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Liufang Ni

Fujian Agriculture and Forestry University

Xingmei Lu

Fujian Agriculture and Forestry University

Jing Yu

Fujian Agriculture and Forestry University

Changmei Lin

Fujian Agriculture and Forestry University

Xiaoxia Cao

Fujian University of Technology

Shilin Cao

Fujian Agriculture and Forestry University

Xiaojuan Ma (✉ 1212juanjuan@163.com)

Fujian Agriculture and Forestry University <https://orcid.org/0000-0001-5927-2658>

Haili Gao

Fujian Agriculture and Forestry University

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4 Liufang Ni^{1,2}, Xingmei Lu¹, Jing Yu¹, Changmei Lin¹, Xiaoxia Cao², Shilin Cao^{1*}, Xiaojuan
5 Ma^{1*}, Haili Gao^{1*}

6 *1. College of Materials Engineering, Fujian Agriculture and Forestry University,*

7 *Fuzhou 350002, China*

8 *2. School of Ecological Environment and Urban Construction, Fujian University of Technology,*

9 *Fuzhou 350002, China*

10 *Corresponding Author: Dr. Shilin Cao, Dr. Xiaojuan Ma, Dr. Haili Gao

11 College of Materials Engineering

12 Fujian Agriculture and Forestry University

13 Fuzhou 350002, China

14 E-mail: 1212juanjuan@163.com (Xiaojuan Ma)

15 E-mail: scutcs1@163.com (Shilin Cao)

16 **Abstract:** Ionic liquids are potential and successful cellulose solvent but still suffer technical and
17 economic issues in the cellulose commercialization. In this work, a relative low-viscosity
18 aqueous 1-ethyl-3-methylimidazole acetate (EmimAc with 10% water) was used instead of
19 EmimAc to dissolve cellulose; the results showed that adding NaOH to water can significantly
20 accelerate cellulose dissolution and the cellulose solubility increased with the NaOH
21 concentration in the EmimAc/10% water solution. NaOH can weaken the strong interaction
22 between water and EmimAc because it can bond preferentially with water by hydrogen bonding
23 and therefore release Ac^- from Ac^- -water cluster; which can enhance the reaction between Emim^+
24 and Ac^- and therefore improve the cellulose dissolution. Unfortunately, the NaOH introduction
25 inevitably cause a cellulose degradation via peeling reaction.

26 **Key words:** 1-ethyl-3-methylimidazole acetate; Sodium hydroxide; Cellulose dissolution;
27 Hydrogen bond basicity

28

29 **1. Introduction**

30 Natural cellulose is a kind of crystalline biopolymer which is composed of glucose units
31 connected by β -1-4 bonds forming a stacked layer through strong hydrogen bonding network of
32 intramolecular and intermolecular hydrogen bond connections. The special hydrogen bond
33 interactions endow natural cellulose with high chemical and mechanical stability, insoluble in
34 water and most organic solvents (Pinkert et al., 2010; Gericke et al., 2012; Andanson et al., 2014;
35 Grøssereid et al., 2019). However, the dissolution of cellulose is very important for the
36 subsequent high-value utilization (such as cellulose film, coating, etc.). Therefore, how to
37 effectively dissolve cellulose for subsequent high-value utilization is still a challenge.

38 In the past twenty years, ionic liquids have been demonstrated a promising green solvent for
39 cellulose dissolution due to their good physical properties and designability. Among the ionic
40 liquids, ionic liquids with acetate anion are widely used because of their higher hydrogen bond
41 alkalinity and greater solubility for cellulose (Fukaya et al., 2006; Kosan et al., 2008; Xu et al.,
42 2010; Zakrzewska et al., 2010; Zhao et al., 2012; Shi et al., 2014). Although the ionic liquids are
43 potential and successful cellulose solvents, they still suffer technical and economic issues. Ionic
44 liquids are usually viscous (Gardas et al., 2008; Xu et al., 2012), moreover, the cellulose
45 dissolution could further increase the viscosity of the system (Schlufter et al., 2009; Lovell et al.,
46 2010). The resistance of mass transfer from the viscose can not only impede the subsequent mass
47 cellulose dissolution but also cause difficulties in the separation of biomass and solute.
48 Additionally, the high price of ionic liquids are the other obstacle to the large-scale application of
49 ionic liquids (Andanson et al., 2014; Shi et al., 2014).

50 In order to decrease the viscosity of ionic liquids, some polar aprotic solvents (i.e., DMSO,
51 DMF, DMI, etc.) are suggested to be mixed with ionic liquids for cellulose dissolution. Studies

52 have shown that polar aprotic solvents can promote cellulose dissolution under the premise of
53 reducing viscosity (Huo et al., 2013; Andanson et al., 2014; Wang et al., 2014; Minnick et al.,
54 2016). However, the toxicity and difficulties in ionic liquids recovery have become new
55 issues (Xu et al., 2010). For this purpose, another kind of cosolvent-polar protic solvents (i.e.,
56 water, alcohols, etc.) have been proposed to be used as cosolvent. Recent studies have
57 demonstrated that the ionic liquids/water mixture are low-viscose solvent systems (Shi et al.,
58 2014; Roselli et al., 2017; Ni et al., 2021). Whereas, water is usually used as an antisolvent as the
59 driving force to separate cellulose and ionic liquids (Liu et al., 2010; Shi et al., 2014; Roselli et
60 al., 2017), since the solubility of cellulose in ionic liquids decrease with water content (Hauru et
61 al., 2012; Olsson et al., 2014).

