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Organic electrolyte solutions as versatile media for the dissolution and regeneration of cellulose

Matthew T. Clough

Organic electrolyte solutions – mixtures of a (room-temperature) ionic liquid with a neutral, organic, polar co-solvent – are attracting increasing attention as solvents for the regeneration and derivatisation of cellulose. Despite advantages (in comparison to simple ionic liquid analogues) associated with rapid or instantaneous dissolution, reduced viscosity, enhanced thermal stability and fine-tunable physicochemical properties, a firm understanding of the precise solvent–solute interactions and the relative kinetic *versus* thermodynamic contributions to dissolution remains elusive. The incorporation of a co-solvent introduces an additional layer of complexity, therefore an informed choice of both ionic liquid and co-solvent is necessary in order to achieve the desired properties. This article first provides an overview of the structure and bonding properties of native and non-native cellulose allomorphs, and a brief history of strategies for cellulose dissolution. Subsequently, organic electrolyte solutions are introduced as versatile solvents for cellulose, and the underpinning thermodynamic, kinetic and mechanistic phenomena behind cellulose solubility are critically discussed. The final sections summarize recent advances in the development of organic electrolyte technologies for derivatisation and regeneration of cellulose and critically discuss whether organic electrolytes can, or could be, rightly regarded as 'green solvents'.

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Matthew T. Clough (United Kingdom, 1989) obtained his PhD from Imperial College London, UK (2015), supervised by Prof. Tom Welton and Dr. Patricia Hunt, on a combined experimental and computational project investigating the thermal and chemical stabilities of ionic liquids and their mixtures with carbohydrates. Subsequently, he was a Postdoctoral Research Fellow at the Max-Planck-Institut für Kohlenforschung, Mülheim-an-der-Ruhr, Germany (2015–2017), in the groups of Dr. Roberto Rinaldi and Prof. Ferdi Schüth, where his research centred on the development and characterisation of solvent systems for cellulose, and catalytic valorisation of lignocellulosic biomass. In April 2017 he joined Syngenta Ltd., UK, as a Senior Analytical Chemist.

1. Introduction

Motivated by the pressing need for sustainable alternatives to fossil fuel resources in order to meet mankind's burgeoning material demands, lignocellulosic biomass has received widespread and growing interest in recent years. Biomass is primarily composed of three tightly-interwoven biopolymers: (i) cellulose, a linear and regular carbohydrate polymer that offers important structural integrity to the cell walls of plant species;[1,2] (ii) lignin, a complex and irregular aromatic polymer constructed from *para*-(propenylated) phenol units that contributes toward cell wall rigidity;[3,4] and (iii) hemicellulose, a comparatively low-molecular-weight branched polymer of (functionalised) pentose and hexose sugars, serving as a cross-linking motif between cellulose microfibrils and lignin.[5] To achieve the maximum economic potential of an integrated biorefinery, challenges associated with the separation, dissolution and upgrading of these three biopolymers must be overcome, exploiting differences in solubility and reactivity under process conditions.[6,7]

An estimated 56×10^9 tonnes of biomass is generated globally each year (as of 2005),[1] of which cellulose accounts for the largest mass fraction (typically ≥40 wt% of dry biomass).[2] In addition to its extraordinary abundance, the high carbon content and homopolymeric structure of cellulose render it an attractive candidate for valorisation to paper products, textile fibres, biofuels and composite materials (Fig. 1). However,

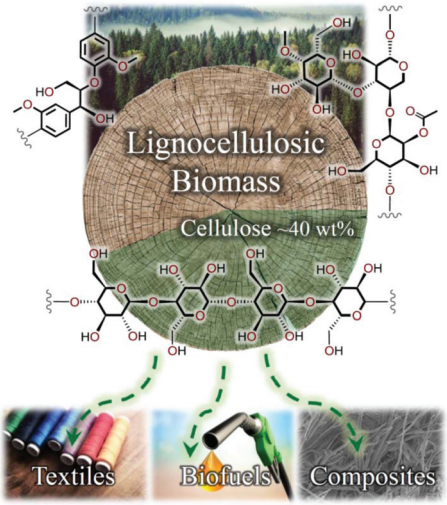

Fig. 1 Selected target materials from cellulose: regeneration (*e.g.*, electrospinning) into textile fibres; depolymerisation and fermentation to biofuels; or derivatisation, mixing and fabrication into composite materials (or hydrogels).

despite the high concentration of hydrophilic hydroxyl substituents along the polymer backbone, cellulose exhibits vanishingly low solubility in water and the majority of conventional solvents because of the extensive network of hydrogen bonds (and van der Waals interactions).

Despite significant historical advances in the development of cellulose dissolution technologies, leading to established and successful large-scale industrial procedures (*e.g.*, the Lenzing process, Austria), frequently-encountered problems associated with solvent toxicity, instability and limited recyclability point out the need for fundamental and applied research toward more sustainable alternatives. A solvent for cellulose should ideally meet several important criteria: (i) high solubility; (ii) rapid dissolution; (iii) facile solvent recyclability; (iv) minimal toxicity and flammability; and (v) insusceptibility to side reactions between solvent and solute. In this context, so-called 'organic electrolyte solutions' (OESs), mixtures of a (room-temperature) ionic liquid with an organic co-solvent, are promising candidates and have received growing attention since their first reports in the literature.[8]

This article is divided into six sections. Initially, a succinct overview of the key structural and bonding properties of cellulose is provided. Secondly, the evolution of cellulose dissolution strategies through the 19th and 20th centuries is described. Thirdly, the properties and behaviour of OES–cellulose systems are reviewed in detail. Next, examples of the successful application of OESs to cellulose derivatisation and valorisation are evaluated. The fifth section addresses the important question as to whether OESs can be considered 'green solvents' and, finally, key conclusions and future prospects of OESs are discussed.

The primary purpose of this review is to clarify the thermodynamic, kinetic and mechanistic properties that underpin cellulose dissolution in OES solvents, and to describe OES-based methodologies for the dissolution and valorisation of isolated cellulose.

OES solvents have been successfully applied to the fractionation of lignocellulose, for example purification of cellulose pulp by selective extraction of hemicelluloses in $[C_2C_1im][OAc]$–EtOH/acetone (IONOCELL-P[9]). Moreover, inclusion of an organic co-solvent (*e.g.*, ethanolamine[10]) during pretreatment has been found to influence the efficiency of enzymatic hydrolysis of cellulose. Nevertheless for brevity, these topics are excluded from this review, instead focusing on procedures for the dissolution and valorisation of pre-isolated cellulosic materials. The interested reader is directed to a recent review article on the fractionation of biomass in ionic liquids and OESs.[11]

2. Cellulose structure and bonding

As the largest single component of hardwoods (43–47 wt%), softwoods (40–44 wt%) and bagasse (*ca.* 40 wt%),[2] cellulose is the world's most abundant bio-renewable resource. It is a strong candidate for targeted upgrading towards textile fibres,[12–18] biofuels,[19–23] (nano)composites[24–28] or hydrogels,[29,30] not only because of its high natural abundance but also because of its well-defined structure of repeating glucopyranose residues, linked *via* β-1,4-glycosidic bonds. The β-configuration at the anomeric carbon gives rise to an extended linear geometry (differentiating cellulose from starch, with α-1,4 configuration and helical structure). The number of glucopyranose residues in a single cellulose chain (denoted the 'degree of polymerisation', DP) may reach 10 000 (*e.g.*, in cotton or bacterial cellulose). Agglomeration of approximately 40–70 individual cellulose strands gives rise to a single 'microfibril', whereby strands are held together through an ordered arrangement of intramolecular and intermolecular hydrogen bonds and van der Waals interactions.[31] Effective dissolution of cellulose hinges on the solvent's ability to dismantle this network of interactions and peel away individual strands from the microfibril.

Various crystalline allomorphs of cellulose exist either in native organisms (cellulose I_α and I_β, collectively referred to as cellulose I), or are attainable through annealing or treatment (cellulose II, III_I, III_{II}, IV_I and IV_{II}).[2] In native cellulose I, each glucopyranose residue participates in two intramolecular hydrogen bonds with neighbouring monomers (specifically O3H···O5 and O2H···O6), and one intermolecular hydrogen bond (linking O3 and O6 groups) with an adjacent strand in the same sheet, *via* the all-equatorial hydroxyl substituents. The arrangement of the heavy atom skeleton is identical in cellulose I_α and I_β although the hydrogen-bonding patterns are subtly different. In contrast to cellulose II, neither cellulose I_α nor I_β contain inter-sheet hydrogen bonds (sheets instead interact *via* van der Waals interactions).[32] In nature, cellulose I_α is always accompanied to some degree by cellulose I_β. The proportion of cellulose I_α may be as high as *ca.* 70% in primitive organisms (*e.g.*, bacteria) and as low as 20% in higher

plants. Diagrams showing representations of structures, hydrogen-bonding patterns and interconversion pathways of different cellulose allomorphs are displayed in Fig. 2.

