Electronic Supplementary Information (ESI)

Cation Does Matter：How Cationic Structure Affects the Dissolution of Cellulose in Ionic Liquids

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^{1}H NMR data:

1-Butyl-3-methylimidazolium acetate (**1**, [C_4mim][CH_3COO]). ^{1}H NMR (400MHz; DMSO-d_6; δ/ppm, relative to TMS): 0.880(t,3H), 1.224(m,2H), 1.548(s,3H), 1.752(m,2H), 3.867(s,3H), 4.182(t,2H), 7.773(s,1H), 7.843(s,1H), 9.972(s,1H).

1-Methoxyethyl-3-methylimidazolium acetate (**2**, [C_1OC_2mim][CH_3COO]). ^{1}H NMR (400MHz; D_2O, δ/ppm, relative to TMS): 1.792(s,3H), 3.269(s,3H), 3.721(t,2H), 3.789(s,3H), 4.280(t,2H), 7.336(d,1H), 7.393(d,1H), 8.629(s,1H).

1-Hydroxyethyl-3-methylimidazolium acetate (**3**, [C_2OHmim][CH_3COO]). ^{1}H NMR (400MHz; DMSO-d_6, δ/ppm, relative to TMS): 1.581(s,3H), 3.687(t,2H), 3.852(s,3H), 4.247(t,2H), 7.691(s,1H), 7.784(s,1H), 9.594(s,1H).

1-Butyl-2,3-dimethylimidazolium acetate (**4,** [C_4dmim][CH_3COO]). ^{1}H NMR (400MHz; D_2O, δ/ppm, relative to TMS): 0.802(t,3H), 1.198(m,2H), 1.661(m,2H), 1.778(s,3H), 2.461(s,3H), 3.640(s,3H), 3.983(t,3H), 7.190(d,1H), 7.224(d,1H).

1-Benzyl-3-methylimidazolium acetate (**5**, [phC$_1$mim][CH$_3$COO]). ^{1}H NMR (400MHz; D$_2$O, δ/ppm, relative to TMS): 1.762(s,3H), 3.727(s,3H), 5.224(s,2H), 7.256-7.343(m,7H), 8.590(s,1H).

N-ethyl-N-methylmorpholium acetate (**6**, [C$_2$mmor][CH$_3$COO]). ^{1}H NMR (400MHz; D$_2$O, δ/ppm, relative to TMS): 1.272(t,3H), 1.795(s,3H), 3.042(s,3H), 3.364(m,4H), 3.424(m,2H), 3.936(s,4H).

N-allyl-N-methylmorpholium acetate (**7**, [C=C$_2$mmor][CH$_3$COO]). ^{1}H NMR (400MHz; D$_2$O, δ/ppm, relative to TMS): 1.803(s,3H), 3.065(s,3H), 3.349(m,2H), 3.421(m,2H), 3.695(t,6H), 5.561(q,2H), 5.935(m,1H).

N-allyl-N-methylpiperidium acetate (**8**, [C=C$_2$mpip][CH$_3$COO]). ^{1}H NMR (400MHz; D$_2$O, δ/ppm, relative to TMS): 1.536(m,2H), 1781(d,4H), 1.801(s,3H), 2.896(s,3H), 3.207(m,4H), 3.818(d,2H), 5.597(t,2H), 5.910(m,1H).

N-butyl-N-methylpiperidium acetate (**9**, [C$_4$mpip][CH$_3$COO]). ^{1}H NMR (400MHz; D$_2$O, δ/ppm, relative to TMS): 0.817(t,3H), 1.235(m,2H), 1.524(m,2H), 1.590(m,2H), 1.729(s,4H), 1.762(s,3H), 2.871(s,3H), 3.185(m,6H).

