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Manuscript for: *[Green Chemistry]*

**γ -Valerolactone-based organic electrolyte solutions: a benign approach to
polyaramid dissolution and processing**

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Electronic Supplementary Information

Synthetic procedures for polyaramids, methods for calculating the Kamlet-Taft parameters
and complete tables with solubility and Kamlet-Taft data are provided in the Electronic
Supplementary Information (ESI).

Abstract

View Article Online
DOI: 10.1039/D0GC02324H

Polyaramids are polymers that consist of aromatic repeating units that are connected via amide bonds. From their chemical structure, an extensive intermolecular hydrogen-bond network arises, which makes them very difficult to dissolve in conventional organic solvents. A commonly used solvent system is *N*-methylpyrrolidone (NMP) mixed with CaCl_2 , where the chloride ions can break up the intermolecular hydrogen bonds. However, with NMP being a known teratogen, an alternative solvent is needed. *Organic Electrolyte Solutions* (OESs) are proposed as a green alternative solvent system. OESs are created by diluting ionic liquids (ILs) with an organic co-solvent. γ -Valerolactone (GVL) was selected as a green, renewable co-solvent. The solubility in OESs was tested for three commonly produced polyaramids: poly-*p*-phenylene terephthalamide (PPTA), poly-*m*-phenylene isophthalamide (PMIA) and copoly(*p*-phenylene/3,4'-diphenylether terephthalamide) (ODA/PPTA). Some OESs were excellent solvents for PMIA and ODA/PPTA, with $[\text{C}_8\text{MIm}][\text{Cl}]/\text{GVL}$ yielding solubilities as high as 23.7 wt% and 7.4 wt%, respectively, rivalling the currently used solvent systems. PPTA, on the other hand, was completely insoluble in all OESs. GVL was found to work synergistically with ILs, while acetonitrile and ethanol acted as a non-solvent and anti-solvent, respectively. OESs made from GVL and imidazolium ILs were suitable solvents for fiber spinning, as was demonstrated using a 3D-printed spinning setup. The Kamlet-Taft parameters of the OES were determined from which boundary conditions for dissolution were loosely defined as $\beta > 0.85$, $\alpha < 0.60$ and $\pi^* > 0.85$. A dissolution mechanism is proposed, in which the IL interacts with the polymer through hydrogen bonding via the anion, while GVL can undergo dispersion interactions with the aromatic parts of the polyaramid.

Keywords: Ionic liquids; *N*-methylpyrrolidone; Organic Electrolyte Solutions; Polyaramids; γ -Valerolactone.

1 Introduction

2 Polyaramids are polymers that consist nearly entirely of aromatic repeating units that are
3 connected with amide bonds. This chemical structure provides both rigidity and chemical
4 stability to the polymer backbone. Moreover, the individual polymer chains experience a
5 multitude of intermolecular interactions through π -stacking of the aromatic units and
6 hydrogen bonding between the NH group and the carbonyl of the amide functional groups.^{1, 2}
7 The end result is a class of high performance polymers, well-known for their mechanical
8 strength, high Young's modulus, thermal and chemical stability.^{3, 4} However, these superior
9 properties have the drawback of making polyaramids notoriously difficult to dissolve in
10 conventional solvents. Industrial synthesis and/or processing of polyaramids generally
11 requires the use of an amide solvent such as *N*-methyl-2-pyrrolidone (NMP) or
12 dimethylacetamide (DMA), usually in combination with an inorganic salt such as CaCl₂ or
13 LiCl.^{5, 6} The chloride ions provided by the inorganic salt interact with the NH groups of the
14 amide functionalities, preventing the formation of intermolecular hydrogen bonds. However,
15 the amide solvents NMP and DMA have been listed as *Substances of Very High Concern*
16 (SVHC) by the European Commission.⁷ With these solvents now being subject to strict
17 regulations, there is an urgent demand for new solvents for polyaramids.

18 Certain polyaramids can be synthesized via an interfacial polymerization, using water and
19 THF as a biphasic solvent system.⁸ However, this type of polymerization offers poor control
20 of the monomer stoichiometry, generally leading to broad molar mass distributions.
21 Furthermore, these biphasic solvent systems are unsuitable for polymer processing. In recent
22 years, our research group has been investigating the potential of ionic liquids (ILs) as green
23 alternative solvents for polyaramids.⁹⁻¹² ILs are compounds which consist entirely of ions, but
24 are liquid at ambient to moderately elevated temperatures.^{13, 14} The green character of ILs
25 stems from their negligible vapor pressure. This significantly reduces the release of chemicals

1 to the atmosphere. This is a major environmental advantage over conventional *Volatile* View Article Online
DOI: 10.1039/D0GC02324H
2 *Organic Compounds* (VOC's).

3 An important disadvantage to ILs, however, is their high viscosity. This can lead to long
4 dissolution times and engineering issues while handling these viscous solutions. This is
5 especially problematic when dealing with polymer solutions which are already characterized
6 by their high viscosity. An effective way of reducing the viscosity of ILs is to dilute them
7 with co-solvents.¹⁵ This creates a binary solvent system that is referred to as an Organic
8 Electrolyte Solution (OES). This type of solvent system has already been applied with great
9 success in the dissolution of cellulose.¹⁶⁻²² Generally, the OESs displayed significantly shorter
10 dissolution times and were overall much easier to work with. Moreover, some co-solvents
11 worked synergistically with cellulose, greatly surpassing the solubility in the pure IL. OESs
12 have recently also been used in the synthesis of aramids,¹¹ and for processing aramids into
13 porous films.²³ However, in these studies, NMP and DMA were used as co-solvents, which
14 definitely still leaves room for improvement.