Although naturally-occurring cellulose I is metastable, it typically undergoes a transformation to cellulose II during regeneration or mercarisation, suggesting that biosynthesis of cellulose fibrils does not proceed *via* the crystallisation of pre-formed chains. Instead, it has been proposed that chain growth occurs by sequential addition of glucopyranose units concurrent with crystallisation into fibrils. In higher plants, biosynthesis occurs with the participation of cellulose synthase complexes tethered to the cell plasma membrane (the interested reader is directed to recent review literature[33,34]).

When characterizing the mechanism of cellulose dissolution or derivatisation in a given solvent system, an understanding of the changes in (hydrogen-)bonding properties and specific solvent–solute interactions is essential. A brief overview of the history of cellulose dissolution strategies is provided in the next section, highlighting differences between early derivatizing solvent systems and more recent (formally non-derivatizing) technologies.

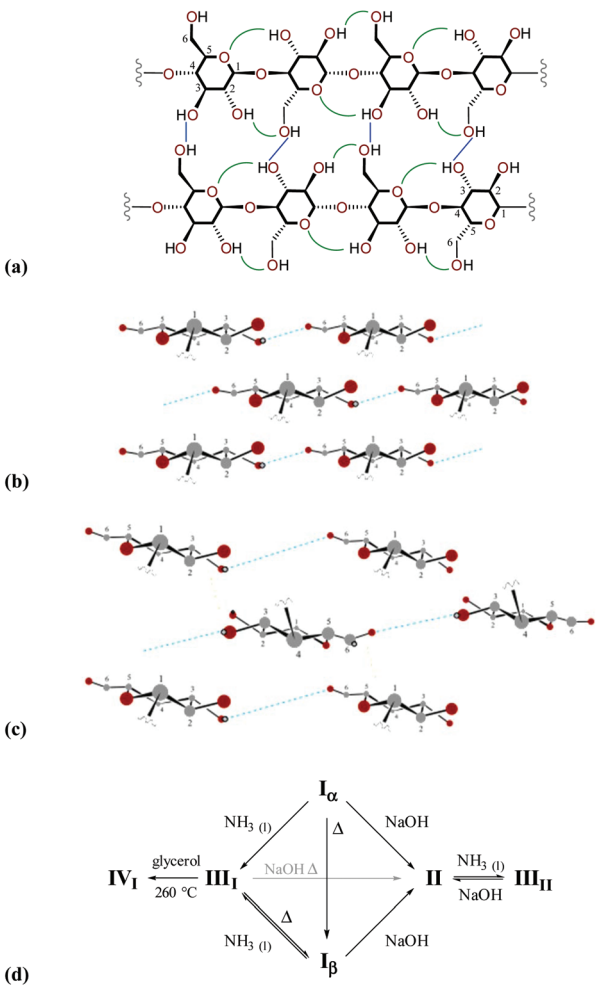

Fig. 2 (a) Diagram highlighting the network of intramolecular (green) and intermolecular (blue) hydrogen-bonding interactions within a sheet of cellulose I; comparison of the arrangement of sheets within a microfibril of cellulose I (b) and cellulose II (c) (only hydrogen atoms that participate in hydrogen-bonding are shown, for clarity); and (d) routes for interconversion of cellulose allomorphs (adapted from D. Klemm *et al.*, in *Biopolymers Online*, Wiley-VCH Verlag GmbH & Co. KGaA, 2005).[2]

3. Evolution of cellulose dissolution strategies

Dissolution is likely to be a crucial stage of any cellulose valorisation technology. However, as discussed in the previous section, dissolving cellulose is challenging on account of the need to break the ordered and extensive network of strong intramolecular and intermolecular hydrogen-bonding[35] and van der Waals[32] interactions. Consequently, cellulose does not dissolve in the great majority of conventional solvents.

Fig. 3 shows the evolution of cellulose dissolution technologies through the 19th and 20th centuries. Early technologies typically involved derivatisation to enhance its solubility (usually in water). In this manner, cellulose was shown to be soluble as cellulose nitrate (Schönbein, 1846), in the form of organo-soluble cellulose acetate (Schützenberger, 1865), or as cellulose xanthogenate, attainable by treatment with NaOH and CS_2 (Cross, 1892).[36] The latter procedure is the so-called 'Viscose' process and is still conducted today at industrial scale. Cellulose was shown to be solubilised by a cuprammonium

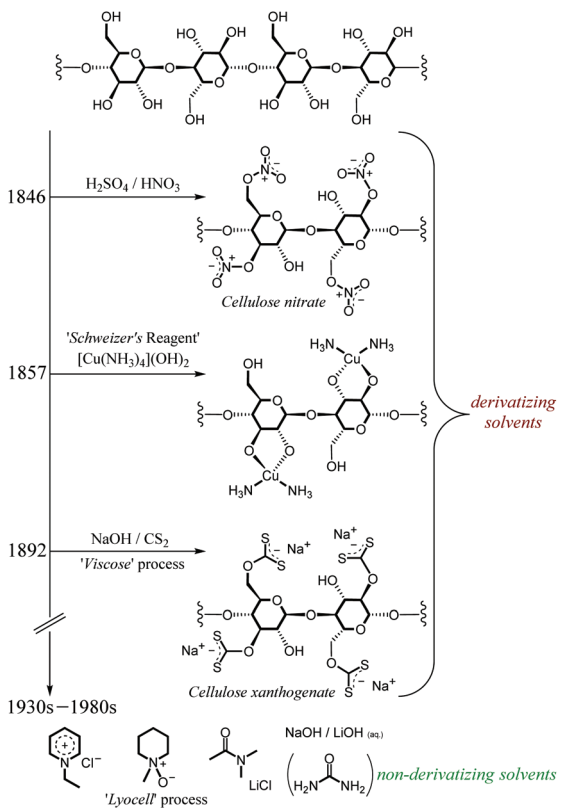

Fig. 3 A simplified diagram representing the evolution of cellulose dissolution strategies through the 19th and 20th centuries.

hydroxide solution (Schweizer, 1857),[37] whereby in the presence of 'Schweizer's reagent' ($[Cu(NH_3)_4](OH)_2$), cellulose reacts to form a complex with copper involving bidentate interaction of the O2 and O3 hydroxyl residues (shown in Fig. 3). In each of the above processes, the added functional group enhances the solubility of the resultant polymer in the solvent media.

In the intervening years, cellulose has been shown to be soluble in a range of (formally non-derivatising) solvents, among them 1-ethylpyridinium chloride (Gränacher, 1934),[38] *N*-methylmorpholine-*N*-oxide ('Lyocell' process, American Enka, 1972),[36] LiCl in dimethylacetamide (DMA) (McCormick, 1978),[39–44] and simple aqueous solutions of group I metal hydroxides (with[45,46] or without[47–49] urea) (Kamide, 1987)[49]. However, such technologies encounter problems associated with solvent toxicity/flammability,[36] severe thermal instability[50–53] or poor recyclability.

