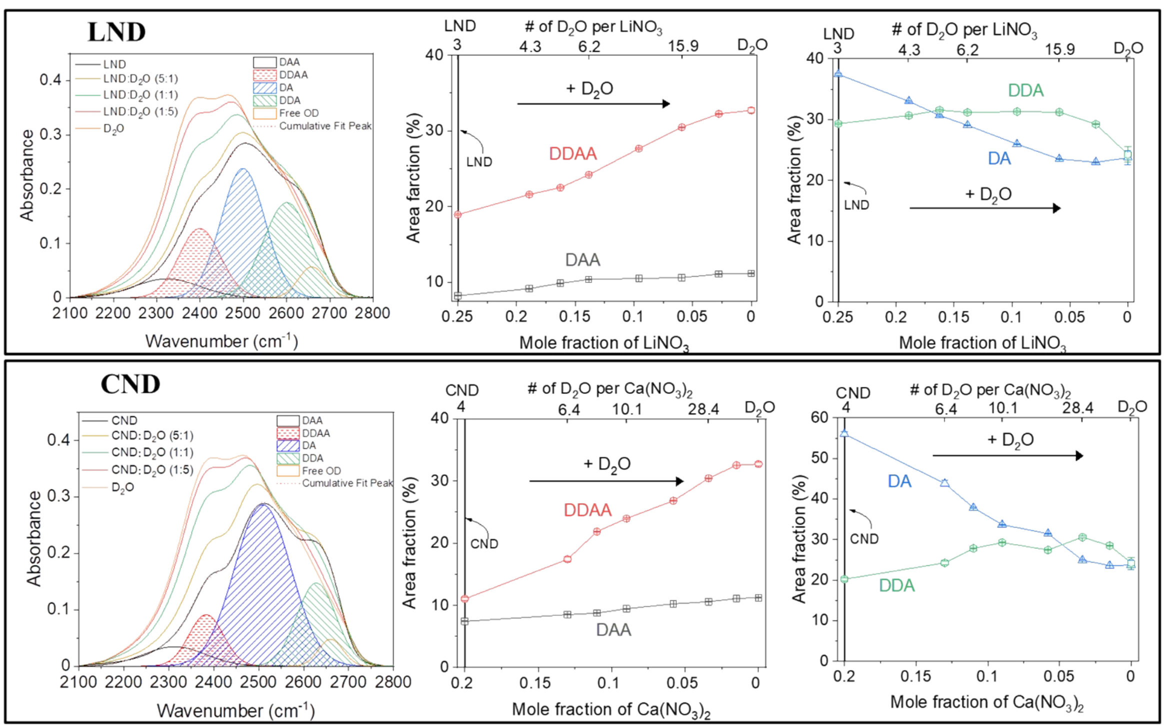

Fig. S1. Effect of dilution by water on -OD stretching vibrational peaks (2100-2800 cm^{-1}) for LND and CND obtained from ATR-FTIR.

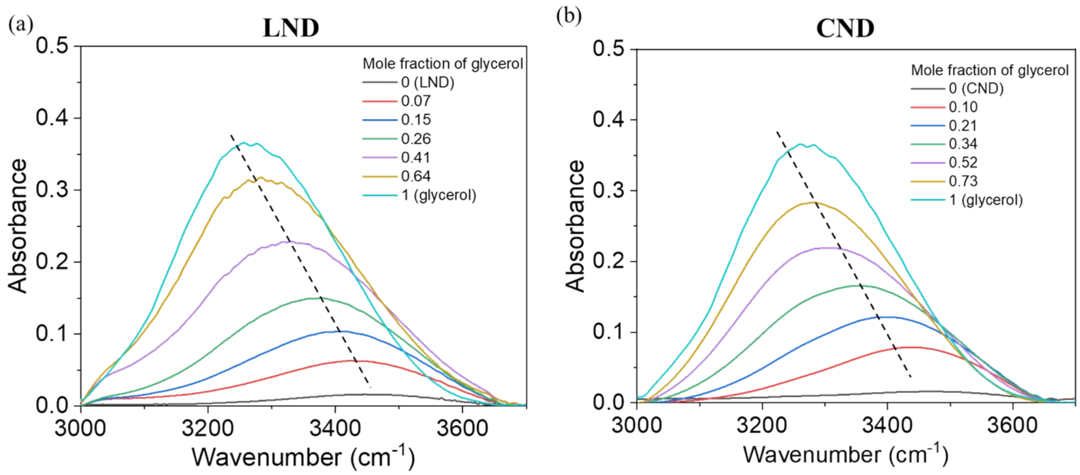

Fig. S2. ATR-FTIR spectra showing changes in the -OH peak of glycerol in mixtures of (a) LND and (b) CND.