15 Of course, the mixing of an IL with organic co-solvents to create an OES negates the
16 environmental benefits of the IL's negligible vapor pressure. As the co-solvent can evaporate
17 and be released to the atmosphere, it is important that this co-solvent is environmentally
18 benign.²⁰ A potential green co-solvent is the bio-based compound γ -valerolactone (GVL).
19 This compound is readily derived from cellulosic biomass, making it very abundant and
20 renewable.²⁴ Other beneficial properties are biodegradability and a low toxicity.²⁵ While it is
21 commonly used as a precursor to value-added chemicals or fuels,²⁶⁻²⁸ it can also be employed
22 as a (precursor to a) bio-based polar solvent^{29, 30} and it has already been successfully used in
23 combination with ILs in the dissolution of cellulose.²⁰ The green credentials of GVL, its
24 structural resemblance to NMP and the solvating capacity of ILs make GVL-based OESs an
25 interesting and promising solvent system.

1 Dissolution of polyaramids requires interactions between the solvent and the polymer that
2 outcompete the interactions between the polymers themselves. These interactions include
3 hydrogen bonding with the amide functionalities, and dispersion interactions with the
4 aromatic parts of the polymer. A commonly used method of assessing a solvent's ability to
5 undergo hydrogen bonding or dispersion interactions is via the Kamlet-Taft parameters.³¹⁻³⁷
6 These solvatochromic parameters give an indication of a solvent's hydrogen-bond acidity (α),
7 hydrogen-bond basicity (β) and polarizability (π^*). Our previous work, as well as extensive
8 work done in the field of cellulose dissolution have shown that the solubility is related to
9 these parameters. In this regard, the use of OESs can prove extra beneficial, as altering the
10 mixing ratios can be used to tune the Kamlet-Taft parameters of binary solvent systems.³⁸

11 This paper explores the potential of GVL-based OESs as green alternative solvents for the
12 three most commonly produced polyaramids: the *para*-aramid poly-*p*-phenylene
13 terephthalamide (PPTA), the *meta*-aramid poly-*m*-phenylene isophthalamide (PMIA) and the
14 copolymer copoly(*p*-phenylene/3,4'-diphenylether terephthalamide) (ODA/PPTA). Several
15 ILs were mixed with GVL at different molar ratios and screened for their ability to dissolve
16 polyaramids. Acetonitrile (ACN) and ethanol (EtOH) were also used as co-solvents to study
17 their respective influence on the solubility compared to GVL. After screening the solubility,
18 the spinnability of several polyaramid solutions was tested using a 3D-printed spinning setup.
19 The Kamlet-Taft solvent parameters of the OESs were determined and cross-examined with
20 the solubility data. This allowed us to shed light on the role of each component of the OES in
21 the solvation mechanism, which might aid in the design of potential new ILs and co-solvents.

Experimental

Products

The ionic liquids were purchased from IoLiTec (Heilbronn, Germany). Isophthaloyl chloride ($\geq 99\%$), α -picoline (lonza quality, $\geq 99\%$), *N*-methylpyrrolidone (extra dry (99.5%), ethanol (anhydrous), Reichardt's dye (dye content 90%), *N,N*-diethyl-4-nitroaniline, 4-nitroaniline ($\geq 99\%$) and terephthaloyl chloride ($\geq 99\%$) were purchased from Sigma–Aldrich (Diegem, Belgium). Sulfuric acid (96%), *p*-phenylenediamine ($>99\%$), γ -valerolactone (98%) and acetonitrile (extra dry, 99.9%) were purchased from Acros Organics (Geel, Belgium). Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was purchased from Merck (Overijse, Belgium). *m*-Phenylenediamine (99%) was purchased from Chem-Lab (Zedelgem, Belgium) and 3,4-oxydianiline (95%) was purchased from Fluorochem Limited (Hadfield, UK). *p*-Phenylenediamine (99+%), 3,4-oxydianiline (95%) and *m*-phenylenediamine (99%) were purified extensively prior to use. Ethanol, γ -valerolactone and α -picoline were dried using molecular sieves (4 Å) until the water content was below 50 ppm. All other compounds were used as received, without any further purification. The synthesis and characterization of the polyaramids, as well as the purification methods for the diamines are described in the Electronic Supplementary Information (ESI).

Instrumentation

Dissolution tests were carried out using a Nemus Life Thermo Shaker TMS-200. Water content was measured on a Karl Fischer coulometer (Mettler-Toledo DL39). The inherent viscosity of the polyaramids was determined using a certified calibrated Ubbelohde 10–100 mm^2/s (0.1 K) capillary viscometer from SI analytics in a Lauda thermostated water bath. A UV-Vis-NIR spectrophotometer (Agilent Cary 6000i) was used to record the UV-Vis spectra required for the determination of the Kamlet-Taft parameters.

Dissolution experiments

All compounds used in the dissolution experiments were thoroughly dried beforehand. The polyaramids were initially dried overnight in a vacuum oven at 50 °C and stored there for the duration of the experiments. Organic solvents that were not purchased as 'extra dry' were dried by addition of 4Å molecular sieves. ILs were dried overnight using a vacuum line at 90 °C. Appropriate amounts of organic solvents and ILs were then mixed to obtain 2 g of organic electrolyte solutions with the desired co-solvent/IL ratios. The water content of the organic electrolyte solutions was determined via coulometric Karl Fischer titration and the solvent considered acceptable when its water content was below 200 ppm. The dissolution experiments were carried out in a thermo-regulated vortexer, shaking at 1500 rpm at 70 °C. Glass vials with a plastic cap, sealed with Teflon® tape were used to prevent losses due to evaporation. From each of the organic electrolyte solutions, an aliquot of 0.5 g was transferred to the glass vial and polyaramid was added in aliquots of 5 mg. The saturation points of the solutions were defined as the polymer concentration at which the solutions were no longer transparent but looked more turbid. The dissolution experiments were repeated a second and third time, starting at a concentration up to 5 wt% below the previously determined saturation point and with addition of aliquots of 2.5 mg of the polymer.

Determination of the Kamlet-Taft parameters

The Kamlet-Taft parameters of the OESs were determined by dissolving solvatochromic dyes and determining their peak maxima using UV-Vis spectroscopy. The three dyes used were Reichardt's Dye (RD), 4-nitroaniline (NA) and *N,N*-diethyl-4-nitroaniline (DENA). The dyes were dissolved in such a concentration as to keep the absorbance below 1. The samples were then placed between 2 quartz cuvette plates, yielding a measuring cell with an optical path length of 0.1 mm. All UV-Vis spectra were measured with a resolution of 0.1 nm. The peaks

were fitted using a Gram-Charlier peak function (GCAS) to accurately determine the peak maxima. Details on the calculations of the Kamlet-Taft parameters can be found in the ESI.