Contemporary ionic liquids (ILs), salts that are molten at (or close to) ambient temperatures, were first successfully applied to the dissolution of cellulose by Swatloski *et al.* in 2002.[54] The authors noted that up to 25 wt% of high-molecular-weight cellulose (DP ≈ 1000) dissolved in the archetypal IL 1-butyl-3-methylimidazolium chloride, $[C_4C_1im]Cl$, assisted by 3–5-second microwave heating pulses, leading to a clear viscous solution. Moreover, this article first demonstrated the strong sensitivity of IL–cellulose mixtures to the anti-solvent effect of water, a recurrent theme in subsequent literature.[55–59] It is now established that pairing strongly hydrogen bond-basic anions (*e.g.* Cl^-, $[OAc]^-$, $[HCO_2]^-$ or $[(CH_3O)_2PO_2]^-$), contributing to 'Kamlet–Taft' (KT) β values ≥0.8 (ref. 60–62) with moderately hydrogen bond-acidic cations (*e.g.*, 1-alkyl-3-methylimidazolium, $[C_nC_1im]^+$; 1,8-diazabicyclo[5.4.0]undecenium, $[HDBU]^+$; tetraalkyl-phosphonium) generates ILs that are effective cellulose-dissolving agents (Fig. 4).[27,54,61–72] Hauru *et al.* proposed that the difference between hydrogen bond basicity and acidity is a useful parameter for predicting the ability of a solvent to dissolve cellulose, whereby effective solvents exhibit $\beta - \alpha$ values in the range *ca.* 0.35–0.9.[73] Although the associated cost[74,75] and susceptibility to undergoing side reactions with cellulose[76–82] have to be considered carefully, ILs could nevertheless offer profound benefits over traditional cellulose dissolution systems on account of their typically low toxicities (low vapour pressures) and their potential for continuous recycling.[83–85]

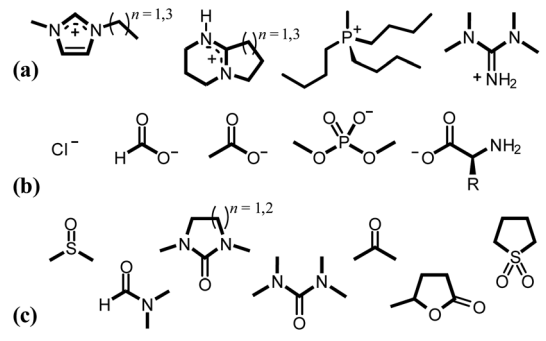

Fig. 4 Typical cations (a), anions (b) and co-solvents (c) incorporated into (IL and) OES solvents for the dissolution of cellulose.

Questions on the mechanism of cellulose dissolution in ILs, and the specific roles of the cation and anion in dismantling the network of hydrogen-bonded strands, have formed the basis of various experimental[72,86–89] and theoretical[55,59,90–97] studies. There is a broad concensus that bonding interactions between the IL anion and cellulose are the predominant driving force for dissolution of the biopolymer.[59,87,90,92] It has been suggested that in $[C_4C_1im]Cl$–cellulose mixtures, the anion interacts with the equatorial hydroxyl substituents in a specific and directional manner (with 1 : 1 stoichiometry between Cl^- anions and hydroxyl residues),[87] although a Molecular Dynamics (MD) investigation of cellulose dissolved in the same IL demonstrated interactions of Cl^- from both axial and equatorial directions.[91] In addition, MD simulations have provided evidence that the cation occupies positions at the upper and lower faces of cellulose, interacting in a relatively non-specific/non-directional manner *via* hydrophobic or dispersion interactions.[59,90,94,96,97] The cation may intercalate between individual cellulose strands,[96] aiding in separation of the chains. Dissolution of cellulose in ILs is likely to be accompanied by increased polymer conformational flexibility[55,86,95] and disruption of the O3H···O5 intramolecular hydrogen bonds between neighbouring glucopyranose monomers.[55] Therefore, the chemical and electronic properties of both the anion and cation are of critical importance for effective cellulose dissolution in an IL.

4. Organic electrolyte solutions and cellulose: thermodynamic and mechanistic considerations

Although electrolytes of inorganic salts have been known as solvents for cellulose for many years (*e.g.*, LiCl in DMA),[39–44] analogous 'organic electrolyte solutions' (OESs) – mixtures incorporating a room-temperature ionic liquid (IL) and a polar organic co-solvent – were characterized in detail only recently (Rinaldi, 2011).[8] Remarkably, it was shown by Rinaldi that complete dissolution of 10 wt% Avicel cellulose was possible even at very low mole fractions of the IL, *e.g.*, χ_{IL} = 0.08 ($[C_4C_1im]Cl$–DMSO), 0.10 ($[C_4C_1im]Cl$–DMF) or 0.18 ($[C_4C_1im]Cl$ with 1,3-dimethyl-2-imidazolidinone, DMI).[8] Moreover, it was observed that complete dissolution was achieved far more rapidly in the OES than in the corresponding neat IL (*e.g.*, <3 min for 10 wt% cellulose in 50 : 50 wt/wt $[C_4C_1im]Cl$–DMI, *cf.* >10 h for 5 wt% cellulose in $[C_4C_1im]Cl$[65]). The inclusion of a co-solvent has, in one instance, been shown to enhance the solubility of cellulose[98] and may even enable dissolution where the neat IL is incapable of doing so.[99] Example ions and co-solvents that contribute to effective cellulose dissolution are shown in Fig. 4. A flow diagram to aid in the appropriate choice of cation, anion and co-solvent combinations for cellulose dissolution is shown in Fig. 5.

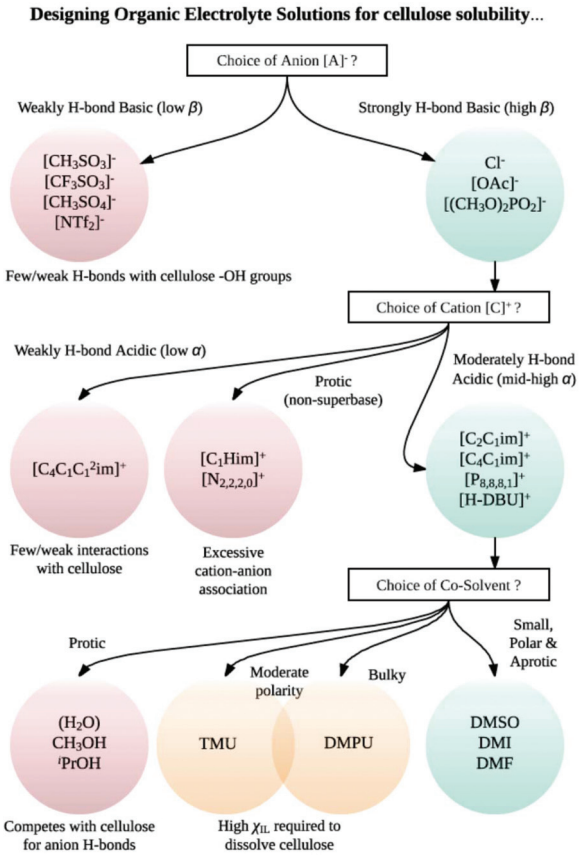

Fig. 5 A flow diagram to aid in the selection of sensible cation–anion–co-solvent combinations for effective cellulose dissolution. The diagram is intended to highlight key structural and electronic factors that influence cellulose solubility, and is not exhaustive. $[NTf_2]^-$ = bis(trifluoromethanesulfonyl)imide; $[OAc]^-$ = acetate; $[C_4C_1C_1{}^2im]^+$ = 1-butyl-2,3-dimethylimidazolium; $[C_1Him]^+$ = 1-methylimidazolium; $[N_{2,2,2,0}]^+$ = triethylammonium; $[C_2C_1im]^+$ = 1-ethyl-3-methylimidazolium; $[C_4C_1im]^+$ = 1-butyl-3-methylimidazolium; $[P_{8,8,8,1}]^+$ = tri(*n*-octyl)methylphosphonium; $[H\text{-}DBU]^+$ = 1,8-diazabicyclo[5.4.0]undecenium; TMU = 1,1,3,3-tetramethylurea; DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone; DMI = 1,3-dimethyl-2-imidazolidinone.

A variety of different experimental methods for dissolving cellulose in OESs have been described. In many instances cellulose was added – either in small aliquots or as a single addition – to a pre-mixed solution containing the desired stoichiometry of IL and co-solvent.[99–102] For instance, Huang *et al.* described addition of various cellulose materials to mixtures of tetra(*n*-butyl)ammonium acetate and DMSO at 25 °C.[101] The authors observed that the time required to dissolve 4 wt% of microcrystalline cellulose (MCC) was influenced by the mass fraction of IL in the solvent, such that complete dissolution was most rapid ($T < 2$ min) at $W_{IL} = 0.15$. Understandably, dissolution time increased incrementally with the DP of the cellulosic material. Comparative studies of this type are of great value in elucidating the little-known effects of *e.g.* IL mole fraction and DP on the practicalities associated with preparing OES-cellulose mixtures.

Another method for preparation of OES–cellulose mixtures is the initial dispersion of cellulose in the co-solvent, followed by addition of the IL. In one early example, cellulose was suspended in DMSO prior to the addition of tetra(*n*-butyl) ammonium fluoride (TBAF), after which complete dissolution was attained within 15 min.[103] Similarly, by first preparing a suspension of Avicel in DMI at 100 °C, agglomeration of biopolymer fibres was prevented; upon subsequent addition of the IL, complete dissolution was attained in a remarkably short time frame (<3 min with $[C_4C_1im]Cl$ or instantaneous with $[C_2C_1im][OAc]$).[8] In preparing dope solutions for electrospinning of cellulose fibers (refer to section 5.1, below), Härdelin *et al.* describe treating small pre-dried square pieces of pulp material first with co-solvent, followed after 1 minute by addition of the IL.[104] The authors observed that complete dissolution was less time-consuming following this procedure, and they rationalised that absorption of the co-solvent enhanced the rate of ion diffusion into the pulp. Future investigations into the exact influence of co-solvent pretreatment on the uptake of IL into the microfibrils would be of significant interest.

