

Effect of cation structure on the cellulose dissolution in aqueous solutions of organic onium hydroxides

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1. Materials

Table S1-1. Assignment of NMR spectra of *N*-butylpyridinium hydroxide ([C₄py]OH)

Nw		Type of H
10	200	
8.85 (d, <i>J</i> = 6.0 Hz, 2H*)	8.84 (d, <i>J</i> = 5.5 Hz, 2H*)	benzene ring
8.54 (t, <i>J</i> = 7.8 Hz, 1H*)	8.53 (t, <i>J</i> = 7.8 Hz, 1H*)	benzene ring
8.07 (t, <i>J</i> = 6.6 Hz, 2H*)	8.05 (t, <i>J</i> = 6.9 Hz, 2H*)	benzene ring
4.80 (s, 21H)	4.79 (s, 401H)	H ₂ O and OH
4.61 (t, <i>J</i> = 7.6 Hz, 2H)	4.60 (t, <i>J</i> = 7.3 Hz, 2H)	NCH ₂
2.04-1.96 (m, 2H)	1.95-2.03 (m, 2H)	NCH ₂ CH ₂
1.41-1.32 (m, 2H)	1.30-1.40 (m, 2H)	N(CH ₂) ₂ CH ₂
0.94 (t, <i>J</i> = 7.3 Hz, 3H)	0.93 (t, <i>J</i> = 7.3 Hz, 3H)	N(CH ₂) ₃ CH ₃

*The integral of chemical shift was less than 2H or 1H due to the decomposition of pyridinium ring in alkaline state. The decomposition was observed even diluted state (Nw=200).

Table S1-2. Assignment of NMR spectra of 1-butyl-3-methylimidazolium hydroxide ([C₄mim]OH)

Nw				Type of H
10	15	20	25	
8.32 (d, <i>J</i> = 214.2 Hz, 1H*)	8.53 (d, <i>J</i> = 189.6 Hz, 1H*)	8.50 (d, <i>J</i> = 175.8 Hz, 1H*)	8.52 (d, <i>J</i> = 163.2 Hz, 1H*)	NCHN
7.24-7.45 (m, 2H*)	7.24-7.45 (m, 2H*)	7.25-7.43 (m, 2H*)	7.23-7.43 (m, 2H*)	NCHCHN
4.88 (s, 21H)	4.88 (m, 31H)	4.91 (s, 41H)	4.89 (m, 51H)	H ₂ O and OH
4.11 (t, <i>J</i> = 7.2 Hz, 2H)	4.12 (t, <i>J</i> = 7.2 Hz, 2H)	4.11 (t, <i>J</i> = 7.2 Hz, 2H)	4.13 (t, <i>J</i> = 7.2 Hz, 2H)	NCH ₂
3.80 (t, <i>J</i> = 29.2, 3H)	3.83 (t, <i>J</i> = 19.8 Hz, 3H)	3.82 (t, <i>J</i> = 20.3 Hz, 3H)	3.87 (t, <i>J</i> = 21.5 Hz, 3H)	NCH ₃
1.70-1.75 (m, 2H)	1.72-1.78 (m, 2H)	1.71-1.77 (m, 2H)	1.74-1.80 (m, 2H)	NCH ₂ CH ₂
1.19 (q, <i>J</i> = 7.4 Hz, 2H)	1.22 (q, <i>J</i> = 7.4 Hz, 2H)	1.21 (q, <i>J</i> = 7.4 Hz, 2H)	1.24 (q, <i>J</i> = 7.4 Hz, 2H)	N(CH ₂) ₂ CH ₂
0.71-0.81 (m, 3H)	0.76-0.86 (m, 3H)	0.75-0.85 (m, 3H)	0.78-0.88 (m, 3H)	N(CH ₂) ₃ CH ₃

*The integral of chemical shift was less than 2H designating the de-protonation at the C(2) position of imidazolium ring.