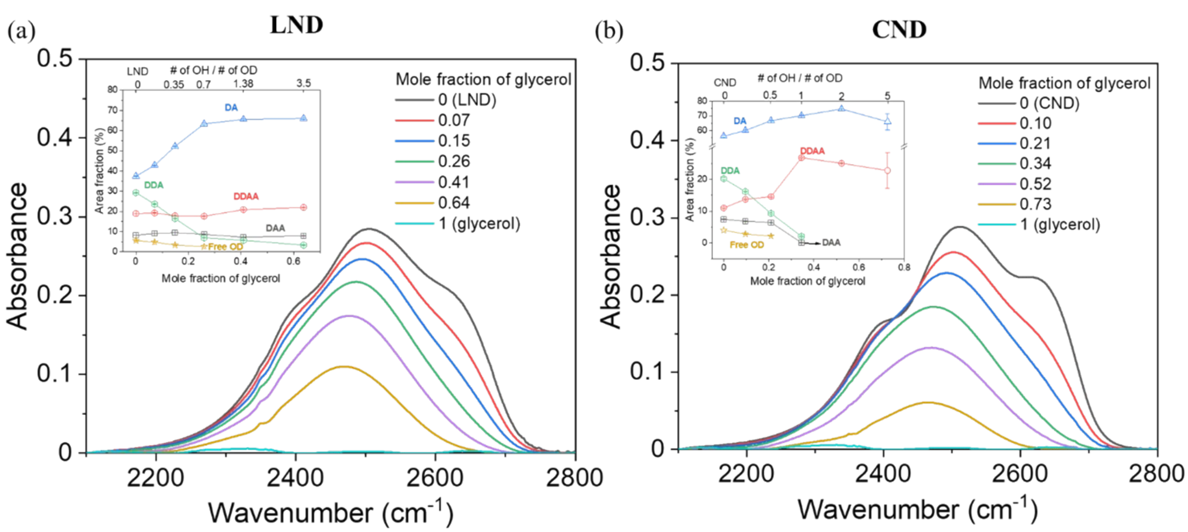

Fig. S3. ATR-FTIR spectra showing -OD stretching vibrational peaks for (a) LND and (b) CND upon dilution with glycerol. Insets show change in area fraction of the hydrogen bonding modes.