Results

The structures of the polyaramids that were used in this work are summarized in Fig. 1. The low solubility of this type of polymers makes it hard to determine their average molar mass using conventional methods. The average molar mass of polyaramids is therefore usually assessed by measuring the inherent viscosity of their solutions in concentrated sulfuric acid. The inherent viscosities of the polymers used in these studies were 2.11 dL.g⁻¹ for PMIA, 2.45 dL.g⁻¹ for ODA/PPTA and 5.17 dL.g⁻¹ for PPTA, which are on par with the industrial standard for each polyaramid.

Figure 1: Chemical structures of the three polyaramids used in this study.

1 Solubility of polyaramids in OESs

2 Organic Electrolyte Solutions were made by mixing 5 different combinations of ILs and
3 organic co-solvents in varying molar ratios. [C₈MIm][Cl], [P₁₄₆₆₆][Cl] and [C₄MIm][NTf₂]
4 were used in combination with GVL, while [C₈MIm][Cl] was also mixed with ACN and
5 EtOH. The [C₈MIm][Cl]/GVL OES thus served as a 'reference solvent' from which the
6 influence of altering the IL and the co-solvent could be studied. Next, the solubility (at 70°C)
7 of the polyaramids in these OESs was determined. Sadly, the *p*-aramid PPTA was not soluble
8 in any of the OESs tested here. Even compared to other polyaramids, PPTA is notoriously
9 difficult to dissolve. Its all-*trans* conformation, and the rigidity of the chain allow for near
10 perfect alignment of the polymer chains, resulting very efficient intermolecular interactions.³⁹
11 In fact, PPTA is known to form thermodynamically stable solutions only in strongly acidic or
12 basic solvents.⁴⁰⁻⁴² The other two polyaramids, PMIA and ODA/PPTA, were readily soluble
13 in some OESs depending on the IL/co-solvent combination and the IL molar ratio (Fig. 2). It
14 is also important to note that the dissolution in OESs proceeded much faster than in pure ILs.
15 In pure ILs, dissolution could take from several hours up to even multiple days if the solution
16 was approaching saturation. In OESs however, the polyaramid could be dissolved in a matter
17 of minutes to a couple of hours, depending on the degree of IL dilution and the amount of
18 polymer being dissolved. This can of course be attributed to the much lower viscosity of the
19 OESs as a result of adding a co-solvent.

20 The [C₈MIm][Cl]/GVL OES was found to be an excellent solvent for PMIA and ODA/PPTA,
21 reaching solubilities as high as 23.7 wt% and 7.4 wt%, respectively. The industrial synthesis
22 and spinning processes utilize solutions with polymer concentrations of 20 wt% and 6 wt%
23 for PMIA and ODA/PPTA, respectively.^{2,4,43,44} The solubility the polyaramids in the
24 [C₈MIm][Cl]/GVL OES is thus on par with that of the established amide solvent/inorganic
25 salt mixtures. Interestingly, the solubility curve passes through a maximum for both

polyaramids. This means that GVL and $[C_8Mim][Cl]$ work synergistically, with their mixture having a higher solubility than the pure components. The maxima occur at rather low IL molar fractions ($x_{IL} = 0.2$ for PMIA and $x_{IL} = 0.4$ for ODA/PPTA), which makes the OES solvent much cheaper than pure $[C_8Mim][Cl]$.

Figure 2: Solubility of PMIA (top) and ODA/PPTA (bottom) in selected OESs with varying solvent composition. A complete table with the solubility data can be found in the ESI (Table S1).

Replacing the IL $[C_8Mim][Cl]$ with $[P_{14666}][Cl]$ or $[C_4Mim][NTf_2]$ generally led to lower solubilities. OESs based on GVL and $[C_4Mim][NTf_2]$ were unable to dissolve any polyaramid, regardless of the IL molar ratio. No synergy was observed for this solvent

1 system. The reduced solubility compared to $[\text{C}_8\text{MIm}][\text{Cl}]$ can be caused by the reduction in
2 length of the alkyl chain on the cation from C_8 to C_4 . However, we would not expect the
3 solubility to drop this significantly. The more probable explanation is the fact that the NTf_2^-
4 anion has poor coordinating properties, and is thus unable to interrupt the intermolecular
5 hydrogen bonds. Interestingly, some $[\text{P}_{14666}][\text{Cl}]$ based OESs were actually capable of
6 dissolving polyaramids, achieving solubilities as high as 18.0 wt% and 3.8 wt% for PMIA and
7 ODA/PPTA, respectively. Synergy was again observed between GVL and the IL. Only this
8 time this synergy was more pronounced, as neither of the pure compounds are able to dissolve
9 polyaramids. Only when combined, these compounds can solubilize the polyaramids. The
10 different behavior of OES based on $[\text{P}_{14666}][\text{Cl}]$ and $[\text{C}_4\text{MIm}][\text{NTf}_2]$ gives an indication of the
11 role of GVL in the dissolution process. It appears that GVL enhances the solubility of an IL
12 by substituting for an inappropriate cation, but it cannot do the same by substituting for an
13 inappropriate anion. Therefore, whatever the role of the cation is in the dissolution
14 mechanism, it can be performed by GVL as well.