Table S1-3. Assignment of NMR spectra of cholinium hydroxide ([Ch]OH)

Nw				Type of H
10	15	20	25	
5.53-5.57 (m, 1H*)	5.36 (s, 1H)	5.22 (s, 1H)	-	CH ₂ OH
5.43 (s, 21H)	5.24 (s, 31H)	5.10 (s, 41H)	-	H ₂ O and OH
3.86 (t, J = 5.7 Hz, 2H)	3.87-3.90 (m, 2H)	3.91-3.94 (m, 2H)	-	NCH ₂ CH ₂
3.26 (t, J = 5.7 Hz, 2H)	3.29 (t, J = 5.7 Hz, 2H)	3.32 (t, J = 5.7 Hz, 2H)	-	NCH ₂
3.07 (s, 9H)	3.08 (s, 9H)	3.11 (s, 9H)	-	NCH ₃

*The integral of chemical shift was less than 1H due to the de-protonation of the hydroxyl group of cholinium cation.

Table S1-4. Assignment of NMR spectra of *N*-butyl-*N*-methylmorpholinium hydroxide ([Mor₁₄]OH) (500 MHz, D₂O)

Nw				Type of H
10	15	20	25	
5.06 (s, 21H)	5.02 (s, 31H)	4.98 (s, 41H)	4.95 (s, 51H)	H ₂ O and OH
3.84-3.92 (m, 4H)	3.91 (t, J = 4.9 Hz, 4H)	3.92 (t, J = 4.6 Hz, 4H)	3.95 (t, J = 4.6 Hz, 4H)	CH ₂ OCH ₂
3.28-3.35 (m, 6H)	3.31-3.38 (m, 6H)	3.32-3.39 (m, 6H)	3.34-3.43 (m, 6H)	NCH ₂ and CH ₂ NCH ₂
3.03 (s, 3H)	3.06 (s, 3H)	3.07 (s, 3H)	3.09 (s, 3H)	NCH ₃
1.59-1.63 (m, 2H)	1.63-1.66 (m, 2H)	1.64-1.67 (m, 2H)	1.67-1.70 (m, 2H)	NCH ₂ CH ₂
1.22-1.26 (m, 2H)	1.26-1.30 (m, 2H)	1.27-1.31 (m, 2H)	1.29-1.34 (m, 2H)	N(CH ₂) ₂ CH ₂
0.81 (t, J = 7.4 Hz, 3H)	0.85 (t, J = 7.4 Hz, 3H)	0.86 (t, J = 7.4 Hz, 3H)	0.88 (t, J = 7.4 Hz, 3H)	N(CH ₂) ₃ CH ₃

Table S1-5. Assignment of NMR spectra of *N*-butyl-*N*-methylpiperidinium hydroxide ([Pip₁₄]OH) (500 MHz, D₂O)

Nw				Type of H
10	15	20	25	
5.04 (s, 21H)	5.03 (s, 31H)	4.99 (s, 41H)	4.97 (s, 51H)	H ₂ O and OH
3.12-3.18 (m, 6H)	3.14-3.19 (m, 6H)	3.17-3.22 (m, 6H)	3.19-3.24 (m, 6H)	NCH ₂ and CH ₂ NCH ₂
2.86 (s, 3H)	2.88 (s, 3H)	2.90 (s, 3H)	2.91 (s, 3H)	NCH ₃
1.67-1.74 (broad, 4H)	1.71 (broad, 4H)	1.75 (broad, 4H)	1.76 (broad, 4H)	CH ₂ CH ₂ NCH ₂ CH ₂
1.44-1.58 (m, 4H)	1.45-1.60 (m, 4H)	1.47-1.64 (m, 4H)	1.49-1.66 (m, 4H)	N(CH ₂) ₂ CH ₂ (in ring) and NCH ₂ CH ₂
1.18-1.25 (m, 2H)	1.20-1.27 (m, 2H)	1.22-1.30 (m, 2H)	1.25-1.32 (m, 2H)	N(CH ₂) ₂ CH ₂
0.80 (t, J = 7.4 Hz, 3H)	0.82 (t, J = 7.4 Hz, 3H)	0.85 (t, J = 7.4 Hz, 3H)	0.86 (t, J = 7.4 Hz, 3H)	N(CH ₂) ₃ CH ₃