An important, recurring observation in studies of OESs and cellulose is that the specific electronic (and steric) properties of the co-solvent are of critical importance in determining cellulose solubility. For example, from the outset it was noted that OESs derived from DMI and 1,1,3,3-tetramethylurea (TMU), close structural analogues, required vastly different quantities of $[C_2C_1im][OAc]$ for complete dissolution of 10 wt% cellulose ($\chi_{IL} = 0.18$ and 0.59, respectively).[8] Similarly Holding and co-workers demonstrated that, although OES solvent systems composed of tri(*n*-octyl)methylphosphonium acetate and DMSO were capable of dissolving up to 19 wt% cellulose, the analogous mixtures with DMF exhibited negligibly low cellulose solubility.[99] Pinkert put forward a qualitative argument for the difference in co-solvent capability of DMI and TMU, suggesting that the increased structural rigidity of DMI and static nature of the *N* π-orbitals (which can readily hybridize to sp^2) enables DMI to better assist with correct positioning of the ions at the hydrophilic and hydrophobic sites of cellulose.[105] However, gas-phase Natural Bonding Orbital (NBO) calculations suggested that the energies of DMI and TMU frontier molecular orbitals are approximately equal.[106] More likely, differences in dipole moment and subtle steric properties explain the contrasting abilities of co-solvent species to aid in cellulose dissolution (Fig. 6).[106]

The capabilities of IL solvents to dissolve cellulose have been shown to correlate[62] with the KT empirical solvation parameters α (hydrogen bond acidity),[107] β (hydrogen bond basicity)[60] and π^* (polarity/polarisability).[108] Interestingly, for OES solvents derived from $[C_2C_1im][OAc]$ and DMI, the β and π^* values do not change significantly over the range χ_{IL} = 0.1–1.0. The hydrogen bond basicity (β, largely influenced by the nature of the anion) and polarisability properties are therefore not significantly perturbed up to $\chi_{DMI} \approx 0.90$. By contrast, the hydrogen bond acidity (α, largely influenced by the nature of the cation) appears to partially decrease in the direction $\chi_{IL} = 1.0 \rightarrow 0.1$.[8] Below $\chi_{IL} \approx 0.1$ the β, α (and to a lesser extent π^*) values fall sharply, associated with the observed loss

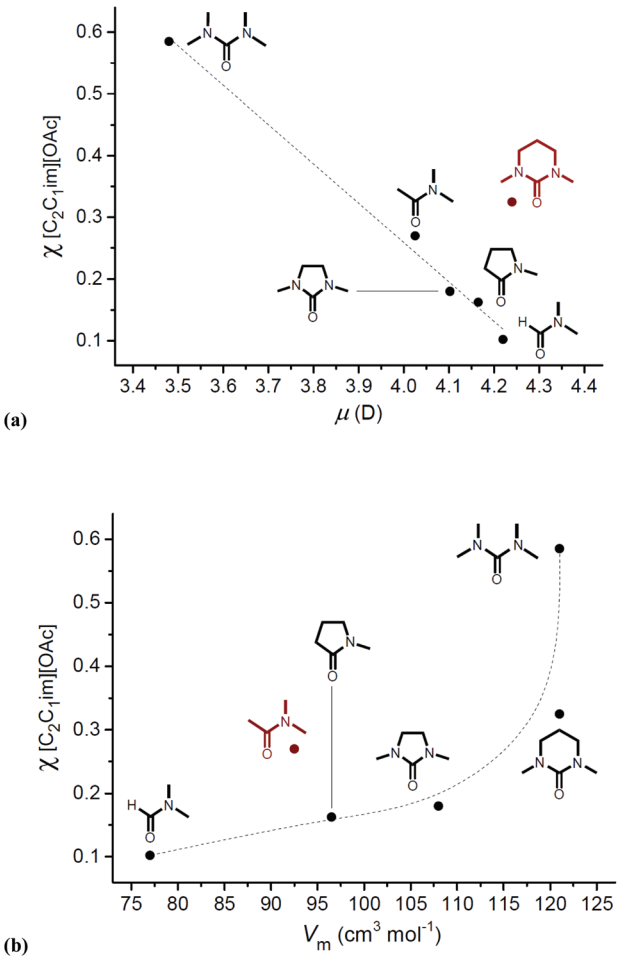

Fig. 6 Understanding the factors contributing to an effective OES co-solvent: relationship between minimum $[C_2C_1im][OAc]$ mole fraction required for 10 wt% cellulose dissolution, χ_{IL}, and the co-solvent dipole moment (μ), (a), and molar volume (V_m), (b). Adapted with permission from *J. Chem. Eng. Data*, 2012, **57**, 1341–1343. Copyright 2012 American Chemical Society.

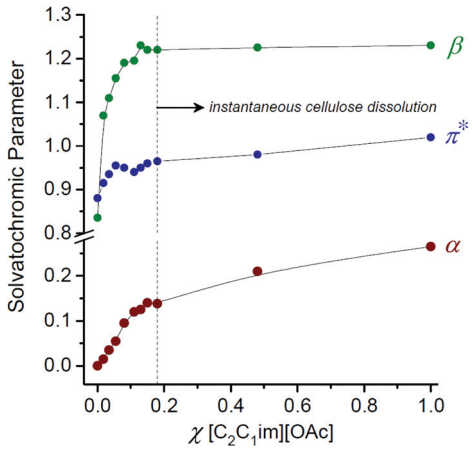

Fig. 7 The influence of solvent composition on the Kamlet–Taft empirical solvation parameters α, β and π^*, for $[C_2C_1im][OAc]$–1,3-dimethyl-2-imidazolidinone (DMI) solvents. Adapted from ref. 8 with permission from the Royal Society of Chemistry.

in cellulose solubility (Fig. 7).[8] Gericke *et al.* studied the influence of adding aliquots of a co-solvent (or co-solvent binary mixture) to 10 wt% cellulose solutions in the ILs 1-allyl-3-methylimidazolium chloride ($[C_1{=}C_2C_1im]Cl$), $[C_4C_1im]Cl$ and $[C_2C_1im][OAc]$.[109] It was concluded that, in order to be miscible with the initial mixtures of IL and cellulose, a co-solvent must typically have solvent parameter values within certain thresholds ($\beta > 0.4$, $\pi^* > 0.8$, normalized empirical polarity (E_T^N) > 0.3). Strongly dipolar and hydrogen-bond-basic co-solvents (*e.g.* DMSO, DMF) could be added in ≥1 : 1 $wt_{co\text{-}solvent}/wt_{IL\text{–}cellulose}$ quantities before cellulose precipitation occurred, for all three investigated ILs. By contrast, protic co-solvents, characterized by high α values, caused immediate and permanent cellulose precipitation at 0.2 : 1 $wt_{co\text{-}solvent}/wt_{IL\text{–}cellulose}$, attributed to the tendency of the co-solvent to compete with cellulose for interactions with the IL anions.

Although OESs have emerged as an independent class of solvent for cellulose, the mechanisms that underpin dissolution remain only partially understood. As for pure ILs,[59,87,90,92] there is almost unanimous agreement that strong, directional hydrogen-bonding interactions that form between the anions and the hydroxyl residues of cellulose are the driving force behind dissolution in an OES.[101,110–113] Nevertheless, the precise role of the co-solvent in enabling rapid or instantaneous cellulose dissolution is the subject of some debate.