62 Water is absolutely a clean and inexpensive cosolvent, if aqueous ionic liquids can dissolve
63 cellulose, the inexpensive, low-viscosity ionic liquids might have a bright future. Adding water
64 to EmimAc for selective separation of hemicellulose from cellulosic fiber have been
65 substantiated (Froschauer et al., 2013; Ni et al., 2021). Our previous attempts testified that
66 instead aqueous NaOH (NaOH-a) of water could not only further reduce the viscosity of the
67 EmimAc, but also enhance the hemicellulose separation from wood fibers (Ni et al., 2021). If the
68 use of EmimAc/10% NaOH-a system can also achieve good dissolution effect for cellulose, it
69 will be more advantageous and less cost than the use of anhydrous EmimAc. In this purpose, 90%
70 EmimAc mixing with 10% aqueous NaOH-a was used to dissolve cellulosic fibers, the NaOH
71 effects have been investigated.

72 **2. Experimental Section**

73 **2.1 Materials**

74 Cellulose sample, dissolving pulp was provided by Qingshan pulp mill (Fujian, China). The
75 ionic liquid, 1-ethyl-3-methylimidazolium acetate (EmimAc) (purity, 99%) was purchased from
76 Sigma and used directly without purification. The three dyes: Reichardt's dye (RD), 4-
77 Nitroaniline (NA) and N, N-diethyl-4-nitroaniline (DNA) were purchased from Aladdin
78 chemical reagent. Other chemicals used in the experiment were all of analytical grade and
79 purchased from Sinopharm Chemical Reagent Co., Ltd., Xiya Reagent, respectively. Sodium
80 hydroxide (analytical grade) purchased from West Asia reagent.

81 **2.2 Cellulose dissolution**

82 In the experiment, the air dried cellulose sample (2 wt%, based on the absolutely dry weight)
83 was slowly added to aqueous EmimAc solution in a 100-mL beaker and treated at 80 °C in an oil
84 bath until the cellulose is completely dissolved. The water content of the aqueous EmimAc was
85 kept at 10%. The other experiments were conducted by adjusting water to aqueous 5% NaOH.
86 The cellulose dissolution state was observed with polarizing microscope (XPL-60, Bing Yu).
87 After completely dissolution, the cellulose was precipitated by adding enough distilled water to
88 the viscose solution. The regenerated cellulose was then washed several times with deionized
89 water to remove the residual EmimAc. After that, the regenerate cellulose was dried for the
90 further analysis.

91 **2.3 Analysis**

92 Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-IR) equipped with
93 diamond crystal with incident angles of 45° (Nicolet IS 50, Thermo Fisher Scientific, America)
94 was applied for the cellulose samples and solvent analysis. For each sample, the scanning range
95 was 650-4000 cm^{-1} , a resolution of 2 cm^{-1} with 32 scans. All samples were dried at 80 °C for 12
96 hours before analysis. Gaussian fitting were analyzed by Omnic software.

97 Crystalline structures of the cellulose samples were performed by the X-ray diffractometer
98 (XRD, Ultima TV, Japan) under the voltage of 40 kV and current of 40 mA. The scanning range
99 (2θ) was from 10° to 60° . The crystallinity of samples were calculated from the XRD patterns by
100 peak height method according to the Penttilä method (Penttilä et al., 2010).

101 The viscosity of cellulose-EmimAc/10% water, cellulose-EmimAc/10% NaOH-a were
102 measured according to the earlier reported procedure (Le et al., 2012; Froschauer et al., 2013)
103 and analyzed under nitrogen gas atmosphere at the temperature of 80°C and shear rate of 0.1-
104 100 s^{-1} . The viscosity of EmimAc/10% water, EmimAc/10% NaOH-a were measured by
105 Rotational viscometer (DV3T, Brookfield, America) at the temperature of 80°C at shear rate of
106 28 s^{-1} and the speed of 100 rpm.

107 The Kamlet Taft (K-T) parameters were determined spectrophotometrically using a series
108 of dyes according to Doherty's report (Doherty et al., 2010; Barba et al. 2019). The three dyes:
109 RD, NA and DENA were dissolved in ethanol. The concentration of all three dyes was 1 mg/mL.
110 The absorbance spectra of each sample were collected using an UV-vis spectrometer (750,
111 Perkin Elmer) at the temperature of 80°C in the range 250-700 nm. All the K-T parameters (v_{max} ,
112 ET (30), π^* , α , β) were calculated by the method referred in Ni's report (Ni et al., 2021).

113 In order to investigate the effect of NaOH-a addition on EmimAc. EmimAc, EmimAc/10%
114 water and EmimAc/10% NaOH-a were performed by in situ NMR analysis. The solvent samples
115 were transferred into 5mm NMR tubing with 0.3mm capillary inserts containing D₂O for ^{13}C -
116 NMR and ^1H -NMR analyses. All experiments were performed on a NMR spectrometer
117 (AVANCE NEO 600 (liquid), Bruker).

118 DFT calculations are performed using the DMOL3 module included in the Material
119 Studio7.0 software package. The geometry structure and bonding energy of Emim⁺-Ac⁻, OH-
120 water, Ac⁻-water, etc., are optimized by GGA/PW91/ method.