Table S1-6. Assignment of NMR spectra of *N*-butyl-*N*-methylpyrrolidinium hydroxide ([Pyr₁₄]OH) (500 MHz, D₂O)

Nw				Type of H
10	15	20	25	
5.07 (s, 21H)	5.02 (s, 31H)	4.97 (s, 41H)	4.94 (s, 51H)	H ₂ O and OH
3.30-3.38 (m, 4H)	3.33-3.39 (m, 4H)	3.34-3.43 (m, 4H)	3.35-3.44 (m, 4H)	CH ₂ NCH ₂
3.15-3.18 (m, 2H)	3.17-3.21 (m, 2H)	3.20-3.24 (m, 2H)	3.21-3.26 (m, 2H)	NCH ₂
2.88 (s, 3H)	2.90 (s, 3H)	2.93 (s, 3H)	2.95 (s, 3H)	NCH ₃
2.04 (broad, 4H)	2.07 (broad, 4H)	2.10 (broad, 4H)	2.12 (broad, 4H)	CH ₂ CH ₂ NCH ₂ CH ₂
1.57-1.62 (m, 2H)	1.61-1.65 (m, 2H)	1.63-1.69 (m, 2H)	1.65-1.73 (m, 2H)	NCH ₂ CH ₂
1.20-1.25 (m, 2H)	1.23-1.28 (m, 2H)	1.26-1.32 (m, 2H)	1.26-1.35 (m, 2H)	N(CH ₂) ₂ CH ₂
0.80 (t, J = 7.4 Hz, 3H)	0.82 (t, J = 7.3 Hz, 3H)	0.86 (t, J = 7.6 Hz, 3H)	0.87 (t, J = 7.3 Hz, 3H)	N(CH ₂) ₃ CH ₃

Table S1-7. Assignment of NMR spectra of tetrabutylammonium hydroxide ($[N_{4444}]OH$)

Nw				Type of H
10	15	20	25	
4.82 (s, 21H)	4.82 (s, 31H)	4.82 (s, 41H)	4.84 (s, 51H)	H_2O and OH
3.18 (t, $J = 7.3$ Hz, 8H)	3.12 (t, $J = 8.1$ Hz, 8H)	3.10 (t, $J = 8.0$ Hz, 8H)	3.10 (t, $J = 8.5$ Hz, 8H)	NCH_2
1.54 (br, 8H)	1.52 (br, 8H)	1.52 (br, 8H)	1.54 (br, 8H)	NCH_2CH_2
1.33 (m, 8H)	1.30 (m, 8H)	1.29 (m, 8H)	1.29 (m, 8H)	$N(CH_2)_2CH_2$
0.88 (t, $J = 7.3$ Hz, 12H)	0.88 (t, $J = 7.3$ Hz, 12H)	0.88 (t, $J = 7.2$ Hz, 12H)	0.88 (t, $J = 7.3$ Hz, 12H)	$N(CH_2)_3CH_3$

Table S1-8. Assignment of NMR spectra of tetrabutylphosphonium hydroxide ($[P_{4444}]OH$)

Nw				Type of H
10	15	20	25	
4.86 (s, 21H)	4.85 (s, 31H)	4.87 (s, 41H)	4.87 (s, 51H)	H_2O and OH
2.14-2.20 (m, 8H)	2.10-2.16 (m, 8H)	2.10-2.15 (m, 8H)	2.09-2.15 (m, 8H)	PCH_2
1.34-1.50 (m, 16H)	1.36-1.47 (m, 16H)	1.39-1.56 (m, 16H)	1.35-1.50 (m, 16H)	$PCH_2CH_2CH_2$
0.89 (t, $J = 6.9$ Hz, 12H)	0.89 (t, $J = 7.1$ Hz, 12H)	0.89 (t, $J = 7.2$ Hz, 12H)	0.89 (t, $J = 7.4$ Hz, 12H)	$P(CH_2)_3CH_3$