Xu *et al.* demonstrated that the addition of aliquots of DMSO to $[C_4C_1im][OAc]$ brought about a considerable increase in ion conductivity (maximum conductivity occurred at $\chi_{DMSO}/\chi_{IL} \approx 5$).[110] They hypothesized that preferential solvation of cations by DMSO helped to increase the availability of dissociated or 'free' $[OAc]^-$ anions, which were capable of accepting hydrogen bonds with the hydroxyl units of cellulose more readily. Similarly, from results of MD simulations on $[C_4C_1im][OAc]$–DMSO and $[C_4C_1im][OAc]$–DMF systems, Zhao and colleagues suggested a partial separation of the cation–anion association by the co-solvent. Once again, a partial breakdown in associative interactions between cations and anions was thought to indirectly account for rapid dissolution of cellulose, though in this instance no preferential solvation of cations or anions by DMSO or DMF was evidenced by the simulations.[111]

Subsequent studies have challenged the concept of ion pair loosening. Andanson *et al.* undertook a comparison of $[C_4C_1im][OAc]$ *vs.* $[C_4C_1im][OAc]$–DMSO (50 : 50 mol/mol), with the use of both experimental (viscometry, conductivity) and computational (MD) techniques.[114] Conductivity was certainly enhanced with the inclusion of DMSO, in agreement with Xu *et al.*[110] However, this was attributed to improved mass transport of ions (lower viscosity) and not due to a significant change to either ion–ion or ion–cellulose interactions, on the basis that the Walden plot indicated no increase in the number of charge carriers with increased DMSO concentration (Fig. 8).[114] This was further supported by an analysis of the

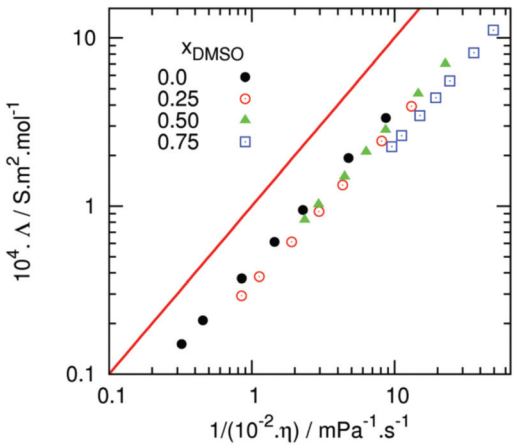

Fig. 8 Walden plot comparing the viscosity and conductivity values for binary [C_4C_1im][OAc]–DMSO mixtures (χ_{DMSO} = 0, 0.25, 0.5, 0.75), reproduced from ref. 107 with permission from the Royal Society of Chemistry. The red line denotes the reference ionicity of 0.01 M aqueous KCl, at 25 °C.

radial distribution functions from MD simulations, which indicated that inclusion of DMSO did not perturb the pre-existing network of hydrogen bonds between cations and anions.[114] An MD study of the dissolution of a 36-strand cellulose microfibril in equimolar [C_4C_1im][OAc]–DMSO indicated that DMSO does not establish specific associative interactions with either ions or cellulose.[113] On this basis, Velioglu *et al.* referred to DMSO as an 'innocent' co-solvent.

Overall, considering this collective data on [C_4C_1im][OAc]–DMSO OESs, despite apparent separation of [C_4C_1im][OAc] ion pairs, closer inspection indicates that strong cation–anion association is not significantly perturbed by addition of DMSO to the parent IL.

The extent of ion pair loosening may vary considerably between different IL–co-solvent combinations; trends that have been observed for [C_4C_1im][OAc]–DMSO OESs therefore may not be replicated in all instances. As an example, Huang *et al.* recently proposed that mixtures of tetra(*n*-butyl)ammonium acetate and DMSO exhibit distinct 'ion-split' and 'ion-paired' stages (in the absence of cellulose), at different mass fractions of the IL ($0.05 \leq W_{IL} \leq 0.15$ and $0.15 \leq W_{IL} \leq 0.25$, respectively).[101] The authors recognised that balancing the ion concentration and ion 'mobility' was the key to ensuring maximum solubility of cellulose, occuring at W_{IL} = *ca.* 0.15 for this specific OES. A recent NMR relaxometry investigation highlighted a similar duality for 1-allyl-3-methylimidazolium chloride–DMSO mixtures: at low χ_{DMSO}, evidence suggested that the co-solvent molecules insert into the IL phase and loosen the cation–anion interactions, whereas high χ_{DMSO} values (>0.5) promote clustering of ions, restricting the ability of ions to form favourable hydrogen-bonding interactions with cellulose.[115] These data confirm a phenomenon noted in the earlier literature – that subtle differences in electronic and steric properties of the IL ions and co-solvent may strongly influence the cellulose-solvating behaviour of the resultant OES.[8,105,106]

The above-described improvement in mass transport of ions in an OES, relative to a simple IL, probably explains the high rate at which cellulose dissolves,[8] whereby cations and anions can rapidly orientate themselves along the cellulose backbone and participate in favourable hydrogen-bonding interactions. Although this kinetic effect has been noted in multiple literature reports, thermodynamic data relating to dissolution of cellulose in OESs is relatively scarce. Polymer dissolution in a molecular solvent is usually an endothermic event (favoured by operating at higher temperatures).[116] However, cellulose dissolution in ILs is typically exothermic (ΔH < 0 kJ mol^{-1}, whereby formation of ion–cellulose interactions more than compensates for breaking of cellulose–cellulose and ion–ion interactions). Dissolution of any polymer is usually accompanied by a small entropic gain (ΔS > 0 J mol^{-1}).[117] Therefore, to maintain spontaneous cellulose solubility in an OES (ΔG < 0 kJ mol^{-1}), the enthalpy term must remain approximately neutral or exothermic after dilution by the co-solvent ($\Delta G = \Delta H - T\Delta S$).

Andanson *et al.* used solution calorimetry to compare the heat of cellulose dissolution in [C_2C_1im][OAc] against dissolution in equimolar [C_2C_1im][OAc]–DMSO.[89] The inclusion of 50 mol% DMSO brought about a surprisingly minimal reduction in exothermicity (at 80 °C), from −132 ± 8 J g^{-1} to −106 J g^{-1}, despite a significant dilution of ions. In a subsequent study, solution calorimetry was also used to measure and compare the enthalpies of mixing for cellobiose (as a model for cellulose) in IL and OES solvents, $\Delta_{mix}H_{(CB)}$.[118] The mole fractions of IL ([C_4C_1im]Cl or [C_4C_1im][OAc]) and co-solvent (DMSO, DMI or DMF) were systematically varied, and the $\Delta_{mix}H_{(CB)}$ values were determined (at 25 °C). The $\Delta_{mix}H_{(CB)}$ profiles as a function of χ_{IL} for mixtures with DMSO, DMI and DMF were strikingly different (Fig. 9). For the [C_4C_1im]Cl–DMI and [C_4C_1im][OAc]–DMSO series, $\Delta_{mix}H_{(CB)}$ rose sharply

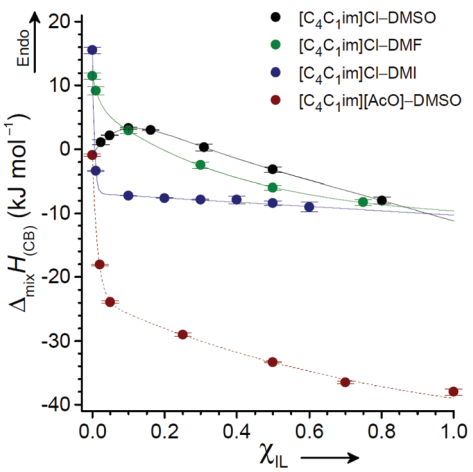

Fig. 9 Relationship between χ_{IL} and the heat of cellobiose mixing, $\Delta_{mix}H_{(CB)}$, for OES solvents derived from [C_4C_1im]Cl or [C_4C_1im][OAc] with DMSO, DMI or DMF. Measurements were obtained at 25 °C. Adapted with permission from *ChemSusChem*, 2015, **8**, 1577–1584. Wiley-VCH Verlag GmbH & Co. KGaA, 2015.

towards endothermic values from χ_{IL} = 0.1 → 0. However, in agreement with the observation of Andanson *et al.*,[89] changes in $\Delta_{mix}H_{(CB)}$ in the broad range χ_{IL} = 0.1–1 were comparatively small for all mixture series. Therefore despite a small loss in exothermicity by inclusion of a co-solvent, the dissolution of cellulose in an OES is likely to be rapid on account of both thermodynamic and kinetic favourability. When χ_{IL} falls below a particular threshold (dependent on the specific choice of IL and co-solvent), cellulose solubilisation is no longer thermodynamically preferable, and spontaneous dissolution of cellulose does not occur.

5. Cellulose derivatisation and valorisation

Building on the success of ILs for the dissolution, derivatisation and regeneration of cellulosic materials,[27,62,71] OESs have received growing attention on account of the additional 'handle' for controlling the physicochemical properties of the solvent. Foremost, the ability to modify viscoelastic and rheological properties by inclusion of a co-solvent, whilst still retaining high cellulose solubility, is an attractive aspect. Key examples of the implementation of OES systems toward cellulose derivatisation and valorisation are summarized in the following subsections.