1-Butyl-1-methylPyrrolidinium acetate (**10**, [C$_4$mPyr][CH$_3$COO]). ^{1}H NMR (400MHz; D$_2$O, δ/ppm, relative to TMS): 0.908(t,3H), 1.337(m,2H), 1.732(m,2H), 1.881(s,3H), 2.159(s,4H), 2.986(s,3H), 3.276(t,2H), 3.451(s,4H)

1-Butyl-3-ethylbenzimidazolium acetate (**11**, [C$_4$ebim][CH$_3$COO]). ^{1}H NMR (400MHz; D$_2$O, δ/ppm, relative to TMS): 0.806(t,3H), 1.224(m,2H), 1.485(t,3H), 1.784(s,3H), 1.826(q,2H), 4.366(m，4H), 7.539(m,2H), 7.740(m,2H), 9.188(s,1H).

1,3-Diethylbenzimidazolium acetate (**12**, [C$_2$ebim][CH$_3$COO]). ^{1}H NMR (400MHz; DMSO-d$_6$; δ/ppm, relative to TMS): 1.53(m,9H), 4.52(q,4H), 7.68(m,2H), 8.07(m,2H),

10.17(s,1H).

1-Butyl-3-ethylbenzotriazolium acetate (**13**, [C_4ebt][CH_3COO]). ^{1}H NMR (400MHz; DMSO-d_6; δ/ppm, relative to TMS): 0.921(t,3H), 1.386(m,2H), 1.645(t,3H), 1.693(s,3H), 2.003(m,2H), 5.046(m,4H), 7.995(m,2H), 8.479(m,2H).

Table S1 Thermal properties of the ionic liquids

Entry	IL	T_m/°C [a]	T_g/°C [a]	T_d/°C [b]
1	[C_4mim][CH_3COO]	c	-58	221
2	[C_1OC_2mim][CH_3COO]	c	-54	217
3	[C_2OHmim][CH_3COO]	57	c	234
4	[C_4dmim][CH_3COO]	52	c	223
5	[phC_1mim][CH_3COO]	c	-23	211
6	[C_2mmor][CH_3COO]	47	c	177
7	[C=C_2mmor][CH_3COO]	c	-33	160
8	[C=C_2mpip][CH_3COO]	78	c	171
9	[C_4mpip][CH_3COO]	c	-54	183
10	[C_4mpyr][CH_3COO]	60	c	165
11	[C_4ebim][CH_3COO]	c	-27	209
12	[C_2ebim][CH_3COO]	55	c	204
13	[C_4ebt][CH_3COO]	c	-53	162

[a] Temperature at signal peak, [b] temperature for 10% weight loss under N_2 gas, [c] not observed.

Table S2 Impurity contents in the ionic liquids

Entry	IL	[Cl^-]/mol.kg^{-1}	[Br^-]/mol.kg^{-1}	H_2O/ppm
1	[C_4mim][CH_3COO]	0.011		589
2	[C_1OC_2mim][CH_3COO]	0.013		355
3	[C_2OHmim][CH_3COO]	0.015		466
4	[C_4dmim][CH_3COO]	0.0085		519
5	[phC_1mim][CH_3COO]	0.012		527
6	[C_2mmor][CH_3COO]		0.00028	521
7	[C=C_2mmor][CH_3COO]	0.014		422
8	[C=C_2mpip][CH_3COO]	0.010		405
9	[C_4mpip][CH_3COO]	0.0095		428
10	[C_4mpyr][CH_3COO]	0.010		420
11	[C_4ebim][CH_3COO]	0.0082		468
12	[C_2ebim][CH_3COO]		0.0028	489
13	[C_4ebt][CH_3COO]		0.0030	396