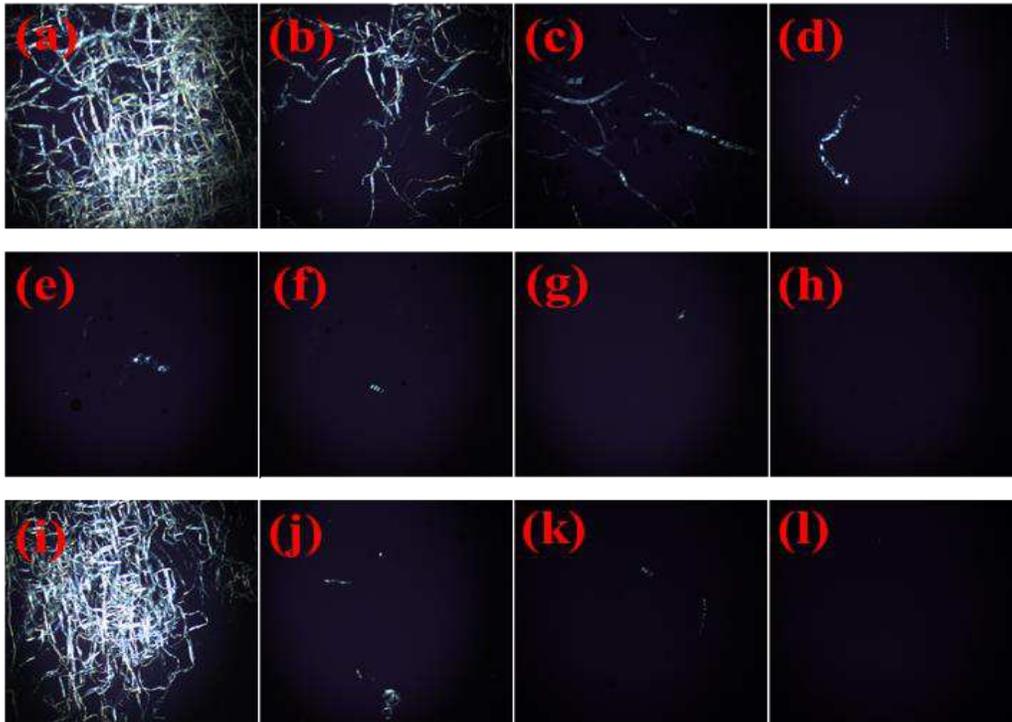
121 **3. Results and discussions**

122 **3.1 NaOH-a addition can promote the cellulose dissolution in aqueous EmimAc/10% water**

123 The dissolution state of cellulose in aqueous EmimAc were observed by polarizing
124 microscope, as shown in Fig. 1. At the beginning of dissolution, in both cellulose-EmimAc/10%
125 water and cellulose-EmimAc/10% NaOH-a cosolvent system, cellulose has a bright eyeshot
126 because of the crystalline structure. After 2 mins, only a small amount of insoluble cellulose can
127 be seen in the cellulose-EmimAc/10% NaOH-a system; but lots of insoluble cellulose in the
128 cellulose-EmimAc/10% water system. It is referred that NaOH-a introduction can significantly
129 accelerate cellulose dissolution. Furthermore, it is obvious that 2% cellulose can be completely
130 dissolved in EmimAc/10% NaOH-a system within 30 mins, but 180 mins in the EmimAc/10%
131 water system. The addition of NaOH-a to the aqueous EmimAc curtail the dissolution time from
132 180 mins to 30 mins, the dissolution time reduced by more than 7 times. Besides, increase of
133 NaOH concentration can further accelerate cellulose dissolution; while the amount is not yet
134 increased prominently (Table 1).

135 It is reported that the cellulose dissolution conform two modes. Mode 1 is descried as fast
136 dissolution by disintegration into rod-like fragments, which was instantaneous and homogeneous
137 without any sign of heterogeneous fiber swelling (Olsson et al., 2014). Mode 2 is that cellulose
138 dissolution suffer large swelling by ballooning, and then completely dissolution (Cuissinat et al.,
139 2008; Olsson et al., 2014). Cellulose dissolution in the pure ionic liquids is accepted to conform
140 the mode 1 that cellulose is dissolved instantaneous and homogeneous without any sign of

141 heterogeneous fiber swelling. But for the cellulose dissolution in EmimAc/10% water and
142 EmimAc/10% NaOH-a, it is predicated that Mode 2 is more suitable for explaining cellulose
143 dissolution in the aqueous EmimAc.



144

145 **Fig. 1** Polarizing microscope images of the cellulose dissolved in aqueous EmimAc at 80°C, 0
146 min (a); 2 min (b); 15min (c); 40 min (d); 70 min (e); 120 min (f); 150min (g); 180min (h) for
147 EmimAc/10% water; 0 min (i);2 min (j);15 min (k);30 min (l) for EmimAc/10% NaOH-a.