5.1 Fibre electrospinning

Continuous and regulated production of biopolymer fibres can be achieved with the use of an 'electrospinning' apparatus. Electrospinning functions by applying a high voltage difference between a solvent–polymer solution, contained within a syringe, and a collection vessel. A syringe pump regulates the rate at which the solvent–polymer solution is dispensed from the syringe, through a narrow 'spinneret' (often a needle). A pendant droplet forms at the spinneret and, once the voltage difference becomes great enough, the droplet deforms into a conical tip denoted a 'Taylor cone'.[119] A thin and heavily-charged stream of solvent–polymer solution is then drawn towards the collection vessel. When a volatile organic solvent is used, solvent evaporation occurs at this stage. Conversely with (non-volatile) IL or OES solvents,[13,14,18,120,121] the solution is discharged into a collection bath (*e.g.* water[14] or EtOH[122]), causing precipitation of the polymer fibres. Therefore, use of an IL (or OES incorporating a relatively non-volatile co-solvent) mitigates environmental concerns associated with the release of volatile and hazardous organic components, which are typically not recycled.[123] A simplified diagram representing an IL or OES electrospinning apparatus is shown in Fig. 10.

Electrospun fibers typically exhibit the beneficial properties of high porosity,[124] large specific surface area[125] and well-regulated fibre diameter. Such properties are readily controllable by modification of process parameters (*e.g.* the field strength, feed rate, distance between spinneret and collection vessel), solution parameters (*e.g.* concentration, polymer molecular weight, surface tension, viscosity),[126–129] or ambient conditions.[130,131] Considering solution parameters, it is established that low viscosity is a key property that broadly differentiates OESs from their corresponding ILs. For example, Lv *et al.* studied solutions of a cotton-derived cellulose (DP = 650) in $[C_4C_1im]Cl$–DMSO and $[C_1{=}C_2C_1im]Cl$–DMSO solvents, at 25 °C.[132] For mixtures incorporating 1.5 wt% cellulose, exponential reduction in viscosity was observed in the range χ_{DMSO} 0 → 0.7, mirroring the behaviour of OES solvents without cellulose. In a later investigation of $[C_4C_1im]Cl$–DMSO–cellulose mixtures by Saba *et al.* (5 wt% cellulose, DP = 500), non-linear viscosity behaviour was observed in the range 5–8 wt% DMSO, at temperatures of 50–80 °C (Fig. 11).[133] The non-linearity was attributed to microscopic aggregation or phase separation in this region. Although in one instance a higher viscosity was observed for an OES–cellulose mixture ($[C_2C_1im][OAc]$/DMSO 90 : 10 wt/wt) than the equivalent neat IL–cellulose solution,[104] the general trend of decreasing viscosity upon addition of the molecular co-solvent still holds.

Prior to OESs emerging as an independent class of solvents for cellulose,[8] the inclusion of a co-solvent had been used as a strategy for controlling the rheological properties of IL–cellulose mixtures for electrospinning processes. For example, Xu and co-workers explored the influence of DMSO concentration on the electrospinning properties of cellulose (from cotton linters, DP = 1600) dissolved in $[C_1{=}C_2C_1im]Cl$.[12] DMSO reduced the viscosity,[114,132–134] surface tension and entanglement density, thereby contributing toward a continuous electrospinning jet. The authors identified that a sufficient cellulose loading was necessary to ensure effective entanglement. At a fixed cellulose loading of 5 wt%, excessive quantities of DMSO (*e.g.*, 8 : 1 DMSO/$[C_1{=}C_2C_1im]Cl$ wt/wt) led to electrospraying of the mixture. Insufficient DMSO (*e.g.* 1 : 1 DMSO/$[C_1{=}C_2C_1im]Cl$ wt/wt) afforded a mixture with poor electrospinning capability, on account of the high viscosity. Therefore, it is worth noting that the solution para-

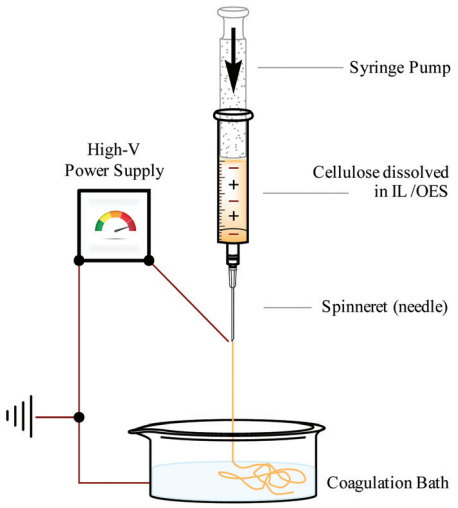

Fig. 10 Apparatus (simplified) for continuous and regulated electrospinning of cellulose fibers from an IL or OES solvent system, adapted from ref. 10 with permission from the Royal Society of Chemistry.

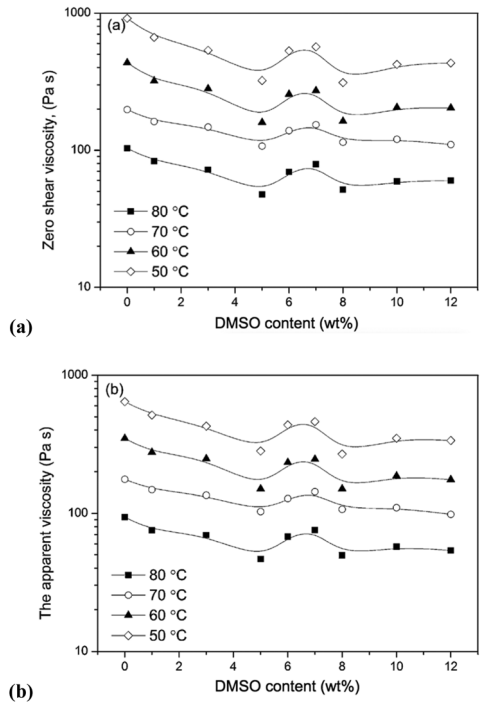

Fig. 11 Influence of DMSO content (wt%) on zero-shear-rate viscosity, (a), and apparent viscosity at shear rate 1 s^{-1}, (b), for $[C_4C_1im]Cl$–DMSO–cellulose ternary mixtures (5 wt% cellulose), at 50–80 °C (solid lines are provided to guide eyes). Adapted from ref. 126 with permission from the Royal Society of Chemistry.

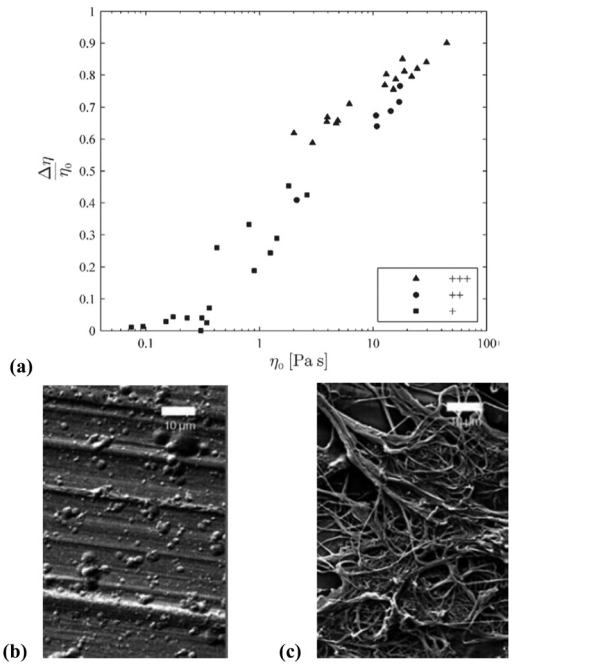

Fig. 12 (a) Relationship between shear thinning of OES–cellulose mixtures, and the propensity for fibre formation: + denotes no fibre formation; ++ denotes partial fibre formation; +++ denotes good fibre formation. Scanning Electron Microscopy (SEM) images for example '+' and '+++' cellulose electrospinning experiments are shown in (b) and (c), respectively (scale bars denote 10 μm). Reproduced and adapted with permission from *J. Appl. Polym. Sci.*, 2012, **125**, 1901–1909. Wiley-VCH Verlag GmbH & Co. KGaA, 2012.

meters cannot be considered in isolation when developing OES–cellulose electrospinning processes.[12]

Härdelin *et al.* conducted a detailed investigation of the influence of DMA, DMF and DMSO co-solvents on the ability of $[C_2C_1im][OAc]$ to electrospin cellulose fibres (from dissolving pulp, DP = 750).[104] Interestingly, although each of the three co-solvents brought about a reduction in the surface tension of the mixture, DMA and DMF had a significantly more pronounced effect than DMSO. The OES–cellulose mixtures incorporating DMSO exhibited the greatest degree of 'shear thinning', leading to optimal fibre formation (Fig. 12).