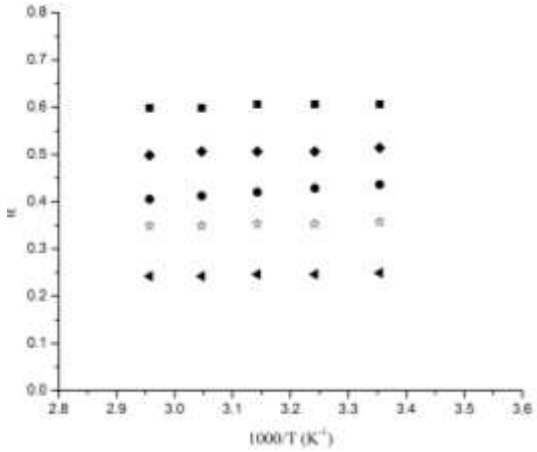

Fig. S1 Temperature dependence of α parameter of the ILs: (■), [C_4mim][CH_3COO]; (◆), [C_1OC_2mim][CH_3COO]; (●), [phC_1mim][CH_3COO]; (☆), [C_2mmor][CH_3COO]; and (◀) [C=C_2mmor][CH_3COO].

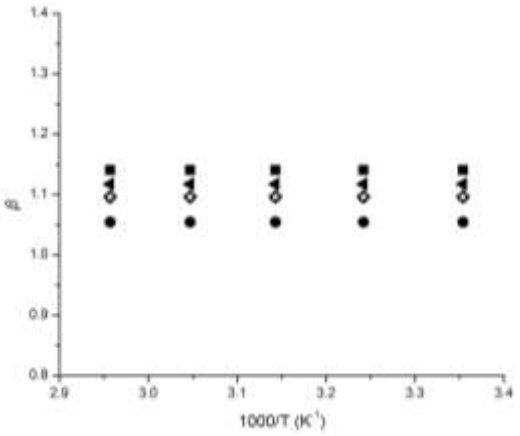

Fig. S2 Temperature dependence of β parameter of the ILs: (■), [C_4mim][CH_3COO]; (◆), [C_1OC_2mim][CH_3COO]; (●), [phC_1mim][CH_3COO]; (☆), [C_2mmor][CH_3COO]; and (◀) [C=C_2mmor][CH_3COO].

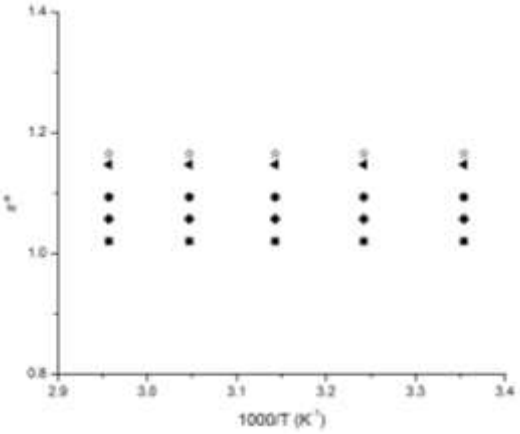

Fig. S3 Temperature dependence of π* parameter of the ILs: (■), [C_4mim][CH_3COO]; (◆), [C_1OC_2mim][CH_3COO]; (●), [phC_1mim][CH_3COO]; (☆), [C_2mmor][CH_3COO]; and (◀) [C=C_2mmor][CH_3COO].

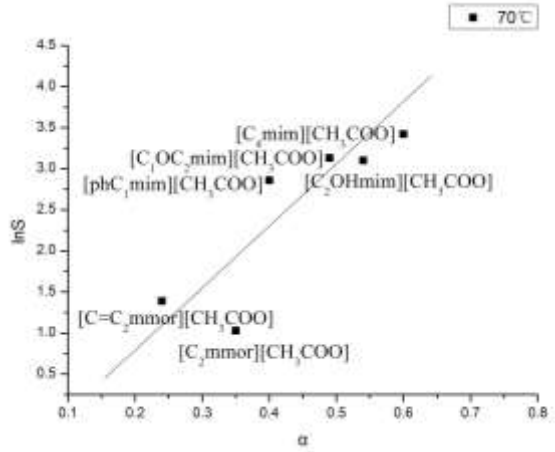

Fig. S4 The linear correlation between solubility of cellulose and α parameter of the ILs at 70°C.

