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Capturing CO₂ for Cellulose Dissolution

Haibo Xie,* Xue Yu, Yunlong Yang and Zongbao Kent Zhao

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The design of a system using 1,1,3,3-tetramethyl guanidine in conjunction of ethylene glycol in DMSO after CO₂ capture created a new solvent capable of dissolving up to 10 wt% of cellulose under mild conditions, which opened a new window for the homogeneous utilization of cellulose for production of sustainable materials, chemicals and energy in the future.

The utilization of both CO₂ and biomass as resources are urgent and challenging research topics, because CO₂ is regarded as a main gas responsible for climate change, and its effective capture, storage (CCS) and utilization can reduce the accumulation of CO₂ in the atmosphere;¹,² the utilization of biomass as raw feedstock to produce sustainable materials, energy and chemicals contributes to reduce our current dependence on fossil resources and establish a sustainable economy.³,⁴ Development of reversible CO₂ capture systems with strong ability to dissolve cellulose after CO₂ capture is highly desirable for efficient integration of CCS and cellulose utilization processes.

![Scheme 1](image)

Scheme 1 TMG-based reversible mono-anionic and di-anionic ionic compounds screened in this study

Cellulose, a linear and semi-flexible polymer, is the most abundant renewable resource. Since cellulose cannot be melted and dissolved easily in conventional solvents, dissolution has become a major obstacle preventing its subsequent processing in various forms (e.g. fibres, films), derivatisation as well as catalytic conversion. Therefore, the search of effective solvents for the dissolution of cellulose has been a popular research topic since its isolation in the nineteenth century.⁵ To date, a rather limited number of solvents are available via non-derivatising or derivatising pathways, such as cuprammouium hydroxide solution, monohydrate of N-methyl-N-morpholine oxide (lyocell process), CS₂-NaOH aqueous solution (viscose process), LiCl-based solvents, ionic liquids,⁶ NaOH-urea-water.⁷ The viscose process and lyocell process (production over 3,000,000 tons per year) have dominated the production of regenerated cellulose fibers in fiber industry so far.⁸,⁹ The recently developed ionic liquids and NaOH-urea-water systems have significantly promoted the utilization of biomass in terms of catalytic conversion and sustainable material development under homogeneous conditions.¹⁰⁻¹² However, these processes in general have drawbacks including environmental pollution, high cost and recycling problems, etc. Therefore, the design of environmentally friendly, effective and cheap solvents with good recyclability and reusability for cellulose dissolution processing and conversion is of still prime importance.⁵,¹³

The reversible CO₂ capture based on an exothermic transformation using a strong organic base in conjunction with a proton donor proposed by Jessop et al. is one of the most fascinating strategies for the CCS process.¹,²,¹⁴ With the reversible compositional change under mild conditions from molecular liquids to ionic compounds, in association with other switched properties, such as polarity and viscosity, the proposed system introduced a variety of possible opportunities in catalysis and separation processes.¹⁵⁻¹⁹ Although the formed reversible ionic compounds (RICs) have been used as extracting solvents for fractionation of lignocellulose,²⁰,²¹ they are not successful for full dissolution and processing of cellulose yet. Our results showed that the formed viscous or solid RICs after CO₂ capture when 1,1,3,3-tetramethyl guanidine (TMG) was used as a base, in conjunction with commonly used alcohols, such as methanol,
ethanol, n-propanol and n-butanol (Scheme 1), could only slightly swell microcrystalline cellulose (MCC). The addition of dimethyl sulfoxide (DMSO, one of the commonly used co-solvents; \( X_{RICs} = 0.2, X_{RICs} = \text{the mole fraction of formed RICs after CO}_2 \text{ capture in the mixture} \) can significantly decrease the viscosity of the RICs and enhance their solubility to MCC, but only semi-transparent or opaque cellulose solution achieved under identical conditions. The moderate solubility of these formed reversible RICs was evidenced from the pictures of opaque and viscous cellulose solutions (Fig. 1, top: B, C, D, E) and the results of wide angle X-ray diffraction (WXRD) analysis of the regenerated cellulose by methanol (Fig. 1, bottom panel).