Therefore, in analogy to the differing abilities of co-solvent species to aid and promote cellulose dissolution (see section 4, above), the specific choice of co-solvent plays an important role in determining the precise solution parameters for cellulose electrospinning procedures. Whilst the inclusion of a co-solvent may offer an additional handle for controlling viscoelastic properties of the mixture, the solution parameters must be considered collectively in order for successful electrospinning of cellulose fibres to be achieved.

5.2 Solution-state NMR spectroscopy of cellulose

The low viscosities of OES–cellulose mixtures offer potential benefits beyond tailored electrospinning. Typically, cellulose solutions are of prohibitively high viscosity for high-resolution NMR spectroscopy measurements, with broad and poorly-resolved ^1H signals. Because of this, whilst solid-state (*e.g.*, ^{13}C 'Cross-Polarisation–Magic-Angle Spinning') NMR spectroscopy has been successfully applied to cellulose,[135,136] solution-state measurements are comparatively uncommon.

Nevertheless, Holding *et al.* were able to collect high-resolution 1D and 2D NMR data of high-M_w cellulose, at ≥8 wt% concentration, dissolved in tri(*n*-octyl)methylphosphonium acetate–DMSO-d_6 (50 : 50 wt/wt).[137] The sharpening of cellulose ^1H signals in this low-viscosity medium enabled glucopyranose residues at the reducing and non-reducing ends to be distinguished from those embedded within the chain. Cellulose DP values could therefore be semi-quantified *via* integration of the respective signals. Whilst the DP values of low-M_w celluloses (DP ≤ 100), calculated by NMR, aligned closely with the results of Gel Permeation Chromatography (GPC) analysis, the increased difficulty in spectral resolution for long-chain cellulose polymers (up to DP > 600) led to poor correlation between NMR and GPC assays. In spite of this, such methodologies employing OES solvents hold promise for future *in situ* NMR analyses of cellulose depolymerisation and derivatisation reactions.

5.3 Cellulose derivatisation

The addition of a co-solvent offers a dual benefit for homogeneous cellulose derivatisation reactions performed in IL-type solvents: reduced viscosity, and improved miscibility with hydrophobic reagents.[109] The co-solvent can aid in the misci-

bility of common derivatisation agents for cellulose, such as acetic anhydride or acetyl chloride. As early as 1999, Heinze and co-workers demonstrated the use of an OES-type solvent, tetra(*n*-butyl)ammonium fluoride trihydrate with DMSO, to dissolve high-M_w cellulose (DP > 600).[138] This solvent system was successfully used to carboxymethylate[138] and acylate[103] cellulose samples. Nevertheless, the use of such systems was hampered by hydrolysis of anhydrides and acid chlorides as a result of residual water in the solvent,[103] and the high energy input required for solvent recycling.[139]

More recently, homogeneous acetylation of microcrystalline cellulose (MCC, 5 wt%) was performed in solvent systems comprised of triethyl(*n*-octyl)ammonium chloride with acetone or DMA (9 : 10 wt/wt). Results were compared against reactions carried out in conventional LiCl/DMA and $[C_4C_1im]Cl$ solvents.[140] Strikingly, solvents containing tetraalkylammonium salts were advantageous because they gave rapid dissolution of cellulose, without the need for prior activation or prolonged heating. Using acetyl chloride as the derivatising agent, a similar degree of substitution was observed when comparing reactions performed in the tetraalkylammonium systems against those using LiCl/DMA and $[C_4C_1im]Cl$.

Although examples of procedures for the derivatisation of cellulose using OESs are currently scarce, the potential benefits associated with improved IL–reagent miscibility are significant, serving as another example of how inclusion of a co-solvent could tailor the properties of an IL solvent toward improved outcomes.

5.4 Phase separation

Although OES solvents are capable of dissolving high quantities of cellulose at remarkably low values of χ_{IL}, excessive dilution of the ions (*e.g.*, $\chi_{IL} \leq 0.08$ for $[C_4C_1im]Cl$–DMSO, 10 wt% Avicel cellulose[8]) leads to systems where cellulose dissolution is no longer thermodynamically favourable. Recently, OES–cellulose mixtures that exhibit thermally triggered and reversible phase separation were reported.[141] The mixtures, derived from $[C_2C_1im][OAc]$, DMI and MCC, could be easily handled as a single, homogeneous and low-viscosity mixture at elevated temperatures. Upon cooling, the mixtures passed through a well-defined 'temperature of phase separation' (T_{PS}), and separated into two distinct liquid phases. Cellulose was found to be wholly retained within the lower IL-enriched phase, whereas the upper phase was dominated by the co-solvent, DMI. Interestingly, the T_{PS} parameter could be tailored over a wide range of temperatures ($\Delta T_{PS} \approx 75$ °C) by small changes to the IL and DMI mole fractions ($\Delta\chi \pm 0.05$) (Fig. 13a). Although such phase-separating OES–cellulose mixtures have not yet been applied to cellulose dissolution or derivatisation, it can be envisaged that they may find use for derivatisation to high-value-added products (*e.g.*, chiral stationary phases for liquid chromatography), exploiting trivial separation of the cellulosic product from residual lipophilic reagents.[141]

Holding and co-workers reported a somewhat different phase separation phenomenon, enabling recovery of the expensive IL component tri(*n*-octyl)methylphosphonium

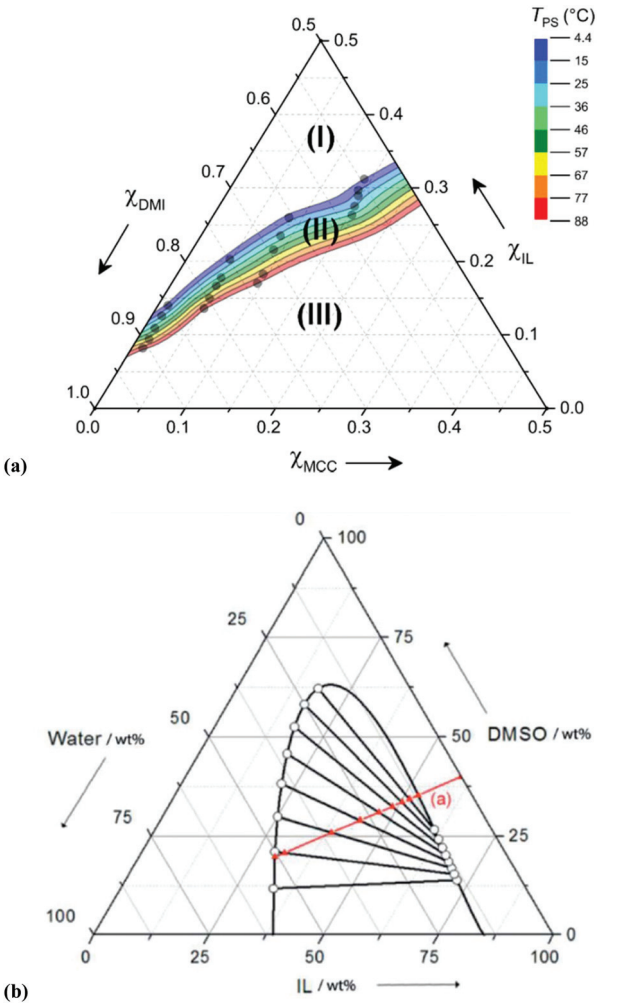

Fig. 13 (a) Composition diagram for thermally triggered phase-separating $[C_2C_1im][OAc]$–DMI–microcrystalline cellulose blends. For T > 4 °C, no phase separation is observed in region I, region II denotes phase separation, and region III indicates compositions at which cellulose is partially insoluble;[141] (b) composition diagram for phase-separation of $[P_{8881}][OAc]$–DMSO mixtures upon addition of water, line '(a)' (in the absence of cellulose). Ternary mixtures that lie within the biomodal curve are biphasic, consisting of an IL-enriched upper phase and a water-enriched lower phase.[99] Reproduced with permission from *ChemSusChem*, 2016, **9**, 3324–3329, and *ChemSusChem*, 2014, **7**, 1422–1434, respectively. Wiley-VCH Verlag GmbH & Co. KGaA, 2016, 2014.

acetate, $[P_{8881}][OAc]$, from OES mixtures with DMSO.[99] The addition of water or aqueous sodium acetate to blank OES solvents brought about division into two phases, namely, an upper phase rich in the IL and a lower aqueous-rich phase (Fig. 13b). This strategy was then applied to 5 wt% MCC solutions in $[P_{8881}][OAc]$–DMSO (55 : 45 wt/wt), whereby addition of 10 wt% aqueous sodium acetate caused simultaneous phase separation and precipitation of the MCC. The costly phosphonium IL could be recovered in close to quantitative yield and high-purity, and the cellulose could be obtained as a white powder having undergone significant conversion from cellulose I to cellulose II (*cf.* Fig. 2).