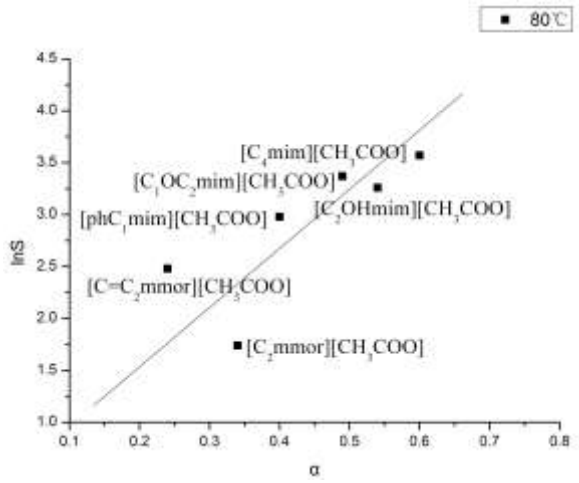

Fig. S5 The linear correlation between solubility of cellulose and α parameter of the ILs at 80°C

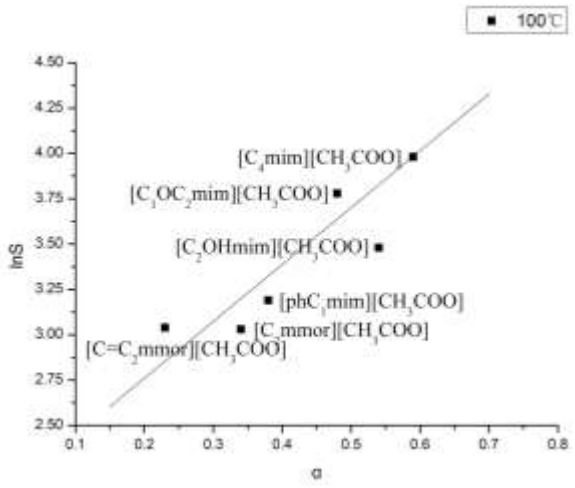

Fig. S6 The linear correlation between solubility of cellulose and α parameter of the ILs at 100°C.

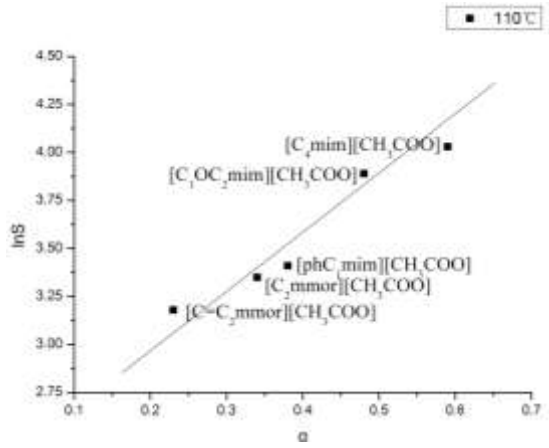

Fig. S7 The linear correlation between solubility of cellulose and *α* parameter of the ILs at 110°C.

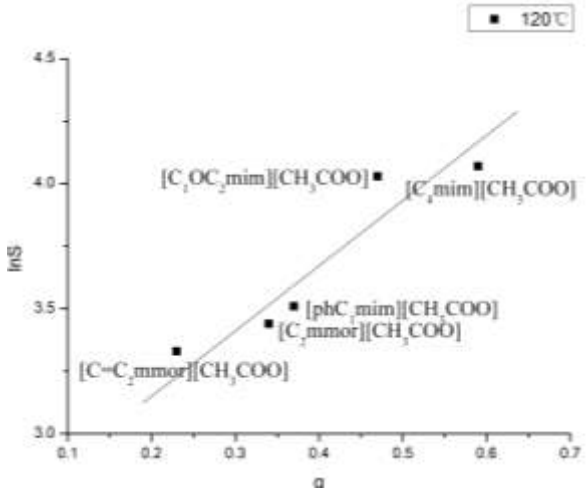

Fig. S8 The linear correlation between solubility of cellulose and *α* parameter of the ILs at 120°C.