Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

NMR Study on the Cellulose Dissolution Mechanism in $CaCl_2 \cdot 6H_2O$-LiCl Molten Salt Hydrate

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KEYWORDS: Cellulose; Molten salt hydrate; Solid-state NMR; Dissolution; Role of Li^+ ions

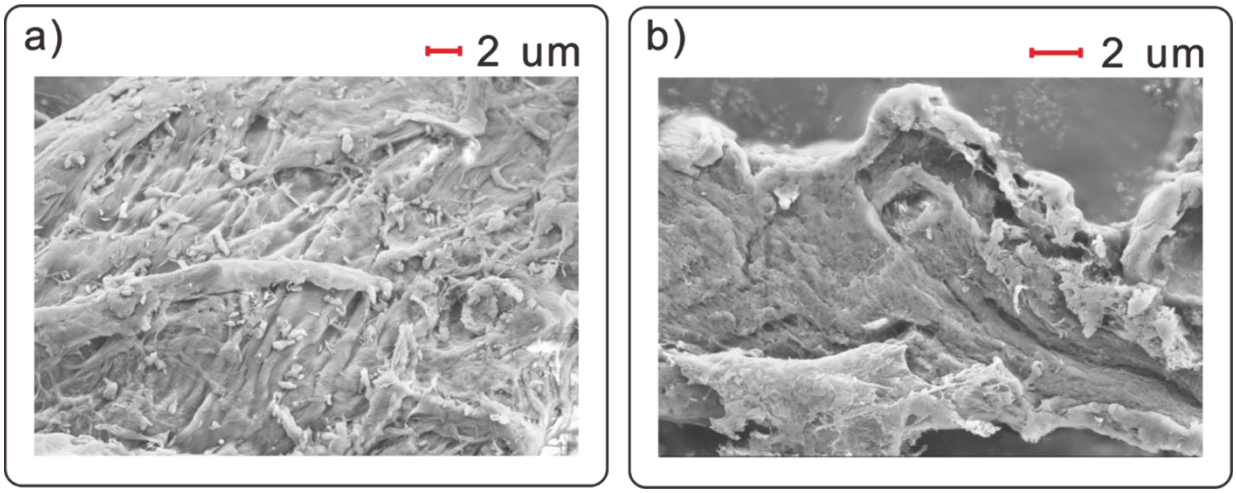

Figure S1. SEM photos of a) cellulose and b) regenerated cellulose.

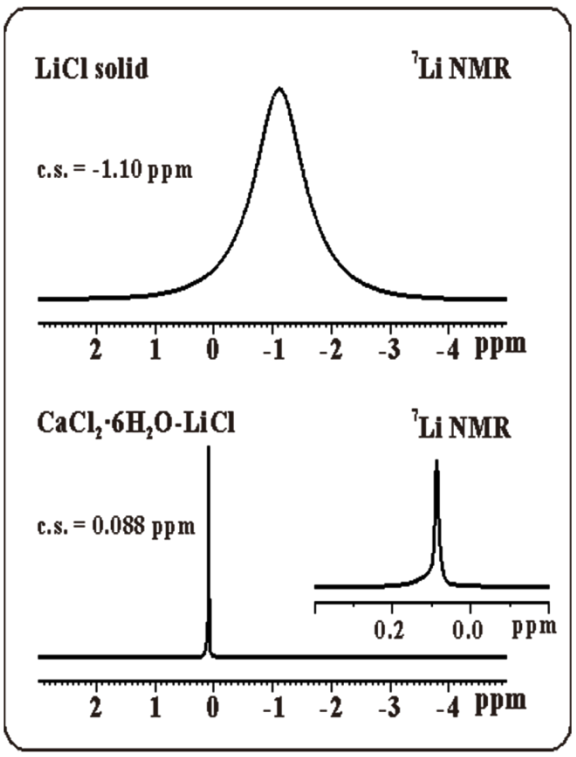

Figure S2. ^{7}Li NMR spectra of LiCl solid salt and $CaCl_2 \cdot 6H_2O$-LiCl molten salt hydrate at room temperature.