Table S1-9. Assignment of NMR spectra of *N,N*-dibutylpyrrolidinium hydroxide ($[Pyr_{44}]OH$)

Nw	Type of H
10	
4.93 (s, 21H)	H_2O and OH
3.39 (broad, 4H)	CH_2NCH_2
3.09 (t, $J = 8.2$ Hz, 4H)	NCH_2
2.02 (broad, 4H)	$CH_2CH_2NCH_2CH_2$
1.55-1.47 (m, 4H)	NCH_2CH_2
1.23 (q, $J = 7.3$ Hz, 4H)	$N(CH_2)_2CH_2$
0.79 (t, $J = 7.3$ Hz, 6H)	$N(CH_2)_3CH_3$

Table S1-10. Assignment of NMR spectra of *N,N*-dibutylmorpholinium hydroxide ($[Mor_{44}]OH$)

Nw	Type of H
10	
4.87 (s, 21H)	H_2O and OH
4.03 (t, $J = 4.6$ Hz, 4H)	CH_2OCH_2
3.49 (t, $J = 5.0$ Hz, 4H)	CH_2NCH_2
3.40-3.44 (m, 4H)	NCH_2
1.65-1.73 (m, 4H)	NCH_2CH_2
1.44-1.34 (m, 4H)	$N(CH_2)_2CH_2$
0.95 (t, $J = 7.3$ Hz, 6H)	$N(CH_2)_3CH_3$

2. Methods

2.1 Kamlet-Taft parameter calculation

Three solutions having 30.0 mL of dehydrated methanol and 0.03 g of each dye were prepared. 0.075 mL of either dye_{NN} and dye_{4N} solution or 0.15mL of dye_{Rei} solution was separately transferred to an empty vial and dried under vacuum at 60 °C for 6 h. To these vials, 0.3mL of the chloride solutions were added and stirred gently. The sample solutions were placed in a quartz cell with a light path length of 0.1 mm and their UV-vis spectra were recorded. The Kamlet-Taft parameters were calculated according to the following equations (Equation (1) – (4)):

$$E_T(30) = 0.9986(28592 / \lambda_{\max(\text{Rei})}) - 8.6878 \dots (1)$$

$$\pi^* = 0.314(27.52 - \nu_{\text{NN}}) \dots (2)$$

$$\alpha = 0.0649 E_T(30) - 2.03 - 0.72\pi^* \dots (3)$$

$$\beta = (1.035\nu_{\text{NN}} + 2.64 - \nu_{4\text{N}}) / 2.80 \dots (4)$$

where, $\lambda_{\max(\text{dye})}$ is the maximum absorption wavelength of the dye and ν_{dye} is given as $1 / (\lambda_{\max(\text{dye})} \times 10^{-4})$.

3. Results

Table S2. Viscosity of OHAS with different Nw at 25 °C.

Type of OHAS	Viscosity / cP			
	$Nw^a = 10$	$Nw^a = 15$	$Nw^a = 20$	$Nw^a = 25$
[Ch]	^b	2.43	1.35	0.79
[Mor ₁₄]	9.61	4.80	2.93	1.98
[Pip ₁₄]	6.60	6.20	3.18	2.07
[Pyr ₁₄]	7.04	4.24	2.27	2.09
[N ₄₄₄₄]	N.A.	N.A.	N.A.	N.A.
[P ₄₄₄₄]	12.6	5.36	4.66	4.95

^a Ratio of H₂O/OH (mol/mol), ^b not evaluated due to the decomposition of cation structures