148

149 **Table 1** The impact of NaOH concentration on cellulose dissolution time and dissolution amount

NaOH Concentration (%)	Time for completely dissolving 2% cellulose (min)	Maximum dissolved amount at 180 min
0	180	2.5
3	160	---
5	30	3
7	27	3.2
10	25	3.3

150

151 **3.2 Crystal and macromolecular structure of cellulose**

152 Fig. 2 indicated that the raw cellulose sample shows the typical lattice structure of cellulose

153 I. When cellulose was dissolved in the aqueous EmimAc solution, the regenerated cellulose

154 exhibits the characteristic diffraction pattern of cellulose II; notably the disappearance of the

155 peak at 35.0° indicated the complete dissolution (Cheng et al., 2012; Lethesh et al., 2019). By

156 contrast to the raw cellulose sample, the peak of the regenerated cellulose at $\sim 20.5^\circ$ has a large

157 half-height width, indicating the penetration of EmimAc molecules into the pores between the

158 hydrogen bond sheets in cellulose I during dissolution; the expanded lattice structure remains

159 even after the EmimAc molecules were washed away. When water was replaced by NaOH-a, the

160 crystallinity index decreased from 44.6% to 43.9%. Unfortunately, addition of NaOH-a would

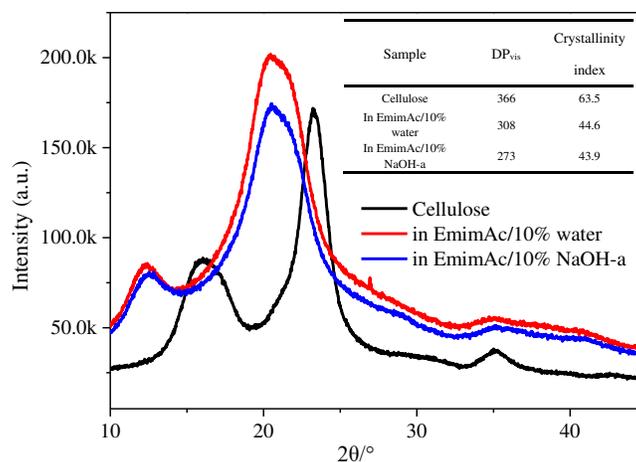
161 cause cellulose degradation and results in a lower DP (Fig. 2 insert table). The elimination

162 reaction toward β -alkoxy group in the reducing end groups on cellulose molecular chain in the

163 alkaline medium might be the main reason for the DP decrease (Yan et al., 2007; Fu et al., 2011),

164 besides, the cellulose dissolution could prompt the reaction.

165



166

167 **Fig. 2** WAXS spectra of the raw cellulose and the cellulose regenerated from cellulose
 168 dissolution in EmimAc/10% water and EmimAc/10% NaOH-a system. The insert is the
 169 calculated crystallinity index and DP of the cellulose sample.

170

171 3.3 Viscosity of the cellulose-EmimAc/10% NaOH-a system

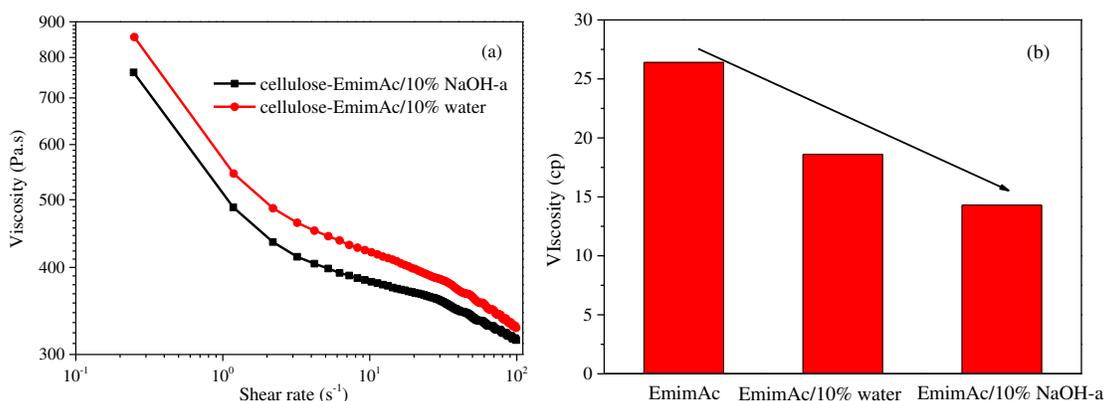
172 As observed in Fig. 3a, the cellulose solution was shear thinning, which was caused by the
 173 reduction of the number of tangles induced by shear and the desolvation of macromolecules at a
 174 high shear rate. The results showed that although the solution was transparent and the
 175 undissolved particles could not be seen under the optical microscope, as listed in Fig. 1, the
 176 properties of the cellulose solution changed.

177 Theoretically, the rheological curves of the cellulose samples that dissolved in both
 178 EmimAc/10% NaOH-a and EmimAc/10% water should be similar. However, the viscosity of the
 179 cellulose-EmimAc/10% NaOH-a was lower than that of cellulose-EmimAc/10% water. On the
 180 one hand, the cellulose sample with higher DP might entangle more in EmimAc/10% water
 181 system and result in the higher viscosity (Olsson et al., 2014). On the other hand, as shown in
 182 Fig.3b, the addition of NaOH-a can reduce the viscosity of EmimAc, and the increase of NaOH-a

183 concentration can further reduce the viscosity, leading to the lower viscosity of EmimAc/10%
184 NaOH-a.