15 No synergy was observed when ACN or EtOH were used instead of GVL. Adding these co-
16 solvents to $[\text{C}_8\text{MIm}][\text{Cl}]$ decreased the solubility for both polyaramids. For ACN, this
17 decrease was less pronounced, and a high solubility could be maintained for PMIA up to an
18 IL molar ratio as low as $x_{\text{IL}} = 0.4$. In the presence of EtOH, on the other hand, the solubility
19 decreased more rapidly, with even small amounts added being enough to render ODA/PPTA
20 completely insoluble. This was expected as it is known that protic co-solvents can interfere
21 with the dissolution process of cellulose by shielding the IL anion from the polymer.¹⁹

1 *Table 1: Solubility of PMIA and ODA/PPTA in a range of OESs at 70 °C.*View Article Online
DOI: 10.1039/D0GC02324H

Solvent Composition		x_{IL}	Solubility (wt%)	
Ionic Liquid	Co-solvent		PMIA	ODA/PPTA
[C ₈ MIm][Cl]	GVL	0.1	18.0	2.0
		0.2	23.7	6.5
		0.4	23.1	7.4
		0.6	21.9	5.7
[C ₄ MIm][Cl]	GVL	0.1	17.4	0.0
		0.2	22.5	2.9
		0.4	21.9	5.2
		0.6	20.6	3.8
[C ₂ MIm][Cl]	GVL	0.1	16.0	0.0
		0.2	21.9	2.0
		0.4	21.3	3.8
		0.6	18.0	2.9
[C ₂ MIm][PO ₄ Et ₂]	GVL	0.1	13.8	2.0
		0.2	18.7	4.8
		0.4	20.6	7.4
		0.6	18.7	7.0
[P ₂₄₄₄][PO ₄ Et ₂]	GVL	0.1	14.5	2.9
		0.2	19.4	5.7
		0.4	22.5	9.1
		0.6	14.5	7.4
[P ₁₄₆₆₆][Cl]	GVL	0.1	15.3	2.0
		0.2	18.0	3.8
		0.4	13.8	2.9
		0.6	1.0	0.0
[P ₁₄₆₆₆][Cl]	ACN	0.1	3.8	0.0
		0.2	5.7	0.0
		0.4	0.0	0.0
		0.6	0.0	0.0
[C ₈ MIm][Cl]	ACN	0.1	10.7	0.0
		0.2	16.0	1.0
		0.4	19.4	2.9
		0.6	20.0	3.8

2

3

1 More solubility tests were performed to screen the solvating capacity of other ILs when mixed
2 with co-solvents (Table 1). Knowing that optimal solvent efficiency occurs at lower IL
3 concentrations, only OES with x_{IL} in the 0.1–0.6 range were considered. In addition to ILs,
4 the inorganic salts $CaCl_2$ and $LiCl$ were also tested, but they were not sufficiently soluble in
5 GVL. This demonstrates another benefit of using ILs as organic electrolytes, as they are more
6 readily soluble in a broad range of organic solvents compared to inorganic salts.

7 Again, none of the tested solvents were able to dissolve the *p*-aramid PPTA, but they did
8 display solubility for PMIA and ODA/PPTA with varying degrees of success. OESs made
9 with $[C_4Mim][Cl]$ and $[C_2Mim][Cl]$ had systematically lower solubilities for polyaramids
10 than OESs with $[C_8Mim][Cl]$, which is the same trend as established in our previous work.⁹
11 Nevertheless, they were still able to dissolve large amounts of PMIA. This means ILs with
12 shorter alkyl chains can also be employed instead of the more expensive $[C_8Mim][Cl]$,
13 without sacrificing much in terms of dissolution potential. This also confirms that the inability
14 of $[C_4Mim][NTf_2]$ to dissolve polyaramids is largely due to the poorly coordinating anion,
15 and not due to the reduction in alkyl chain length on the cation. The OESs containing
16 $[P_{2444}][PO_4Et_2]$ and $[C_2Mim][PO_4Et_2]$ also turned out to be excellent solvents. Just like Cl^- ,
17 the $PO_4Et_2^-$ anions are strongly coordinating and capable of forming hydrogen bonds with the
18 polymer. These OESs even outperformed $[C_8Mim][Cl]/GVL$ in the solubility of ODA/PPTA,
19 with $[P_{2444}][PO_4Et_2]/GVL$ at a molar ratio of $x_{IL} = 0.4$ reaching a solubility of 9.1 wt%.
20 Finally, the poor solubility of polyaramids in $[P_{14666}][Cl]/ACN$ demonstrates that there is little
21 to no synergy between the IL and ACN. It is evident that GVL has an essential role in the
22 solvation mechanism that cannot be taken over by ACN.

23

Polyaramid processing in OESs and solvent regeneration

View Article Online
DOI: 10.1039/D0GC02324H

The spinnability of the polyaramid solutions in OESs was evaluated using a small spinning setup, consisting of a syringe pump and a 3D-printed precipitation bath and winder. More details on this setup and the 3D-model can be found the ESI. The processing of PMIA in pure ILs through wet-spinning and electro-spinning has already been reported in the literature.^{45, 46} However, to the best of our knowledge, this is the first attempt at spinning polyaramid fibers from OESs. These spinnability tests were meant to serve as a ‘proof of principle’. Optimizing the spinning parameters and post-processing and in-depth characterization of the fibers are beyond the scope of this work.

PMIA fibers were spun using solutions with polymer concentrations of 10 wt%, 15 wt% and 20 wt%, while ODA/PPTA was spun at a concentration of 6 wt%. All IL/GVL combinations from Table 1 were tested, as long as they could dissolve polyaramids in the above mentioned concentrations. For PMIA, only OESs with a molar ratio of $x_{IL} = 0.1$ and 0.2 were used, as these usually had a high enough solubility, while keeping the amount of expensive IL used to a minimum. The polymer solutions were heated up to 90 °C, pushed into a water bath using a syringe pump and pulled from the water bath using a 3D-printed winder attached to a step motor (Fig. 3).