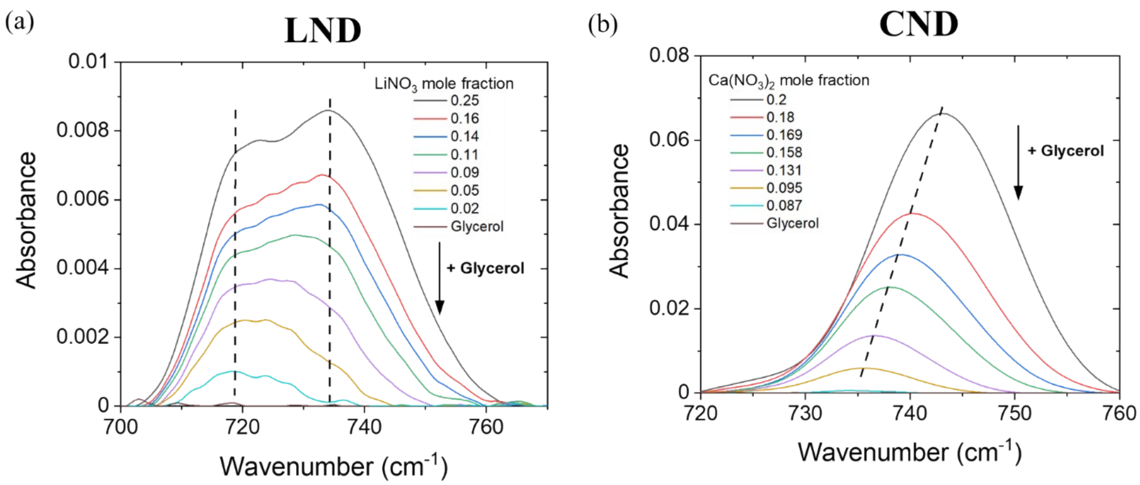

Fig. S4. ATR-FTIR spectra showing nitrate in-plane deformation (IPD) peaks of nitrate ions for (a) LND and (b) CND upon dilution with glycerol.

Fig. S5. 5 wt% PVA (90 kDa, 98% hydrolyzed) in molten LNH (left) and CNH (right).

Table S1. Examples of cations and anions in ILs[1]

Cation	Anion
1,3-Dialkylimidazolium 1,3-Dialkyl-2-methylimidazolium 1-Alkylpyridinium 1,1-Dialkylpyrrolidinium 1,1-Dialkylmorpholimium 1-Alkylpyrazolium Tetraalkylammonium Tetraalkylphosphonium	Cl^-, Br^-, $[Cl/AlCl_3]^-$, $[BF_4]^-$, $[PF_6]^-$, $[P(OH)_2O_2]^-$, $[PO_4]^{3-}$, $[N(SO_2CF_3)_2]^-$ $[NO_3]^-$,$[N(CN)_2]^-$

Table S2. Peak wavenumbers for hydrogen bonding bands from -OD peak (2100-2800 cm^{-1}) analysis in D_2O, LND, and CND.

	D_2O	LND	CND
DAA	2300	2323	2313
DDAA	2386	2399	2383
DA	2479	2499	2509
DDA	2574	2600	2628
Free OD	2668	2658	2660

Table S3. Phase change properties of ILs vs. Inorganic salt hydrates.

	IL	Melting point (˚C)	Heat of fusion (J/g)	Ref.
IL	[EMIM][BF4][1]	14.5	48.5	2
	[BMIM][BF4][2]	−87.5	47	2
	[DMPI]Im[3]	11.5	50	2
	[Gdm][4] [NTf$_2$]	100	69	3
	[Gdm][Val]	157	100	3
	[Gdm][Tf]	160	130	3
	[Gdm][Tar]	170	121	3
	[Gdm][Ms]	208	190	3
	[Gdm][NO$_3$]	217	174	3
	[C$_{10}$MIM]Br[5]	74	66	4
	[C$_{16}$MIM]Br	74	152	4
	[C$_4$MIM]Cl[6]	60	53	4
	[C$_4$MMIM]Cl	92	76	4
	ChCl/ ZnCl$_2$[7]	89	85	5
	[TEA][BF4][8]	72	65	4
	[DEA][BF4][9]	30	37.5	4
	[MEA][BF4][10]	33	58	4
	[C$_{16}$MMIM][11],Br	98	126	4
	[C$_{10}$MMIM]Br	68	75	4
	[C$_4$MMIM]Br	76	67	4
	[C$_2$MIM]tosylate	50	69.5	6
	[C$_4$MIM]octylsulfate	34	36.44	6
	[C$_1$MIM][Ntf2][12]	26	64.94	6
	[C$_2$MIM][Ntf2]	-3	55.2	6
	[C$_4$MIM][Ntf2]	-4	53.49	6
	[C$_6$MIM][Ntf2]	-7	63.2	6
	[C$_8$MIM][Ntf2]	-23	52.96	6
	[C$_4$MMIM]Cl	92.89	76.38	4
	[C$_4$MMIM]Br	76.66	66.98	4
	[C$_{10}$MMIM]Br	68.35	95.4	4
	[Pyr][BF4][13]	87.12	134.81	7
	[C$_2$Py][Ntf2][14]	31	19.85	6
	[C$_3$Py][Ntf2][15]	45	30.12	6
	[C$_4$Py][Ntf2][16]	26	27.7	6
	[C$_5$Py][Ntf2][17]	0	51.55	6
	[N1114][Ntf2][18]	17	16.15	8
	[N1123][Ntf2][19]	-11.7	54.5	9
	KF·4H$_2$O	~ 18.5	~ 245	10
	CaCl$_2$·6H$_2$O	~ 29	~ 170	11
	Na$_2$SO$_4$·10H$_2$O	32	254	11