185 Notably, according to the Stokes-Einstein diffusion equation, the lower viscosity of the
186 solution refers higher diffusion rate of the cellulose in the solution, which corresponds to an
187 increase in mass transfer, thus increasing the reaction rate (Kostag et al., 2019). This might be
188 one of the reasons that EmimAc/10% NaOH-a solvent system can accelerate cellulose
189 dissolution, as described in section 1.

190



191
192 **Fig. 3** Viscosity of cellulose-EmimAc/10% NaOH-a and cellulose-EmimAc/10% water system
193 (a); viscosity of EmimAc, EmimAc/10% water and EmimAc/10% NaOH-a system (b).

194

195 3.4 K-T parameters of EmimAc/10% NaOH-a

196 The π^* value in K-T parameters represent the dipolarity/polarizability effects. With the
197 addition of water or NaOH-a to the EmimAc, π^* value increases significantly (Table 2).
198 Theoretically, addition of water or NaOH-a can cause delocalization of the charge around the
199 imidazole ring, the polarizability of the delocalized system will increase the π^* value. However,
200 the delocalization also can weaken the Coulomb interaction and cause a decrease of π^* .

201 Considering the increase of π^* , it is referred that polarizability of the solution system are
202 dominant other than Coulomb interaction (Cuissinat et al., 2008; Seoud et al., 2019). The higher
203 polarizability refers a stronger interaction between Emim⁺ ring and Ac⁻ of EmimAc and is
204 unfavorable for cellulose dissolution (Froschauer et al., 2013), this result was consistent with
205 those in Fig. 1, EmimAc/10% NaOH-a system can only dissolve ~3wt% cellulose, but pure
206 EmimAc can dissolve up to 20% cellulose.

207 As reported in the literatures, the hydrogen bond alkalinity (β value) of the ionic liquids is
208 considered to be one of the most important parameters to determine the cellulose dissolution by
209 breaking intermolecular/intramolecular hydrogen bond (Fukaya et al., 2008; Grøssereid et al.,
210 2019). For a binary cosolvent system, differences between β and α (β - α , neat alkalinity) tends to
211 be the favorable parameter for evaluating the cellulose solubility in the system (Hauru et al.,
212 2012; Shi et al., 2014). As listed in Table 2, adding water or NaOH-a to EmimAc can
213 dramatically reduce the α , β and β - α , indicating the decrease of the ability for cellulose
214 dissolution. However, by contrast to the EmimAc/10% water system, instead 5% NaOH-a of
215 water can obviously increase β and slightly decrease α , it is suggested that NaOH-a affected β
216 significantly and can promote cellulose dissolution in the EmimAc/10% water system, which is
217 accorded to the results mentioned in the section 1.

218

Table 2 K-T parameters of the EmimAc/10% NaOH-a at 80°C

Parameters	NaOH concentration / (%)		
	Pure EmimAc	EmimAc/10% water	EmimAc/10% NaOH-a
π^*	0.75	0.98	0.98
α	0.72	0.60	0.59
β	1.19	0.82	0.85
$\beta-\alpha$	0.47	0.22	0.26

220

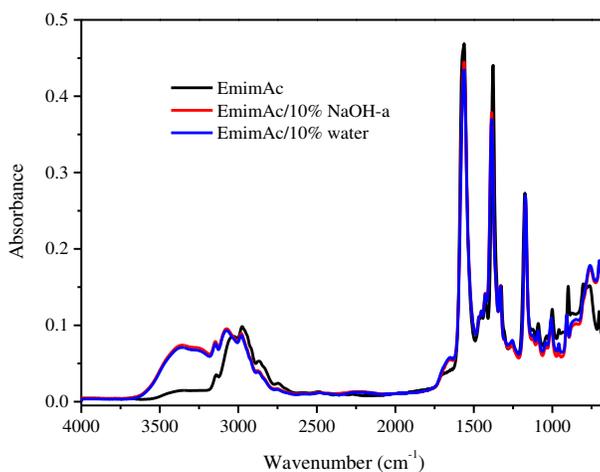
221 **3.5 The action of NaOH on EmimAc/10% water**

222 In order to investigate the NaOH effects, we compared the changes of the ATR-IR spectrum
223 of EmimAc/10% water before and after the addition of NaOH-a. As shown in Fig. 4, the Emim⁺
224 imidazole ring of EmimAc is mainly characterized as the absorption peaks at 3139 cm⁻¹, 3039
225 cm⁻¹ and 2976 cm⁻¹, respectively (Katsyuba et al., 2007; Wang et al., 2007; Zhang et al., 2007;
226 Dhumal et al., 2009; Bogdan et al., 2015); while the Ac⁻ is featured as the adsorption at 1567 cm⁻¹,
227 1427 cm⁻¹ and 1378 cm⁻¹. It is apparent that addition of water cause a broader absorption band
228 at about 3300 cm⁻¹ attributing to the hydroxyl groups from water; specifically, this band is
229 assigned to water aggregates formed around the hydrophilic acetate anion (Ac⁻) in EmimAc
230 (Fazio et al., 2010). Besides, blue shifts of the Emim⁺ ring and Ac⁻ are observed, as we know,
231 water is both a hydrogen bond donor and a hydrogen bond acceptor and can simultaneously
232 interact with the Emim⁺ and Ac⁻ of EmimAc, the detailed shifts are listed in Table S1 and the
233 chemical structure of EmimAc with each atom resonances labelled are shown in Fig. S1 The
234 interaction between EmimAc and water can weaken the hydrogen bonding between Emim⁺ and
235 Ac⁻ and cause blue shifts (Yu. et al., 2014). Specifically, water dissociates the network structure

236 of EmimAc into aggregated ion clusters forming tight ion pairs. The interaction between water
237 and Ac^- can loosen the cohesion of the ion pair, resulting in the reduction of the interaction
238 between the anions and the cations of EmimAc (Yu. et al., 2014; Bogdan et al., 2015). In
239 addition, water reduce the positive charges of Emim^+ significantly and weaken the electrostatic
240 interaction, thus leading blue shifts.