With the exception of solutions that used phosphonium-based ILs, all polyaramid solutions were readily spinnable. PMIA produced clear white fibers that were still rather fragile due to non-optimized spinning parameters. Although all the imidazolium-based OESs were suitable for PMIA processing, OESs of [C₄MIm][Cl] and [C₂MIm][Cl] are by far the cheapest options and have no major disadvantages over the other solvent systems. ODA/PPTA made light yellow fibers that were much stronger than the PMIA fibers. Due to the lower solubility of ODA/PPTA, only [C₈MIm][Cl]/GVL and [C₂MIm][PO₄Et₂]/GVL were found to be adequate for spinning. It was not possible to produce fibers using OESs of [P₂₄₄₄][PO₄Et₂] and

[P₁₄₆₆₆][Cl]. Phosphonium-based ILs generally have a reduced miscibility with water, which led to a slow and messy precipitation of the polyaramid. The fibers would still be partially dissolved as the polymer solution came out the syringe, making it too weak to pull through the water bath and onto the winder.

Figure 3: Spinning process for PMIA from [C₈MIm][Cl]/GVL. a) polymer solution in the syringe pump. b) polymer solution precipitates upon contact with water. c) polymer fiber being formed by drawing it from the syringe needle. d) fiber being pulled through and out of the water bath. e) polymer collected on a winder connected to a step motor. f) Resulting fiber after washing and drying.

To test the recyclability of the solvent system, a recycling experiment was performed in which [C₈MIm][Cl]/GVL was recovered from the water bath after spinning. GVL has a boiling point of 212 °C at atmospheric pressure and does not form an azeotrope with water.⁴⁷ Hypothetically, it should be possible to selectively distil off the water from the OES at the right experimental conditions. However, ILs are known to increase the boiling point of water,

acting as entrainers when applied in extractive distillation.⁴⁸ This can raise the boiling point of water to be closer to that of GVL. For the sake of simplicity, it was opted to recycle GVL and [C₈MIm][Cl] separately in a two-step process. In a first step, water and GVL were removed simultaneously on a rotary evaporator at 60 °C, with the pressure stepwise lowered to 65 mbar. The final traces of water and GVL were evaporated from the IL on a vacuum line at 0.6 mbar with a temperature of 90 °C. The IL was recovered with a yield of 86%. Losses could be due to spillage when transferring the mixture from the spinning setup, and to some IL still impregnated in the polyaramid fiber. This latter issue can be mitigated by more thorough washing. Finally, with the IL removed, water could simply be distilled off, leaving pure GVL with a yield of 73%. Losses could be due to the same reasons as mentioned above, as well as extra losses by incomplete removal from the IL. Regardless, both components of the OES could be recovered with acceptable yields and, after properly drying, could be re-used to make a new OES that showed no decline in solubility.

Kamlet-Taft parameters of OESs and influence of solvent composition

The intermolecular forces between the polymer and the solvent molecules play a crucial role in the determination of the solubility of polyaramids. The potential strength of these forces can be estimated by determining the Kamlet-Taft solvatochromic parameters. The Kamlet-Taft parameters have been determined for all the OESs used in the initial solubility tests and are displayed in Fig. 4.

Figure 4: Kamlet-Taft parameters of several OESs as a function of the IL molar fraction: β (top), α (centre) and π^* (bottom). The dyes used for the determination of these parameters were Reichardt's, *N,N*-diethyl-4-nitroanilin and, 4-nitroaniline. A complete table with all the Kamlet-Taft data can be found in the ESI (Table S2).

The β parameter (Fig. 4 top) is a measure for the hydrogen-bond basicity of a solvent. In pure ILs, the hydrogen-bond basicity is largely provided by the anions. When comparing the three pure ILs $[C_8MIm][Cl]$, $[P_{14666}][Cl]$ and $[C_4MIm][NTf_2]$ we see some stark differences in their

1 β parameter. The NTf_2^- anion is quite bulky and its negative charge is highly delocalized, hence it is a rather poorly coordinating anion with a low β parameter. The Cl^- anion on the
2 other hand is small and has a high charge density, making it strongly coordinating. This
3 results in a high β parameter for the chloride-containing ILs. We do however observe a higher
4 hydrogen basicity for $[\text{P}_{14666}][\text{Cl}]$ than for $[\text{C}_8\text{MIm}][\text{Cl}]$, indicating that the β parameter is not
5 solely determined by the anion of the IL.
6

7 The pure organic solvents GVL and ACN have low β parameters, and thus have little
8 hydrogen-bond accepting capacity. However, adding even small amounts of the chloride-
9 containing ILs instantly increases their β parameters to values comparable to that of the pure
10 ILs. This demonstrates that the main source of hydrogen bonding in these OESs comes from
11 the IL anions and why only small amounts of IL are needed to achieve high solubilities. The β
12 parameter of EtOH is quite high compared to those of GVL and ACN. However, β only
13 gradually increases when $[\text{C}_8\text{MIm}][\text{Cl}]$ is added, and is generally lower than for the other two
14 co-solvents.

15 The reason for this lower hydrogen-bond basicity observed in EtOH can be found by looking
16 at the α parameter (Fig. 4 centre), or the hydrogen-bond acidity. EtOH has a very high
17 hydrogen-bond acidity due to its hydroxyl functional group. This hydroxyl functional group
18 will form strong hydrogen bonds with the anions of the IL, effectively shielding them from
19 interactions with other solutes such as the solvatochromic dyes used in these measurements.
20 GVL and ACN have low α parameters, and thus leave the anion 'free' to interact with other
21 solutes.

22 The trends in α can similarly explain why $[\text{P}_{14666}][\text{Cl}]$ has a higher hydrogen-bond basicity
23 than $[\text{C}_8\text{MIm}][\text{Cl}]$. The hydrogen-bond acidity in an IL is generally provided by the cation.
24 Both ILs with imidazolium cations have very similar values for α , which are higher than for

the phosphonium IL. This hydrogen-bond acidity mainly originates in the quite acidic C₂-hydrogen between the nitrogen atoms of the imidazolium cation. This allows the imidazolium cation to form hydrogen bonds with the anion, although to a much lesser extent than EtOH. The final Kamlet Taft parameter is π^* (Fig. 4 bottom), which gives an estimate of the polarizability of the solvent. The polarizability of a solvent determines its potential to interact with the aromatic parts of the polymer through dispersion forces. Imidazolium-based ILs have a higher polarizability than phosphonium-based ILs, although [P₁₄₆₆₆][Cl] still has a quite high π^* parameter due to its long alkyl chains. ACN and EtOH have relatively low π^* values, which rapidly increase when [C₈MIm][Cl] is added. GVL has a higher polarizability than the two other co-solvents, and the effect of adding an IL is less pronounced. This demonstrates a difference between, on one hand OESs of EtOH and ACN, in which the polarizability mainly comes from the IL, while in the OESs of GVL both components contribute to the polarizability.

