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A metrics-based approach to preparing sustainable membranes: application to ultrafiltration

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The purpose of the research is to make a first step towards rationalizing green polymeric membrane preparation. A holistic methodological approach based on metrics that consider technical, environmental, health and safety issues have been suggested to assess sustainability of membrane preparation. Metrics have been applied to solvent substitution in a non-solvent induced phase separation process. The flammability hazard of three shortlisted alternative solvents has substituted the reprotoxicity hazard of common solvents. The ultrafiltration cellulose diacetate membranes prepared with methyl lactate as solvent have a greater renewable intensity and require a lower number of solvents for their preparation. Trade-offs between use of resources (polymer, solvent, energy…) and membrane properties are inevitable. Further socio-economic, risk and life cycle analysis are crucial to fully integrate ecodesign in membrane preparation.

1. Introduction

Membrane technology is well-established in industrial processes as it offers both technical and sustainable performances: high selectivity of specific compounds, excellent waste and energy efficiency, ease of operation and maintenance, simple scale-up and control and good stability.[1,2] One membrane technique is ultrafiltration used, for instance, to separate particulates and pathogens from raw water for drinking water applications or to process proteins in the dairy industry. Mild thermal and chemical operating conditions in water treatment favour polymeric membranes over more expensive ceramic ones.

Most commercialized polymeric membranes are prepared *via* non-solvent induced phase separation (NIPS).[3] A polymer is first dissolved in a solvent usually with an additive. Adding inorganic salts such as lithium chloride (LiCl) or polymers (PEG, PVP) have shown to improve membrane permeability and retention.[4,5] The polymer solution is then cast on a planar support or extruded as a hollow fibre and then immersed in a non-solvent in which it separates into two phases: a polymer rich phase that solidifies into the membrane structure and a polymer lean phase that is washed away and gives the pores.[6–9] The non-solvent is often water as it does not solubilize common used polymers, is inexpensive and easy to handle on an industrial scale. Further steps are membrane rinsing and module preparation. During coagulation and rinsing the polymer lean phase (mainly solvent and additive) is mixed with water and is either recycled or discharged in the sewage network.

Research in membrane preparation has integrated sustainability concerns in response to global concern about preserving finite resources for future generations.[10] Focus in the literature is mainly on the solvents' toxicity. Three of the most common solvents used in membrane preparation (*N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF)) are indeed identified by the European REACH Regulation as substances of very high concern for their potential reproductive toxicity.[11] Furthermore, the initial amount of solvent is entirely found in wastewater after coagulation and rinsing. Razali *et al.* estimate that this wastewater represents more than 95% of the total waste produced during membrane preparation.[12] Figoli *et al.*[13] report on the beginning stages of solvent substitution in membrane preparation with examples of less or non-toxic solvents. Another approach that is also at an early stage of research is to eliminate solvent toxicity by using an aqueous polymer solution and subjecting it to a temperature induced phase separation (TIPS).[14]

Searching for and selecting green solvents is a global issue.[15,16] CHEM21 developed a methodology to rank solvents according to environmental, health and safety criteria aligned with the United Nation's Global Harmonized System (GHS) and European regulations.[17] The resulting solvent selection guide is based on guides previously published by pharmaceutical companies[18–23] and includes newer solvents such as bioderived solvents.[24] Tobiszewski *et al.*[25] rank solvents within clusters according to toxicology and hazard parameters.

Besides the solvent issue, reducing the use of petroleum-based chemicals is another aspect of sustainability. Growing

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attention is for example given to biosourced polymers since carbon composing these polymers originates from atmospheric carbon dioxide and is released back into the atmosphere whenever the polymers are incinerated: no additional carbon dioxide is emitted in this case.[26] Since Dobry's treatment of cellulose esters[27] and Loeb and Sourirajan's preparation of asymetric membranes,[28] membranes prepared with cellulose acetate (CA) offer a bio-sourced alternative to other conventional membranes prepared with petrochemical polyether sulfone (PES), polysulfone or polyvinylidene difluoride.[29] CA membranes were first developed for desalination of water by reverse osmosis[28,30] and are now found in other applications such as hemodialysis or drinking water treament.[31,32] As regards water treatment applications, CA membranes are cheap, easily available and highly resistant to fouling.[33] Cellulose triacetate and diacetate (CTA and CDA respectively) are synthesized from cellulose, the most abundant organic polymer on Earth and industrially extracted from wood pulp or cotton.[34] Krishna Manda *et al.*[35] calculated that CA has a slightly better environmental profile than PES for most impact categories (climate change, human toxicity, marine and freshwater ecotoxicity…). Only the production and disposal of both polymers have been considered; the production and operation of the two associated membranes have been simplistically taken as equal to one another.

Substituting toxic solvents and using renewable feedstocks are only two sustainability improvements and therefore do not fully address the twelve principles of green chemistry as listed by Anastas and Warner.[36] Their framework sets out a broad view on the design and development of greener chemicals, materials and processes. Green metrics have been later developed to quantitatively evaluate sustainability.[37–39] Interestingly, McElroy *et al.*[40] suggest a holistic approach to metrics. The sustainability of chemical reactions are evaluated with a unified metrics toolkit. The aim of such an approach is to study the overall environmental footprint of a given system, thereby taking into account burdens that shift from one subsystem to another or from one impact category to another.

To the best of our knowledge, no holistic approach to assessing sustainability in membrane preparation has been taken in the literature. In our study, metrics that consider technical, environmental, health and safety (EHS) issues are first presented and then applied to solvent substitution in the preparation of ultrafiltration membranes. Both CTA and CDA are tested as polymers. More specifically, Hansen solubility parameters (HSPs) and solubility trials are used for solvent screening. Flat sheet membranes are prepared with the selected solvents and their permeability and retention performances are assessed experimentally.