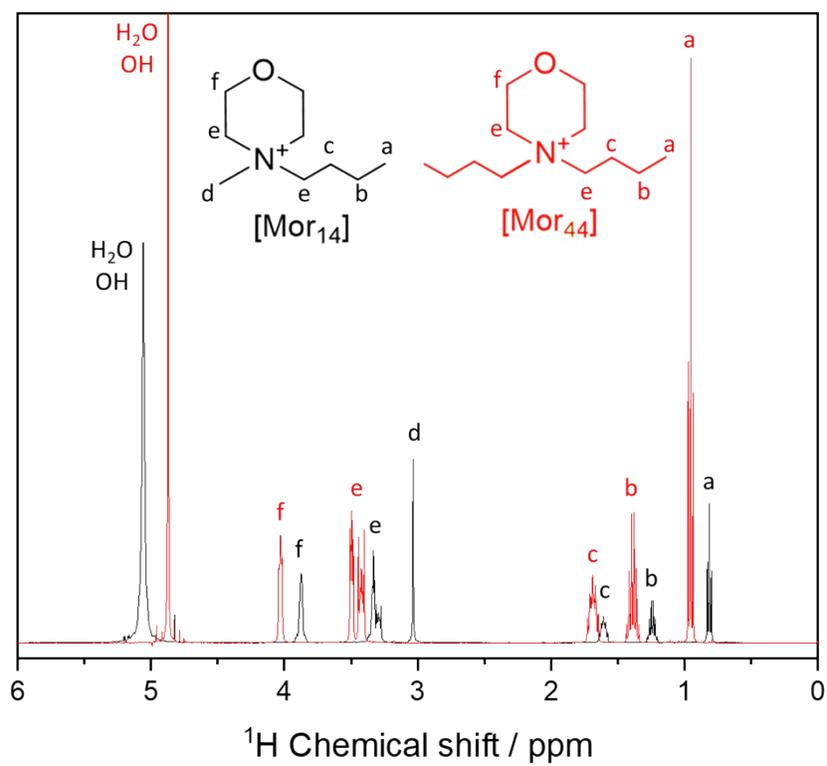
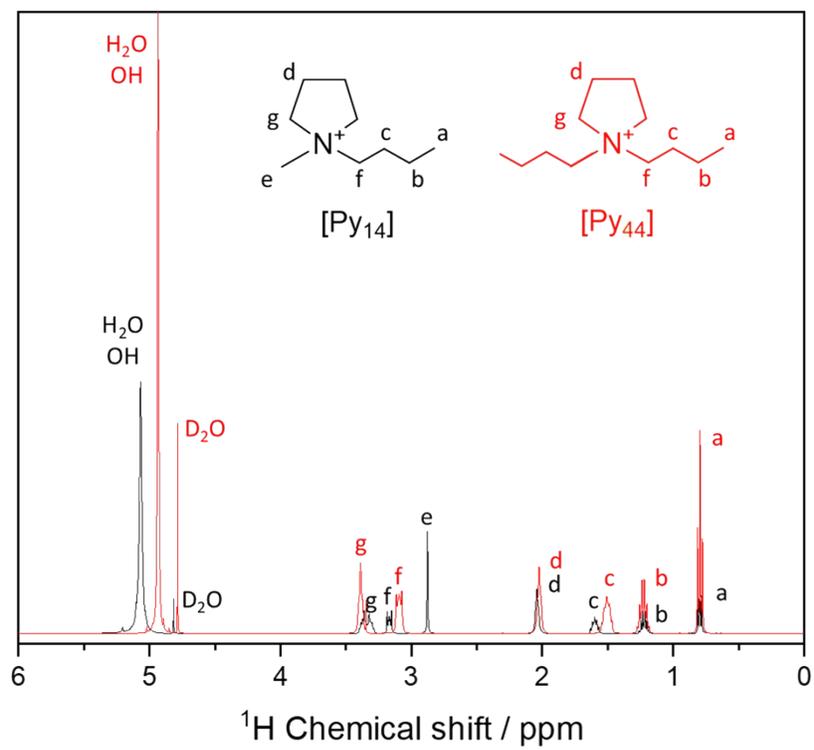


Figure S1. ^1H NMR spectra of [Py₁₄]OH, [Py₄₄]OH, [Mor₁₄]OH, and [Mor₄₄]OH.