Discussion

The Kamlet-Taft parameters for the OESs can be cross-examined with their respective solubilities to yield information about the dissolution mechanism of polyaramids in OESs. The influence of β on the solubility is straightforward. A high hydrogen-bond basicity is required to break up the intermolecular hydrogen bonds in the polyaramid. None of the organic co-solvents or the IL [C₄MIm][NTf₂] have a high β parameter, making them unsuitable to dissolve polyaramids. This also explains the lack of synergy between [C₄MIm][NTf₂] and GVL, as this mixing does nothing to increase the β parameter. The OESs that can dissolve polyaramids all have a high hydrogen-bond basicity, with a β parameter higher than 0.85–0.90 (Fig. 5). The hydrogen-bond basicity in these OESs can almost entirely

be attributed to the chloride ions of the ILs. It appears that the role of the IL in the dissolution mechanism is to provide an anion that can interrupt the hydrogen bonds in the polymer. It is thus important that, when designing an OES for the dissolution of polyaramids, the IL has a sufficiently high β parameter. However, this does not explain why $[P_{14666}][Cl]$, which has a higher β than $[C_8MIm][Cl]$, is able to dissolve polyaramids only when mixed with GVL. As mentioned earlier, it seems that GVL can take over the role of the cation in the dissolution process. Therefore, to explain the difference between $[P_{14666}][Cl]$ and $[C_8MIm][Cl]$, the exact role of the co-solvent in the dissolution mechanism of polyaramids has to be determined.

Figure 5: Solubility data from figure Fig. 2 cross-examined with the β parameters for the respective OESs.

By calculating the number of repeating units dissolved per ionic liquid molecule (RU/IL), it is possible to get a better view of the dissolution mechanism at a molecular level. Fig. 6

1 highlights the differences in behavior between OESs from GVL, ACN and EtOH. Adding
 2 GVL to $[\text{C}_8\text{MIm}][\text{Cl}]$ increases the RU/IL until optimum maximum is reached. This indicates
 3 that GVL plays an active role in the dissolution process and is thus acting as a true co-solvent.
 4 On the other hand, the RU/IL stays remarkably stable if ACN is added instead. For PMIA this
 5 ratio remains constant up to a very low x_{IL} , while for ODA/PPTA it declines, but more
 6 gradually. It appears that ACN is acting more as an ‘innocent bystander’ rather than actively
 7 participating in the dissolution mechanism. Especially for PMIA, it displays the behavior of a
 8 non-solvent. Finally, EtOH reduces the RU/IL of $[\text{C}_8\text{MIm}][\text{Cl}]$, at first gradually for PMIA,
 9 but very rapidly for ODA/PPTA. It is not acting as an ‘innocent bystander’ like ACN, but
 10 rather actively reduces the solvating capability of the IL. EtOH can thus be considered to be
 11 an anti-solvent.

12

13 *Figure 6: Number of repeating units dissolved per ionic liquid molecule at saturation in the solvent.*

The anti-solvent effect of protic solvents is well known in the field of cellulose dissolution, and it can be explained by looking at the α parameter. EtOH, like most protic solvents, has a high α value and thus a high hydrogen-bond acidity. This allows EtOH to coordinate to the anion, effectively shielding it from interactions with the polymer. This is demonstrated by the reduced hydrogen-bond basicity for OESs containing EtOH, compared to GVL or ACN.

The exact role of aprotic co-solvents in the dissolution mechanism of cellulose is still the subject of debate. Some authors claim that the co-solvent preferentially solvates the cation, freeing up the anion to interact with the polymer more effectively.^{17, 19, 22, 49} Others, however, have disputed this hypothesis, claiming that aprotic solvents do not significantly perturb the pre-existing hydrogen-bond networks in ILs.^{18, 50, 51} There is a slight increase of β in the [C₈MIm][Cl]/GVL OES compared to pure [C₈MIm][Cl]. However, there is no similar increase for [P₁₄₆₆₆][Cl]/GVL, so this does not explain the synergistic mechanism in this OES. Furthermore, the β parameters of [C₈MIm][Cl]/GVL are virtually identical to those of [C₈MIm][Cl]/ACN across the whole x_{IL} range. The model of cation solvation does not explain why GVL displays synergy and ACN does not. Some authors have emphasized that dispersion interactions, although much weaker compared to hydrogen-bond interactions, do play a critical role in cellulose dissolution.⁵² Polyaramids have an extended π -electron network, probably making dispersion interactions even more important.

The π^* parameter of GVL is higher than that of ACN, which persists in their OESs at low x_{IL} . This means that GVL is a more polarizable molecule than ACN, making it more suitable to interact with the aromatic parts of the polyaramid through dispersion interactions. This can explain the passive non-solvent behavior of ACN. For PMIA, the RU/IL ratio in [C₈MIm][Cl]/ACN remains more or less constant up until very low x_{IL} . This means that the

1 polymer is surrounded by the same number of [C₈MIm][Cl] molecules in the OES as in the
2 pure IL. ACN is not a part of the first solvation shell, as it is not interacting with the polymer.
3 GVL, on the other hand, can interact with the polymer, relieving the imidazolium cations
4 from that role. In doing so, it frees up more IL molecules that can then interact with the
5 polymer through hydrogen bonding.