241 When water was replaced by aqueous NaOH, the absorption peaks are generally consistent
242 with that of EmimAc/10% water, but the absorption intensity of EmimAc/10% NaOH-a is
243 stronger than that of EmimAc/10% water (Fig. S2a, Fig. S2b, Fig. S2c). As well as we know,
244 both Na^+ and OH^- can combine with water to form hydrate ions, which will compete with the
245 bonding between water and Ac^- . The water captive make more Ac^- bonding with Emim^+ ,
246 indicating that aqueous NaOH can compensate the destruction between the cations and anions
247 that caused by water.

248



249

250 **Fig. 4** ATR- IR spectra of EmimAc, EmimAc/10% water and EmimAc/10% NaOH-a.

251

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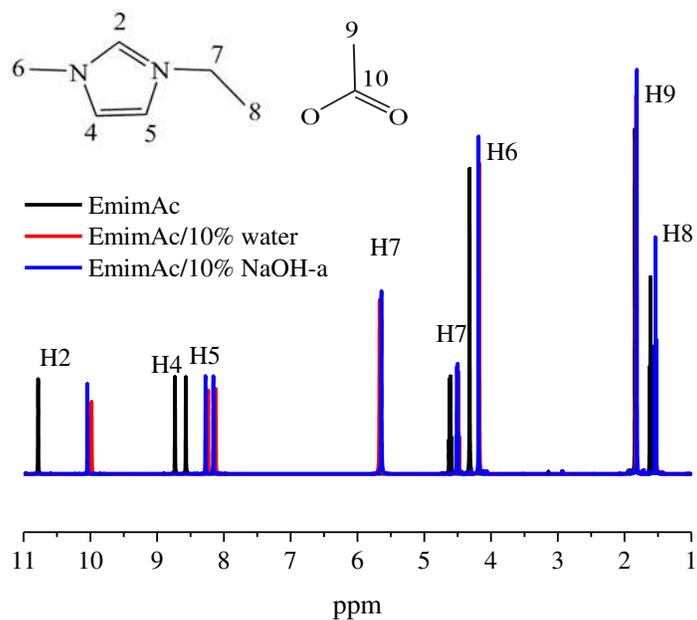
253

254 3.6 NMR studies of the interactions between the EmimAc and NaOH-a

255 To further investigate the NaOH-a effects on cellulose dissolution in the aqueous EmimAc,
256 ^1H -NMR was conducted. As indicated in Fig. 5 and Table 3, adding water or NaOH-a to
257 EmimAc causes all the H of EmimAc shift to upfield. The detailed explanations is shown in the
258 supplementary materials (supplementary NMR analysis). The $\Delta\delta$ on the H2 is much obviously
259 than that of the other H, indicating that water or NaOH-a preferentially combine with hydrogen
260 at C2-H of Emim⁺ position to form hydrogen bonding, the results were consistent with the
261 previous reported data (Cammarata et al., 2001; Ficke et al., 2010; Bogdan et al., 2015). The
262 results were further verified by the ^{13}C -NMR (Fig. 6 and Table 4).

263 Moreover, when water was replaced by NaOH-a, the ^1H -NMR chemical shifts of each
264 proton on the Emim⁺ decreased, suggesting that NaOH-a reduce the electron cloud density on the
265 imidazole ring. Oxygen on OH⁻ is more electronegative than in water which can make the OH⁻
266 more capable of forming hydrogen bonds with Emim⁺. As well as ^1H -NMR, the addition of
267 water or NaOH-a makes the C2, C4 and C5 on the imidazole ring shift to upfield. To be different
268 from H shifts, C10 on the Ac⁻ moves to the downfield. As reported elsewhere, the hydrogen bond
269 between Ac⁻ and water is stronger than that with Emim⁺, resulting in the decrease of the density
270 of C10 electron cloud and the chemical shift of ^{13}C -NMR to downfield. By comparing the
271 absolute value of downfield shift of C10 and upfield shift of C2, the larger shift of C10 might
272 refer that water affects anions more significantly than cations. As listed in Table 3 and Table 4,
273 NaOH-a addition can reduce both the chemical shift of H and C of aqueous EmimAc, it is
274 referred that NaOH-a can protect the structure EmimAc from water damage. We speculated that
275 the combination of water and Na⁺ or OH⁻ reduce the interaction between water and EmimAc.