The degree of de-crystallization of cellulose was closely related to the length of the aliphatic chain; accordingly, the crystallinity index (CrIs) of cellulose was decreased from 0.75 to 0.51, 0.40, 0.18, and 0.14 in the cases of n-butanol, n-propanol, ethanol, and methanol, respectively (Fig. 1, bottom spectra E, D, C, B). The better de-crystallization outcome of \([\text{TMGH}]\text{[O}_2\text{COCH}_2\text{CH}_2\text{O}_2\text{]}\text{[DMSO]} \) (XRICs=0.1) was capable of dissolving up to 10 wt% of MCC at 60 °C in 1 h with 0.5 MPa of CO2 pressure. The solution remained stable for a couple of months. Other commercially available cellulose samples, including \( \alpha \)-cellulose, cellulose powder from spruce and sulfate poplar wood pulp were also examined with appreciable solubility of 10 wt%, 8 wt% and 5 wt% observed respectively under identical conditions.

**Scheme 2** Organic bases used in this study with various pKa of conjugated acids

To better understand the underlying mechanism for the dissolution of cellulose in this new solvent system, other organic bases with various pKa of conjugated acids \(^{22} \) (Scheme 2) were also used to construct the solvent system with methanol and EG in DMSO for this purpose under identical conditions. Beside the TMG-EG-DMSO based system, only DBU-EG-DMSO based system showed moderate solubility to MCC (5 wt%, 0.5 MPa of CO2, 60 °C, 1 h), while the systems based on TBA and TEA are not capable of dissolving MCC, implying that, the structure and the basicity of organic bases were important factors, determining their performance in their solubility to cellulose in DMSO after CO2 absorption. Only strong organic bases, such as DBU and TMG in conjunction with alcohols were able to rapidly capture CO2 for the formation of amidinium/guanidinium alkylcarbonate salt \(^{23} \) as shown in Scheme 1, leading good performance in the dissolution of cellulose.

The formation of \([2\text{[TMGH]}\text{[O}_2\text{COCH}_2\text{CH}_2\text{O}_2\text{]}\text{[DMSO]} \) in DMSO in the presence of CO2 was identified by \( ^1\text{H NMR} \) (ESI, Fig. S1) and \( ^{13}\text{C NMR} \). In the \( ^{13}\text{C NMR} \) spectrum, a new signal at \( \delta = 159.2 \text{ ppm} \) after CO2 addition revealed the formation of carbonate carbon structure between EG and CO2 (Fig. 2) \(^{23, 24} \). Simultaneously, the protonation of TMG resulted in a shift change of the central carbon in TMG from 166.7 to 161.7 ppm, but did not affect the chemical shifts of other carbons both in TMG and ethylene glycol obviously.

The formation and existing state of it during the dissolution process were also monitored by in situ IR (Fig. 3). A strong C=NH stretching vibration absorption band of TMG was detected at 1595 cm\(^{-1} \) before the introduction of CO2 and cellulose.
Fig. 2 The comparative $^{13}$C NMR spectra of TMG/ethylene glycol (2:1, molar ratio) in $d_6$-DMSO without and with CO$_2$ addition. A new signal assigned to the carbonate carbon appeared at $\delta = 159.2$ ppm after CO$_2$ addition, which indicated the formation of 2[TMGH][O$_2$COCH$_2$CH$_2$OCO$_2$]$^2_-$.

Newly formed asymmetric and symmetric carbonyl stretching bands at 1663 and 1410 cm$^{-1}$, asymmetric and symmetric C-O-C, stretching vibrations at 1265 and 1030 cm$^{-1}$, and protonated C=NH$_2^+$ stretching vibration at 1573 cm$^{-1}$ were observed after 0.8 MPa of CO$_2$ was introduced into the DMSO-TMG-EG mixture.$^{25,26}$ The protonation of TMG resulted in a shift of the characteristic C=N stretching vibration band from 1595 to 1601 cm$^{-1}$. These results further indicated the in situ formation of 2[TMGH][O$_2$COCH$_2$CH$_2$OCO$_2$]$^2_-$ in DMSO. The subsequent addition and dissolution of MCC in the formed solvent did not lead to shifts of the characteristic bands related to carbonate ions in 2[TMGH][O$_2$COCH$_2$CH$_2$OCO$_2$]$^2_-$, which implied that 2[TMGH][O$_2$COCH$_2$CH$_2$OCO$_2$]$^2_-$ acted as a stable non-derivitizing solvent for cellulose in this system.

The switchable polarity of the mixed molecular solvents and ionic solvents was assessed by the solvatochromic behavior of Nile red dye. The Nile Red wavelength of maximum absorbance, $\lambda_{\text{max}}$, directly correlates with solvent polarity and has previously been used as a polarity probe with ionic liquids.$^{27}$ The results demonstrated that the ionic solvents were more polar than that of the corresponding molecular solvents, as indicated by larger $\lambda_{\text{max}}$ values of the ionic solvents (Fig. 4). Higher polarity could be achieved with shorter chain aliphatic alcohols applied. The polarity of these systems was correlated to their solubility to cellulose in a certain extent. In general, a solvent with higher polarity had better solubility to cellulose.