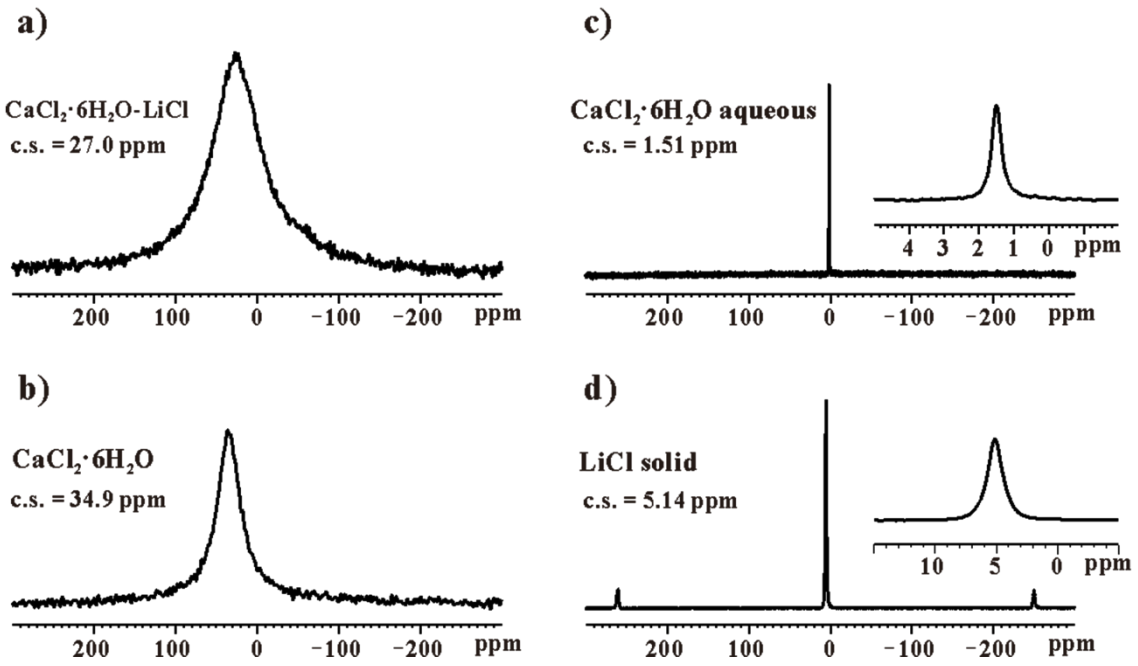

Figure S3. ^{35}Cl NMR spectra of $CaCl_2 \cdot 6H_2O$-LiCl molten salt hydrate at room temperature: a) $CaCl_2 \cdot 6H_2O$ LiCl; b) $CaCl_2 \cdot 6H_2O$; c) $CaCl_2 \cdot 6H_2O$ aqueous; d) LiCl solid salt.