276



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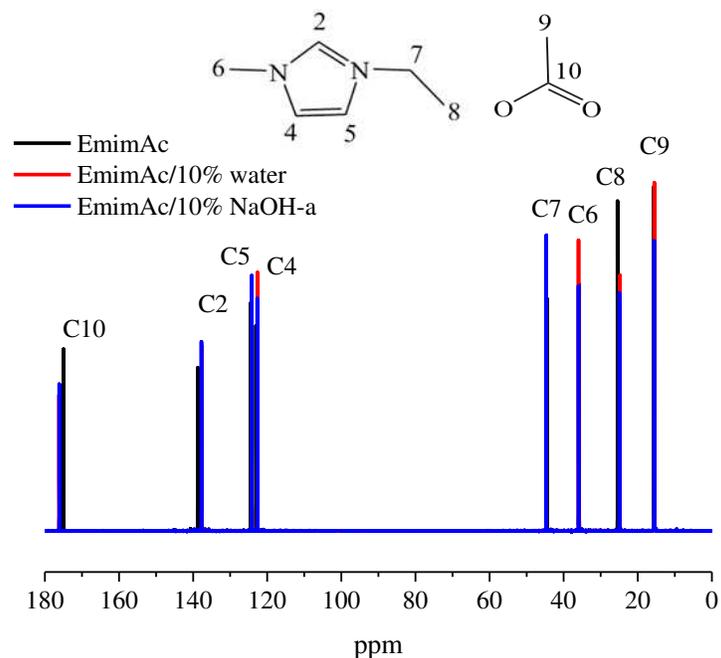
278 **Fig. 5** $^1\text{H-NMR}$ spectrum of EmimAc, EmimAc/10% water and EmimAc/10% NaOH-a.

279

280 **Table 3** $^1\text{H-NMR}$ spectrum data of EmimAc, EmimAc/10% water and EmimAc/10% NaOH-a

	$\delta/(\text{ppm})$						
	H2	H4	H5	H6	H7	H8	H9
EmimAc	10.783	8.733	8.570	4.321	4.618	1.625	1.844
EmimAc/10% water	9.982	8.236	8.123	4.175	4.500	1.536	1.826
EmimAc/10% NaOH-a	10.044	8.277	8.159	4.186	4.510	1.538	1.816
$\Delta\delta$ EmimAc/10% water	0.801	0.497	0.447	0.146	0.118	0.089	0.018
$\Delta\delta$ EmimAc/10% NaOH-a	0.739	0.456	0.411	0.135	0.108	0.087	0.028

281



282

283 **Fig. 6** ^{13}C -NMR spectrum of EmimAc, EmimAc/10% water and EmimAc/10% NaOH-a.

284 **Table 4** ^{13}C -NMR spectrum data of EmimAc, EmimAc/10% water and EmimAc/10% NaOH-a

	δ /(ppm)							
	C2	C4	C5	C6	C7	C8	C9	C10
EmimAc	138.738	123.017	124.452	35.819	44.539	15.627	25.45	174.962
EmimAc/10% water	137.661	122.640	124.179	35.994	44.710	15.534	24.822	176.155
EmimAc/10% NaOH-a	137.755	122.669	124.201	35.986	44.688	15.561	24.959	176.118
$\Delta\delta$ EmimAc/10% water	1.077	0.377	0.273	-0.175	-0.171	0.093	0.628	-1.193
$\Delta\delta$ EmimAc/10% NaOH-a	0.983	0.348	0.251	-0.167	-0.149	0.066	0.491	-1.156

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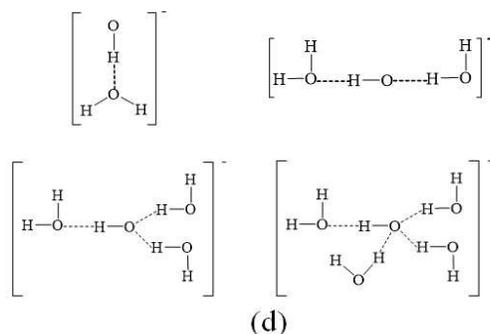
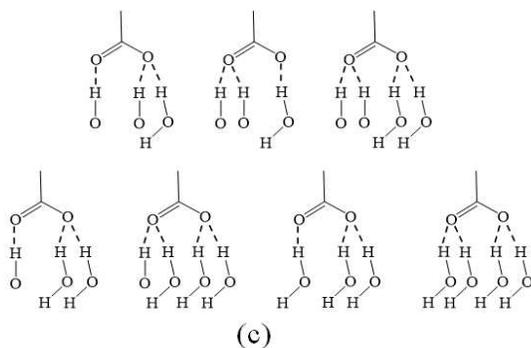
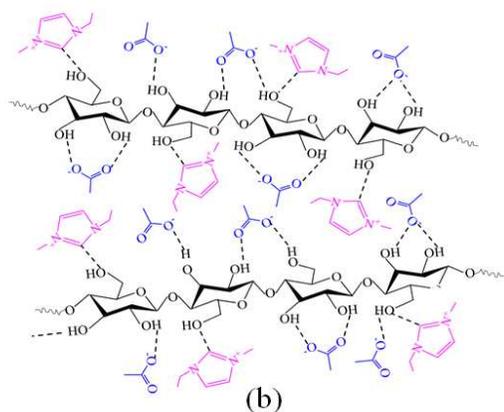
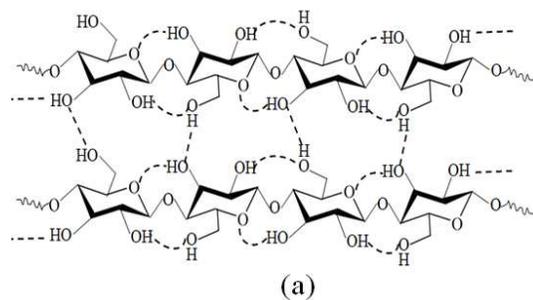
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287 **3.7 Mechanisms of the NaOH-a promotion on cellulose dissolution in aqueous EmimAc**