However, the polarity of [TMGH][O$_2$COCH$_2$]/DMSO...
Figure 4. Switchable $\lambda_{\text{max}}$ of Nile red dye in the mixed molecular solvents and corresponding mixed ionic solvents: 
1. [TMGH][O$_2$COCH$_2$CH$_3$]/DMSO (X$_{\text{RIC}}$=0.2); 
2. [TMGH][O$_2$COCH$_2$CH$_2$O]/DMSO (X$_{\text{RIC}}$=0.2); 
3. [TMGH][O$_2$COCH$_2$CH$_2$O]/DMSO (X$_{\text{RIC}}$=0.2); 
4. [TMGH][O$_2$COCH$_2$CH$_3$]/DMSO (X$_{\text{RIC}}$=0.2); 
5. [TMGH][O$_2$COCH$_2$OCO$_2$]/DMSO (X$_{\text{RIC}}$=0.1).

Figure 5. The TGA graphs (A): [TMGH][O$_2$COCH$_2$]; (B): 2[TMGH][O$_2$COCH$_2$OCO$_2$];
2[TMGH][O$_2$COCH$_2$CH$_2$O]/DMSO (X$_{\text{RIC}}$=0.1).

The reaction between TMG and alcohols in the presence of CO$_2$ was enthalpically favored while the reverse was entropically favored. Comparative TGA analysis demonstrated that 2[TMGH][O$_2$COCH$_2$CH$_2$O]/DMSO (X$_{\text{RIC}}$=0.1) had higher thermal stability than [TMGH][O$_2$COCH$_2$] (Fig. 5). These observations were consistent with the research for ionic liquids that the di-cationic or di-anionic ionic liquids had better thermal stability than mono-ionic liquids. The better thermal stability was anticipated to determine the effective concentration of the ionic compounds at 60 °C, which might explain their differences in solubility of cellulose. The concept of CO$_2$ capture for facile dissolution and regeneration of cellulose based on the reversible properties was easily appreciated by the means of microscopic imaging (Fig. 6).

In conclusion, the study demonstrated a facile dissolution of cellulose in DMSO-TMG-EG mixture at 60 °C, which might explain their differences in solubility of cellulose. The formed carbonate ions acted as hydrogen bond acceptors in the mixed solution, which then interacted with the hydroxyl groups and ether bonds of the cellulose and by disrupting and breaking the intramolecular hydrogen-bonding network, thus leading to the dissolution of cellulose, which was similar with the role of ionic liquids for cellulose dissolution.

A major obstacle to the broader application of cellulose lies in its facile dissolution. Herein, we demonstrated that a novel invented system based on TMG in conjunction of EG in DMSO after CO$_2$ capture could dissolve up to 10 wt% of cellulose under mild conditions. We proposed that the interactions of the in situ formed carbonate anions with hydroxyl groups in cellulose acted as driving forces for cellulose dissolution in 2[TMGH][O$_2$COCH$_2$CH$_2$O]/DMSO (X$_{\text{RIC}}$=0.1) under mild conditions. In conclusion, the study demonstrated a facile integrated strategy for CCS and cellulose dissolution processing and conversion by using cheap, commercially available compounds under mild conditions with good recyclability and reusability, which offered insights in the design of solvents for biopolymers and opportunities on both of CO$_2$ and biomass utilization.
Fig. 7 MCC suspension in scintillation bottles and its microscopic images. A: Suspension of 5 wt% MCC powder in DMSO-TMG-EG (X_RICs=0.1); B: 5 wt% MCC [2(TMGH)O2COCH2CH2OCO2]2-/DMSO (X_{IRC}=0.1) solution; C: Cellulose gel regenerated from 5 wt% of MCC [2(TMGH)O2COCH2CH2OCO2]2-/DMSO (X_{IRC}=0.1) solution by N2 at 70 °C for 20 min.

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10 Notes and references

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Dalian National Laboratory for Clean Energy 457, Zhongshan Rd., Dalian, P. R. China

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Graphical Abstract

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Haibo Xie,* Xue Yu, Yunlong Yang and Zongbao Kent Zhao

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Dalian National Laboratory for Clean Energy 457, Zhongshan Rd., Dalian, P. R. China (116023) E-mail: hbxie@dicp.ac.cn

The design of organic liquids in DMSO after CO$_2$ capture created a new solvent capable of dissolving up to 10 wt% of cellulose under mild conditions.