salt hydrates	$Na_2HPO_4 \cdot 12H_2O$	36.5	279	[12]
	$Zn(NO_3)_2 \cdot 6H_2O$	36	147	[11]
	$FeCl_3 \cdot 6H_2O$	37	186	[12]
	$CaCl_2 \cdot 4H_2O$	44	100	[13]
	$LiNO_3 \cdot 3H_2O$	30	270	[14]

References

1. Davis Jr, J.; Gordon, C.; Hilgers, C.; Wasserscheid, P., Ionic liquids in synthesis. *Wiley-VCH Verlag GmbH & Co., New York* **2003**.
2. Van Valkenburg, M. E.; Vaughn, R. L.; Williams, M.; Wilkes, J. S., Thermochemistry of ionic liquid heat-transfer fluids. *Thermochimica Acta* **2005,** *425* (1-2), 181-188.
3. Vijayraghavan, R.; Rana, U. A.; Elliott, G. D.; MacFarlane, D. R., Protic ionic solids and liquids based on the guanidinium cation as phase-change energy-storage materials. *Energy Technology* **2013,** *1* (10), 609-612.
4. Zhu, J.; Bai, L.; Chen, B.; Fei, W., Thermodynamical properties of phase change materials based on ionic liquids. *Chemical Engineering Journal* **2009,** *147* (1), 58-62.
5. Fanglong, Q.; Jinhe, S.; Shaolei, X.; Chenglong, S.; Yongzhong, J., Preparation and thermal property of ionic liquid based on $ZnCl_2$/ChCl. *International Proceedings of Chemical Biological and Environmental Engineering* **2015,** *90*, 70-75.
6. Marcus, Y., Room Temperature Ionic Liquids. In *Ionic Liquid Properties: From Molten Salts to RTILs*, Springer International Publishing: Cham, 2016; pp 123-220.
7. Domańska, U., Thermophysical properties and thermodynamic phase behavior of ionic liquids. *Thermochimica Acta* **2006,** *448* (1), 19-30.
8. Kazakov, A. M., J.W.; Chirico, R.D.; Paulechka, E.; Diky, V.; Muzny, C.D.; Kroenlein, K.; Frenkel, M., NIST Standard Reference Database 147: NIST Ionic Liquids Database - (ILThermo). 07/02/2021 ed.; National Institute of Standards and Technology: Gaithersburg MD, Vol. 2.
9. Hayashi, E.; Thomas, M. L.; Hashimoto, K.; Tsuzuki, S.; Ito, A.; Watanabe, M., Application of Protic Ionic Liquids to CO_2 Separation in a Sulfonated Polyimide-Derived Ion Gel Membrane. *ACS Applied Polymer Materials* **2019,** *1* (6), 1579-1589.
10. Shamberger, P. J.; Reid, T., Thermophysical properties of potassium fluoride tetrahydrate from (243 to 348) K. *Journal of Chemical & Engineering Data* **2013,** *58* (2), 294-300.
11. Abhat, A., Low temperature latent heat thermal energy storage: heat storage materials. *Solar Energy* **1983,** *30* (4), 313-332.
12. Guion, J.; Sauzade, J.; Laügt, M., Critical examination and experimental determination of melting enthalpies and entropies of salt hydrates. *Thermochimica Acta* **1983,** *67* (2-3), 167-179.
13. Ushak, S.; Cruz, M. J.; Cabeza, L. F.; Grágeda, M., Preparation and characterization of inorganic PCM microcapsules by fluidized bed method. *Materials* **2016,** *9* (1), 24.
14. Shamberger, P. J.; Reid, T., Thermophysical properties of lithium nitrate trihydrate from (253 to 353) K. *Journal of Chemical & Engineering Data* **2012,** *57* (5), 1404-1411.