288 It is accepted that ionic liquids can adsorb onto the cellulose surface and disrupt the
289 hydrogen bonding within the amorphous and crystalline regions and therefore release the
290 cellulose chains in free state into the ionic liquids solution. As shown in Fig.7a, a compact
291 hydrogen bonding network (intra- intermolecular bonds) is observed between the cellulose
292 chains. Since the cellulose is dissolved in the EmimAc, the hydrogen bonds between the
293 opposing cellulose was destroyed and new hydrogen bonds between hydroxyl groups on
294 cellulose and Ac^- are formed (Fig.7b). The tight bonding of the Ac^- cause an effective charging
295 of the cellulose chains that further reduce the propensity of the cellulose chains. Where, Ac^- can
296 bonds with OH with different state because Ac^- has two sites bonding with OH (Rabideau et al.,
297 2015). For the cations of the ionic liquids, the acidic H on the Emim^+ forms hydrogen bond C-
298 $\text{H}\cdots\text{O}$ with the ether O in the cellulose, the disruption of the rigid hydrogen bonding network
299 results a cellulose dissolution.

300 When water was added into the EmimAc, the anions Ac^- will acts with water to form
301 hydrogen bonds as shown in Fig.7c, indicating as the water crowds the hydrogen bond-accepting
302 sites of the anions, results in a reduction in the frequency of hydrogen bonding between OH on
303 cellulose and Ac^- and therefore decrease the cellulose dissolution. In our study, EmimAc with 10%
304 water can completely dissolve 2% cellulose within 180 mins, when 10% water was replaced by
305 NaOH-a (5%), the hydrogen bonding network will suffer extensive disruption and rearrangement.
306 As well as Ac^- , OH^- can associate with water by the means of hydrogen bonds (Fig.7d). DFT
307 results confirmed that the bonding energy (ev) for OH^- -water is much higher than Ac^- -water
308 (Table S2). It is referred that bonding between OH^- and water is domain that release the Ac^- to
309 act with hydroxyl on cellulose. In addition, NaOH addition can increase the alkalinity of the

310 solvent and cause the deprotonation of hydroxyl groups on the cellulose chain, the increasing
311 negative charges of cellulose will improve the cellulose dissolution. Furthermore, the polarity of
312 NaOH-a was greater than that of water, which can reduce the interaction of hydrogen bond and
313 van der Waals force between cellulose molecules and make the dissolution faster (Bialik et al.,
314 2016; Kostag et al., 2019). Additionally, Na^+ can interact with the hydroxyl oxygen O(3) of
315 cellulose, which destroyed the intermolecular hydrogen bond (O(6) H...O(3)) between cellulose,
316 thus accelerating the dissolution of cellulose (Xu et al., 2010). Even so, it is definitely that the
317 OH^- play the important role in the cellulose dissolution in aqueous EmimAc. OH^- can also bond
318 with cellulose, the higher bonding energy of OH^- -OH-Cell (vs Ac^- -OH-Cell) (Table S2) might
319 refer another possibility that NaOH addition cause a conversion of EmimAc to EmimOH and the
320 latter is much efficient for cellulose dissolution. Because of the difficulties in the preparation of
321 purification of EmimOH, the above predication is not proved, the mechanism of the cellulose
322 dissolution require further investigation.



323
 324 **Fig. 7** Hydrogen bonding network of cellulose (a); schematic representation of the mechanism of
 325 cellulose dissolution in EmimAc (b); typical path of Ac⁻ form Hydrogen bonding with H₂O (c);
 326 hydrogen bond between water and OH⁻(d).

327 **4. Conclusions**

328 In this work, a novel EmimAc/10% NaOH-a system was proposed to dissolve cellulose.
329 The addition of NaOH to aqueous EmimAc can greatly shorten the cellulose dissolution time and
330 slightly improve the dissolved cellulose amount. Additionally, the NaOH introduction causes a
331 cellulose degradation because of the β -alkoxy elimination reaction and a larger changes of the
332 crystal structure. More importantly, the viscosity of the system decreased benefiting from the
333 lower viscosity of EmimAc/10% NaOH-a and decreased DP of cellulose.

334

335 **Supporting Information**

336 Detailed explanation of the changes in NMR spectra of EmimAc after the addition of
337 NaOH-a and water; Chemical structure of Emim⁺ and Ac⁻ of EmimAc with the proton
338 resonances labeled; Local magnification spectrogram of ATR-IR spectra of EmimAc,
339 EmimAc/water and EmimAc/NaOH-a; Detailed vibrational frequencies of EmimAc,
340 EmimAc/water and EmimAc/NaOH-a; DFT calculation of interaction energy for Emim⁺-Ac⁻,
341 Emim⁺-OH⁻, Emim⁺-water, Ac⁻-water, OH⁻-water, OH⁻-OH-Cellulose and Ac⁻-OH-Cellulose
342 (PDF).

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348 **Compliance with ethical standards**

349 **Conflict of interest** All authors declare no competing financial interest and have approved the
350 manuscript.

351 **Ethical approval** The study was completed by following ethical standards; no animal or human
352 participants were involved in the study.

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