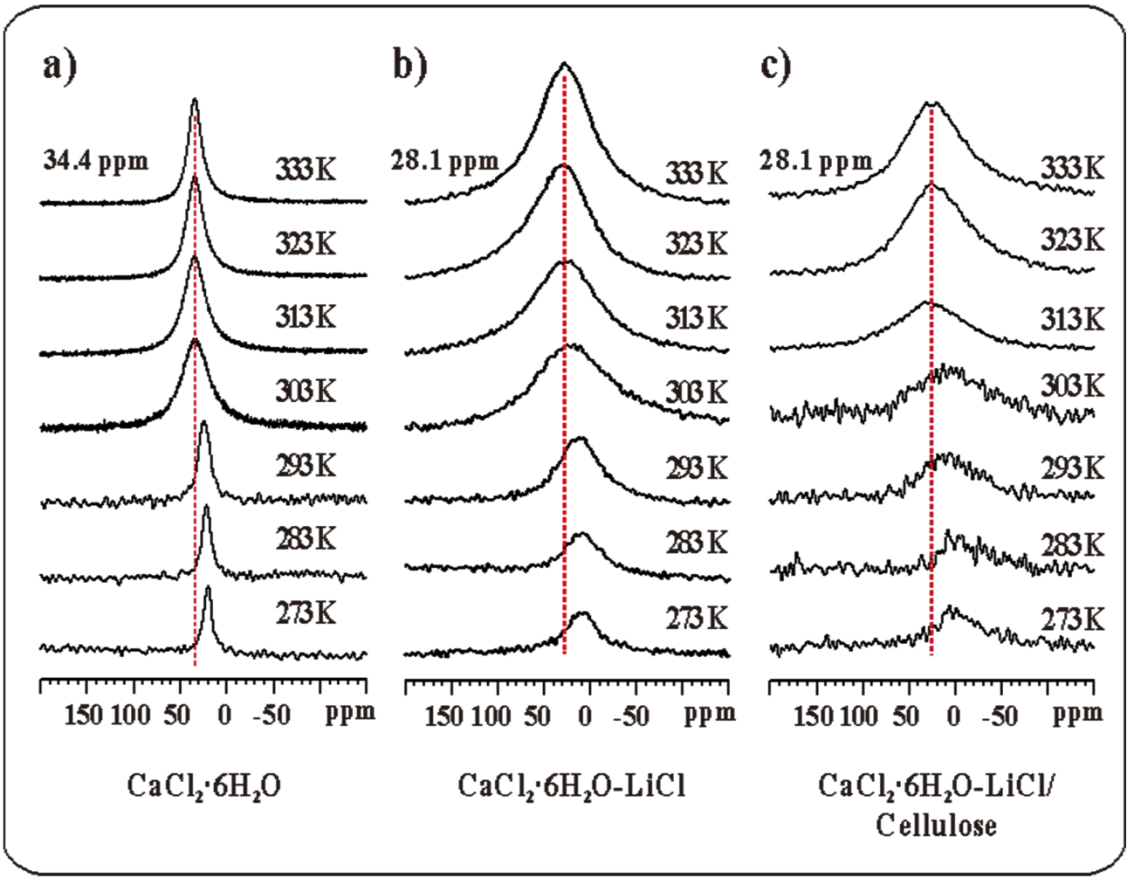

Figure S4. Variable-temperature ^{35}Cl single pulse excitation NMR spectra of $CaCl_2 \cdot 6H_2O$ a), $CaCl_2 \cdot 6H_2O$-LiCl b) and $CaCl_2 \cdot 6H_2O$-LiCl/cellulose system c) at temperature range from 273 K to 333 K.

Table S1. Comparison of $CaCl_2 \cdot 6H_2O$-LiCl with the reported molten salt hydrates in the literatures.

Molten Salt Hydrates Solvents	Melting point	Solubility	Reference
$CaCl_2 \cdot 6H_2O$-LiCl	120 ℃	3.0 %	This work
LiBr (65%, wt)	130 ℃	1.3 %	[1]
$LiBr \cdot 3H_2O$	140 ℃	1.0 %	[2]
$LiI \cdot 2H_2O$	100 ℃	0.25 %	[3]
$LiClO_4 \cdot 3H_2O$	100 ℃	1.6 %	[4]

1. X. Q. Zhang, N. Y. Xiao, H. H. Wang, C. F. Liu and X. J. Pan, *Polymers*, 2018, **10**, 614.

2. L. Zhang, Y. Liao, Y. C. Wang, S. Zhang, W. Q. Yang, X. J. Pan and Z. L. Wang, *Adv. Funt. Mater*, 2020, **30**, 2001763.

3. S. Fischer, W. VOIGT and K. FISCHER, *Cellulose*, 1999, **6**, 213-219.

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Table S2. Parameters of all simulation boxes in AIMD.