Therefore, a variety of phase separation protocols could be envisaged for versatile and sustainable recovery of high-purity IL and cellulosic materials from complex mixtures. Added to those above, various promising strategies have been put forward, incorporating (*e.g.*) kosmotropic salt solutions,[142–145] hydrophobic or fluorinated anions,[146–148] or distillable ILs.[67] These separation methods are likely to be of increasing interest within the field of organic electrolyte solutions.

6. Organic electrolyte solutions – green solvents?

If OESs are to find suitability as solvents for cellulose beyond the laboratory setting, they must not only fulfil various economic criteria, but also satisfy the condition of being 'green solvents'. To state this another way, the OESs themselves – or the processes in which they are involved – ought to meet requirements of (among other factors) waste reduction, energy efficiency and hazard minimization. Questions as to whether ILs are (or could be) green solvents, for example as solvents for catalysis,[149] have been previously addressed.

With reference to the 12 established 'principles of green chemistry',[150,151] OESs could be considered as advantageous or disadvantageous relative to the parent IL, depending on the principle in question or the process/technology in which the solvent is to be used. In the paragraphs below, selected relevant principles of green chemistry are addressed individually, and the extent to which OESs could prove beneficial or problematic for the dissolution and regeneration of cellulose (compared to exisiting alternative solvents) is critically examined.

6.1 Principle 1 – Prevent waste

If a volatile co-solvent (*e.g.*, acetone or DMI) is used, an OES solvent is likely to generate a greater quantity of non-recoverable waste (in the form of solvent vapours) relative to a pure IL with negligibly low vapour pressure under typical conditions of cellulose dissolution or electrospinning.[152,153] However, the co-solvent could in principle be recovered and purified by distillation, whereas the IL is susceptible to gradual (irreversible) decomposition during repeat cellulose dissolution–regeneration cycles.[76–82] Therefore, so long as vaporisation of co-solvent is minimized *via* carrying out a procedure in a closed system, diluting an IL with co-solvent could bring about a significant net reduction in waste by minimizing the fraction of the solvent that undergoes unintended degradation. IL and OES solvents could both offer a potential reduction in waste in comparison to existing industrial technologies (*e.g.*, the Viscose process).

6.2 Principle 3 – Design less hazardous chemical syntheses

Relatively few examples of cellulose derivatization procedures using OES solvents have been shown in the literature.[103,138–140] The flammability, volatility and toxicity of any co-solvent species will present a significant hazard over and above the analogous procedure performed in a pure IL. Nevertheless, the use of an OES–cellulose mixture that exhibits phase separation could offer simplified separation of cellulosic products from unspent toxic organo-soluble reagents.

6.3 Principle 4 – Use renewable feedstocks

Interesting preliminary studies have pointed towards the potential for renewable co-solvents to be used in OES–cellulose mixtures. For example, Gale *et al.* recently identified γ-valerolactone (GVL, Fig. 4c) as a promising co-solvent when paired with $[C_2C_1im][OAc]$.[102] GVL may itself be prepared from biomass,[7] and its credentials as a green solvent have already been established.[154]

6.4 Principles 8 and 12 – Use safer solvents and reaction conditions and minimize the potential for accidents

A severe disadvantage associated with OES solvents is the inclusion of often volatile, flammable and toxic organic species. This presents a significant hazard at large scale. OESs could be regarded as green solvents (according to principles 8 and 12) only where relatively benign co-solvents are used. Accordingly, future research must centre on co-solvents that share properties with DMSO, in contrast to solvents such as DMF or *N*-methylpyrrolidinone (which, *e.g.*, present a risk to reproductive health). In most instances an OES solvent would pose less of a safety risk than *N*-methylmorpholine *N*-oxide or CS_2, used for the established Lyocell and Viscose processes, respectively. However, great care would need to be taken to ensure that toxic co-solvent residues did not find their way into the cellulosic product.

6.5 Principle 9 – Increase energy efficiency

The low viscosities of OES–cellulose blends – in comparison to those based on pure ILs – could bring about a substantial reduction in the energy costs associated with *e.g.* handling or stirring. Moreover, the high rate of cellulose dissolution (at close to ambient temperatures) in OES solvents may also improve energy efficiency, minimizing the extent of heating and stirring required in order to obtain homogenous mixtures. However, the need to prepare mixtures of IL and co-solvent in careful stoichiometric quantities prior to the dissolution of cellulose will likely add at least one extra process stage.

6.6 Principle 11 – Analyze in real time to prevent pollution

As has been demonstrated in recent literature, the low viscosities of OES–cellulose mixtures make possible certain analyses (*e.g.* 2D NMR spectroscopy[137,155]) that are not feasible in pure IL–cellulose blends. Therefore, OESs could represent a more green alternative to pure ILs with respect to in-line analysis of cellulose dissolution and processing, thereby minimizing sampling and affiliated pollution.

In summary, questions as to whether OES-based technologies could be sustainable or 'green' processes must be answered on a case-by-case basis, taking into consideration the specific ions and co-solvent that are incorporated into the mixture. Certainly, there is scope for OESs to improve upon existing technologies in the field of cellulose dissolution, derivatisa-

tion and regeneration. In the scientific literature to date, attempts to evaluate the green credentials of OES solvents are scarce,[102] yet such studies will become increasingly relevant in future.

7. Conclusions

The development of effective, stable and recyclable solvent systems for cellulose has posed a challenge to chemists for many decades. In order to peel away and solvate individual cellulose strands from the solid state, without chemical modification of cellulose itself, the solvent must be capable of participating in strong hydrogen-bonding interactions with the polymer strands. Throughout the 20th and 21st centuries various non-derivatising cellulose solvents have emerged, among which 'organic electrolyte solutions' (OESs) can be considered as a class of solvent in their own right, though sharing certain properties with the ionic liquids (ILs) from which they are derived.

The rapidity with which high quantities of cellulose dissolve in an OES is best explained as a delicate balance between thermodynamic and kinetic properties. So long as the condition of a negative Gibbs free energy is satisfied, enabling the spontaneous dissolution of cellulose, dilution with a co-solvent and the accompanying reduction in viscosity may enhance the mass transport of the ions. Consequently, diffusion of ions into the microfibril and formation of hydrogen bonds between ions and cellulose will occur more rapidly with the aid of the co-solvent. Though the co-solvent appears to 'loosen' the ion pairs, closer inspection of mixtures of [C_4C_1im][OAc] with DMSO[114] suggests that ion–ion interactions are (at least in this instance) not significantly perturbed in the presence of the co-solvent. However, the microscopic and macroscopic properties of the OES hinge upon the specific electronic (and structural) properties of the chosen co-solvent. Therefore, an alternative choice of co-solvent could lead to an OES in which the associative interactions between cations and anions are more heavily disrupted.[155] In this regard, OESs may be considered to share the reputation of ILs as 'designer solvents', whereby physicochemical properties of the solvent can be fine-tuned by choice of cation, anion and co-solvent.

OES solvents have been successfully applied to the electrospinning of high-quality cellulose fibres, to accurate solution-state NMR measurements of cellulose, and also to cellulose functionalisation. Most of these methods benefit from the low viscosity (compared to the parent IL) of the OES solvent. Furthermore, phase-separable OES-cellulose mixtures extend the range of possibilities for cellulose derivatisation, purification, and solvent recycling over and above conventional ILs. Future research is likely to be similarly directed towards improved process sustainability and the development of green OES solvents. As has been demonstrated for ILs,[156] *ab initio* computational calculations could be able to aid the identification of sensible IL–co-solvent combinations, mitigating the need for time-consuming experimental trial and error.

In summary, OESs represent attractive and versatile alternatives to simple ILs for the dissolution, derivatisation and regeneration of cellulose. In light of the additional 'handle' for modifying physicochemical properties by inclusion of a co-solvent, and the flexibility that this affords, they may be expected to attract increasingly widespread interest in the coming years.

Conflicts of interest

There are no conflicts to declare.

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