6 The importance of dispersion interactions can also explain why pure phosphonium ILs cannot
7 dissolve polyaramids like imidazolium ILs can. Although [P₁₄₆₆₆][Cl] has a quite high value
8 for π^* , it has a very bulky cation. One of the shortcomings of the Kamlet-Taft parameters is
9 that it does not measure a bulk solvent property, but rather the interaction between a solvent
10 and a certain solute. Therefore, Kamlet-Taft parameters tend to vary depending on the dye
11 that was used. They do not accurately simulate interactions with sterically hindered solute
12 such as a polymer within a solvation shell.^{33, 53} ILs such as [P₁₄₆₆₆][Cl], or substituted
13 imidazoliums⁹, are too bulky to fit well within a solvation shell and so are unable to
14 effectively interact with the aromatic parts of the polymer. GVL can take up this role and thus
15 work synergistically with [P₁₄₆₆₆][Cl], whereas ACN is less suitable for this task and only
16 marginally increases the solubility.

17 Fig. 7 summarizes a proposed dissolution mechanism of polyaramids in GVL-based OESs, in
18 which the IL provides an anion that can interrupt the intermolecular hydrogen bonds of the
19 polyaramid, while GVL interacts with the polymer through dispersion forces. Some limiting
20 values for the Kamlet-Taft parameters are proposed, which serve as a guide in the design of
21 new potential solvent systems. However, these values are based on a rather small data set and
22 should not be considered as absolute.

23

Figure 7: Proposed solvation mechanism of polyaramids in GVL-based OES.

Conclusion

OESs made by mixing GVL with ILs containing strongly coordinating anions were found to be excellent solvents for the polyaramids PMIA and ODA/PPTA, while PPTA remained insoluble. Maximum solubilities were achieved at rather low IL molar fractions, ranging from $x_{IL} = 0.2$ to 0.4 . These solvent systems have reduced viscosities and show a faster dissolution rate compared to the corresponding pure ILs. Moreover, the reduced IL content also lowers the cost of the solvent. The spinnability of the polyaramid solutions was tested using a 3D-printed experimental spinning setup. OESs from GVL and imidazolium-containing ILs were found to be suitable for spinning PMIA and ODA/PPTA fibers as long as they displayed high enough solubilities. Besides GVL, also ACN and EtOH were tested as co-solvents. It was found that GVL actively participated in the dissolution process, acting as a true co-solvent. ACN did not participate in the dissolution process, but did not harm the solvating potential of the ILs either, and thus displayed non-solvent behavior. The presence of EtOH, on the other hand, did harm the dissolution process by forming hydrogen bonds with the anions, shielding

1 them from interactions with the polymer. The Kamlet-Taft parameters of the OESs were
2 determined, which helped explain the behavior of different co-solvents and ILs. A dissolution
3 mechanism is proposed, along with some loosely defined boundary conditions for the Kamlet-
4 Taft parameters of OESs suitable for polyaramid dissolution. The IL must provide an anion
5 that can interrupt the intermolecular hydrogen-bond network of the polyaramid. The anion
6 must display strong hydrogen-bond basicity, with $\beta > 0.85$. The co-solvent interacts with the
7 aromatic parts of the polymer through dispersion forces. The co-solvent must thus have a high
8 enough polarizability to undergo these types of interactions, with $\pi^* > 0.85$. Finally, the
9 solvent needs a medium to low hydrogen-bond acidity, as a high hydrogen-bond acidity will
10 result in destructive competition with the polymer for interactions with the anion. Therefore,
11 the hydrogen-bond acidity must not exceed an upper value of $\alpha < 0.60$.

13 **Conflict of interest**

14 There are no conflicts to declare.

15 **Acknowledgements**

16 This research was funded by a doctoral (PhD) strategic basic research grant of the Research
17 Foundation Flanders (FWO) to Jonas Winters (1S12717N). The help of Jakob Bussé in the
18 design and building of the 3D-printed spinning setup is greatly acknowledged.

References

View Article Online
DOI: 10.1039/D0GC02324H

1. Rao, Y.; Waddon, A. J.; Farris, R. J. *Polymer* **2001**, *42* (13), 5937-5946.
2. Kwolek, L. S.; Winthrop, M. P.; Richard, S. W. Process of making wholly aromatic polyamides; US Patent 3,063,966 1962.
3. Hearle, J W S. In *High-Performance Fibres*; Woodhead Publishing: Manchester, England, 2001.
4. Ozawa, S. *Polym. J.* **1987**, *19* (1), 119-125.
5. Vollbracht, L.; Veerman, T. J. Process for the preparation of poly-p-phenyleneterephthalamide; US Patent 4,308,374 1981.
6. García, J. M.; García, F. C.; Serna, F.; de la Peña, J. L. *Prog. Polym. Sci.* **2010**, *35* (5), 623-686.
7. Scientific Committee on Consumer Safety (SCCS), "Opinion on N-Methyl-2-pyrrolidone (NMP)", European Union, 2011,
https://ec.europa.eu/health/sites/health/files/scientific_committees/consumer_safety/docs/sccs_o_050.pdf.
8. Morgan, P. W. *Condensation polymers: by interfacial and solution methods*; Interscience Publishers: New York, 1965.
9. Winters, J.; Dehaen, W.; Binnemans, K. *Phys. Chem. Chem. Phys.* **2019**, *21* (7), 4053-4062.
10. Dewilde, S.; Dehaen, W.; Binnemans, K. *Green Chem.* **2016**, *18* (6), 1639-1652.
11. Dewilde, S.; Winters, J.; Dehaen, W.; Binnemans, K. *Macromolecules* **2017**, *50* (8), 3089-3100.
12. Dewilde, S.; Vander Hoogerstraete, T.; Dehaen, W.; Binnemans, K. *ACS Sustain. Chem. Eng.* **2018**, *6* (1), 1362-1369.
13. Seddon, K. R. Ionic Liquids: "Designer" Solvents for Green Chemistry. In *Methods and Reagents for Green Chemistry*; Wiley: Hoboken, NJ, 2007; pp 103-130.
14. Kar, M.; Plechkova, N. V.; Seddon, K. R.; Pringle, J. M.; MacFarlane, D. R. *Aust. J. Chem.* **2019**, *72* (2), 3-10.
15. Seddon, R. K.; Stark, A.; Torres, M.-J. *Pure Appl. Chem.* **2000**, *72* (12), 2275-2287.
16. Rinaldi, R. *Chem. Commun.* **2011**, *47* (1), 511-513.
17. Zhao, Y.; Liu, X.; Wang, J.; Zhang, S. *J. Phys. Chem. B* **2013**, *117* (30), 9042-9049.
18. Andanson, J.-M.; Bordes, E.; Devémy, J.; Leroux, F.; Pádua, A. A. H.; Gomes, M. F. C. *Green Chem.* **2014**, *16* (5), 2528-2538.
19. Minnick, D. L.; Flores, R. A.; DeStefano, M. R.; Scurto, A. M. *J. Phys. Chem. B* **2016**, *120* (32), 7906-7919.
20. Gale, E.; Wirawan, R. H.; Silveira, R. L.; Pereira, C. S.; Johns, M. A.; Skaf, M. S.; Scott, J. L. *ACS Sustain. Chem. Eng.* **2016**, *4* (11), 6200-6207.
21. Clough, M. T. *Green Chem.* **2017**, *19* (20), 4754-4768.
22. Holding, A. J.; Heikkilä, M.; Kilpeläinen, I.; King, A. W. T. *ChemSusChem* **2014**, *7* (5), 1422-1434.
23. Pascual, B. S.; Trigo-López, M.; Reglero Ruiz, J. A.; Pablos, J. L.; Bertolín, J. C.; Represa, C.; Cuevas, J. V.; García, F. C.; García, J. M. *Eur. Polym. J.* **2019**, *116*, 91-98.
24. Wright, W. R. H.; Palkovits, R. *ChemSusChem* **2012**, *5* (9), 1657-1667.
25. Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. *Green Chem.* **2013**, *15* (3), 584-595.
26. Yan, K.; Yang, Y.; Chai, J.; Lu, Y. *Appl. Catal., B* **2015**, *179*, 292-304.
27. Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12* (9), 1493-1513.
28. Velisoju, V. K.; Jampaiah, D.; Gutta, N.; Bentrup, U.; Brückner, A.; Bhargava, S. K.; Akula, V. *ChemCatChem* **2020**, *12* (5), 1341-1349.