System	N(Ca)	N(Cl)	N(H)	N(O)	N(Li)	N(C)	N(cellulose)	a(Å)	Density (g/cm^3)
$CaCl_2 \cdot 6H_2O$-LiCl	6	20	72	36	8	/	/	11.55	1.78
$CaCl_2 \cdot 6H_2O$-LiCl / cellulose	6	20	94	47	8	12	1	12.30	1.78
LiCl/ H_2O	/	1	112	56	1	/	/	12.04	1.0

Table S3. The data of chemical shielding calculations of Li NMR in LiCl/H_2O.

	500fs	**550fs**	**600fs**	**650fs**	**700fs**	**750fs**	**800fs**	**850fs**	**900fs**	**950fs**	**1000fs**	**AVG**
Li1	88.61	88.3	88.95	88.82	87.82	88.86	88.15	88.86	88.95	88.49	88.63	88.59

Table S4. The data of chemical shielding calculations of Li NMR in $CaCl_2 \cdot 6H_2O$-LiCl.

	500fs	550fs	600fs	650fs	700fs	750fs	800fs	850fs	900fs	950fs	1000fs	AVG
Li1	89.41	88.68	89.2	88.97	87.96	88.98	87.97	89.54	88.73	88.22	89.6	88.84
Li2	88.96	88.36	89.05	89.01	88.53	88.76	89.39	89.1	88.87	89	88.89	88.90
Li3	87.54	88.29	88.38	88.2	88.83	88.49	88.44	88.02	88.31	88.18	89.14	88.35
Li4	88.64	88.29	88.01	88.96	88.19	88.54	88.53	88.51	88.96	88.52	88.61	88.52
Li5	89.64	89.46	89.57	88.92	89.34	89.64	88.56	88.96	89.29	88.28	88.42	89.10
Li6	88.99	89.21	88.33	88.82	88.74	88.42	87.66	88.88	88.41	87.95	88.99	88.58
Li7	90.49	89.99	89.69	90.02	90.28	89.45	89.84	89.42	89.27	88.89	88.23	89.60
Li8	88.6	88.26	88.12	87.04	87.94	88.43	88.44	88.7	87.87	88.73	88.31	88.22

The chemical shielding average of all Li ions in $CaCl_2 \cdot 6H_2O$-LiCl system is 88.76 ppm.
The calculation Li NMR in $CaCl_2 \cdot 6H_2O$-LiCl system reference to $LiCl/H_2O$ is -0.17 ppm.
The data of Li NMR in $CaCl_2 \cdot 6H_2O$-LiCl/cellulose.

Table S5. The data of chemical shielding calculations of Li NMR in $CaCl_2 \cdot 6H_2O$-LiCl/cellulose.

	500fs	**550fs**	**600fs**	**650fs**	**700fs**	**750fs**	**800fs**	**850fs**	**900fs**	**950fs**	**1000fs**	**AVG**
Li1	86.89	87.09	86.26	87.04	86.55	87.79	87.76	86.07	88.12	88.53	88.24	87.30
Li2	88.99	88.66	89.79	90.21	90.03	89.83	89.43	89.41	88.3	89.38	88.52	89.32
Li3	88.33	88.82	88.94	88.36	89.34	89.16	88.72	89.33	88.78	89.1	88.71	88.87
Li4	89.39	89.34	87.65	88.78	88.5	88.35	87.99	88.56	88.26	88.83	89.34	88.64
Li5	87.08	87.29	88.21	88.01	89.51	88.48	89.23	89.1	88.18	88.86	88.76	88.43
Li6	88.69	89.64	88.45	89.36	88.11	89.26	88.08	88.76	88.31	89.11	88.84	88.78
Li7	89.49	88.39	88.89	87.77	89.04	88.16	88.58	89.08	89.14	88.17	89.14	88.71
Li8	87.73	87.51	88.58	88.28	87.79	88.69	88.4	88.62	89.36	87.56	88.48	88.27

The chemical shielding average of all Li ions in $CaCl_2 \cdot 6H_2O$-LiCl/cellulose system is 88.54 ppm.
The calculation Li NMR in $CaCl_2 \cdot 6H_2O$-LiCl/cellulose system reference to $LiCl/H_2O$ is 0.05 ppm.