29. Fegyverneki, D.; Orha, L.; Láng, G.; Horváth, I. T. *Tetrahedron* **2010**, *66* (5), 1078-1081.
30. XianRong, S.; DengZhou, X.; YiXin, X.; JianGang, G. *e-Polymers* **2019**, *19* (1), 323-329.
31. Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98* (2), 377-383.
32. Reichardt, C. *Chem. Rev.* **1994**, *94* (8), 2319-2358.
33. Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2003**, *5* (13), 2790-2794.
34. Jessop, P. G.; Jessop, D. A.; Fu, D.; Phan, L. *Green Chem.* **2012**, *14* (5), 1245-1259.
35. Eyckens, D. J.; Demir, B.; Walsh, T. R.; Welton, T.; Henderson, L. C. *Phys. Chem. Chem. Phys.* **2016**, *18* (19), 13153-13157.
36. Kurnia, K. A.; Lima, F.; Claudio, A. F. M.; Coutinho, J. A. P.; Freire, M. G. *Phys. Chem. Chem. Phys.* **2015**, *17* (29), 18980-18990.
37. Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48* (17), 2877-2887.
38. Duereh, A.; Sato, Y.; Smith, R. L.; Inomata, H. *Org. Process Res. Dev.* **2017**, *21* (1), 114-124.
39. Grujicic, M.; Bell, W. C.; Glomski, P. S.; Pandurangan, B.; Yen, C. F.; Cheeseman, B. A. *J. Mater. Eng. Perform.* **2011**, *20* (8), 1401-1413.
40. Ogata, N.; Sanui, K.; Kitayama, S. *J. Polym. Sci., Part A: Polym. Chem.* **1984**, *22* (3), 865-867.
41. Burch, R. R.; Sweeny, W.; Schmidt, H. W.; Kim, Y. H. *Macromolecules* **1990**, *23* (4), 1065-1072.
42. Picken, S. J.; van der Zwaag, S.; Northolt, M. G. *Polymer* **1992**, *33* (14), 2998-3006.
43. Morgan, H. S. Process for spinning wholly aromatic polyamide fibers; US Patent 3,414,645 1968.
44. Trigo-López, M.; García, J. M.; Ruiz, J. A. R.; García, F. C.; Ferrer, R. *Encyclopedia of Polymer Science and Technology* **2018**, 1-51.
45. Zhao, T.; Wang, H.; Zhang, Y.; Wang, B.; Jiang, J. *Int. J. Mol. Sci.* **2007**, *8* (7), 680-685.
46. Yang, W.; Yu, H.; Zhu, M.; Bai, H.; Chen, Y. *J. Macromol. Sci., Part B: Phys.* **2006**, *45* (4), 573-579.
47. Havasi, D.; Mizsey, P.; Mika, L. T. *J. Chem. Eng. Data* **2016**, *61* (4), 1502-1508.
48. Lei, Z.; Dai, C.; Zhu, J.; Chen, B. *AIChE J.* **2014**, *60* (9), 3312-3329.
49. Xu, A.; Zhang, Y.; Zhao, Y.; Wang, J. *Carbohydr. Polym.* **2013**, *92* (1), 540-544.
50. Velioglu, S.; Yao, X.; Devémy, J.; Ahunbay, M. G.; Tantekin-Ersolmaz, S. B.; Dequidt, A.; Costa Gomes, M. F.; Pádua, A. A. H. *J. Phys. Chem. B* **2014**, *118* (51), 14860-14869.
51. Yang, M.; Zhao, W.; Wang, S.; Yu, C.; Singh, S.; Simmons, B. A.; Cheng, G. *Cellulose* **2019**, *26*, 2243-2253.
52. Alves, L.; Medronho, B. F.; Antunes, F. E.; Romano, A.; Miguel, M. G.; Lindman, B. *Colloids Surf., A* **2015**, *483*, 257-263.
53. Duereh, A.; Sato, Y.; Smith, R. L.; Inomata, H. *J. Phys. Chem. B* **2015**, *119* (46), 14738-14749.