2. Metrics for membrane preparation

Membrane preparation is considered in 3 stages (see Table 1), each having specific metrics that allow to compare alternative solvents and their associated membranes. Hotspots such as flammability or energy-intensive fabrication processes are highlighted to either eliminate a solvent from the screening process or take precautionary measures during scale-up. These metrics are relative and can be adapted to the intended application such as ultrafiltration in drinking water treatment, as opposed to absolute metrics solely based on threshold values. For example, there is no threshold value for energy use but rather a comparison to be made with other solvents' fabrication processes.

Table 1 Metrics tables relative to solvent substitution for membrane preparation

Stage	Stage name	Concerned process or chemical composition	Metrics table
I	Alternative solvent shortlisting	Solvent Solvent fabrication	Table 2 Table 3
ii	Solubility trials	Polymer solution	Table 4
iii	Membrane preparation	Membrane Membrane fabrication	Table 5 Table 3

It is interesting to note that McElroy *et al.*[40] adopt a three-coloured flag system applied to their metrics as an attempt to alert on specific issues. Quantified ranges for each colour (green, amber and red) are however defined for only 3 metrics and the lack of justification suggests that these ranges result from an arbitrary choice. These omissions most certainly stem from the difficulty to apply the three-coloured flag system in a thorough and consistent manner. It is indeed very challenging to define meaningful threshold values for each colour, especially considering that thresholds may depend on the intended application or operational conditions. Such a visual aid also aims at putting emphasis on certain metrics rather than on others, which is inconsistent with our holistic approach according to which metrics are to be considered altogether. No visual aid has thus been integrated in our work.

During alternative solvent shortlisting (stage i in Table 1), the technical and EHS compatibility of the shortlisted solvents (Table 2) and their fabrication process (Table 3) are assessed. During solubility trials of stage ii, polymer solution parameters give information on the technical feasibility of membrane preparation with the associated alternative solvent (Table 4). If feasible, membranes are fabricated during stage iii. Either flat sheet membranes or hollow fibres can be prepared. Flat sheet membrane preparation can also be conducted as a feasibility study for hollow fibre preparation.

Technical membrane performances (Table 5) and eco-compatibility of the fabrication process (Table 3) are then studied.

The metrics can be transposed to polymer or additive substitution as well as to other membrane preparation processes (*e.g.* TIPS) provided several adjustements be made. For polymer substitution, water insolubility and solvent solubility are sought, whereas polymer volatility is irrelevant. The fabrication process of the polymer, instead that of the solvent, should be investigated. For a TIPS process, the polymer must be soluble in the solvent at high temperatures (generally 100–200 °C (ref. 41)) and insoluble at ambient temperature.

Table 2 Metrics for the solvent

Criterion	Parameter	Metric
Technical	Solvency	Relative energy difference (solvent and polymer Hansen solubility parameters) Solubility in water
	Stability	Thermal decomposition Chemical degradation
	Volatility	Vapour pressure Boiling point
Safety	Inflammability	Flash point
	Other physical hazard	Explosiveness Self-reactivity Pyrophoricity Oxidizing Corrosivity
Health	Acute toxicity	Acute toxicity estimate values
	Specific target organ toxicity	Single and repeated exposure tests
	Aspiration hazard or irritation	Aspiration hazard Skin corrosion or irritation Serious eye damage or eye irritation Respiratory or skin sensitization
	Carcinogenic, mutagenic, reprotoxic	Germ cell mutagenicity tests Carcinogenicity tests Reprotoxicity tests
Environmental	Biodegradability	Ready biodegradability
	Bioaccumulation	Bioconcentration factor Octanol–water partition coefficient
	Ecotoxicity	Acute aquatic toxicity Chronic aquatic toxicity

For the NIPS process considered in this work, solvent miscibility in water must be sufficient to allow polymer coagulation upon contact of the polymer solution with the non-solvent (see Table 2). The solvent must also dissolve the polymer. Given the large number of existing solvents, screening methods based on the potential solvent solvency of the polymer are necessary to reduce the number of solubility trials to carry out. The relative energy difference (RED), calculated from HSPs, allows to select an appropriate solvent for a polymer[42] (see section 3) and is often used in formulation for its simplicity of use and predictive quality.[43] Solvent stability is a technical prerequisite for the solvent use: no thermal or chemical degradation (hydrolysis, oxidation, autoxidation) that could hamper coagulation should occur under the operational conditions of membrane preparation. Another solvent property considered is volatility. High vapour pressure under operational conditions compels to take precautionary measures to reduce solvent exposure and protect workers' health and safety. EHS criteria in Table 2 are based on the hazards defined and classified by the GHS.[44] Regional or national implementations of the GHS can also be used as reference (*e.g.* the European CLP Regulation). An ideal solvent does not present any hazard and thus does not have any associated H-statement. Should this not be the case, hazard categories reflect the hazard severity. A category 1 solvent has extremely flammable liquid and vapour, whereas a category 4 solvent is a combustible liquid. Being readily biodegradable and not bioaccumulating are two properties reducing the solvent's end-of-life environmental impact, in particular in aquatic environments.

Table 4 Metrics for the polymer solution

Criterion	Parameter	Metric
Technical	Solvency	Polymer and additive dissolution
	Casting capacity	Viscosity
	Stability	Turbidity Gel formation and crystallization

Table 5 Metrics for the membrane

Criterion	Parameter	Metric
Technical	Productivity	Permeability
	Selectivity	Molecular weight cut-off Log removal values Integrity tests
	Mechanical resistance	Tensile stress Compaction pressure
	Chemical resistance	Ageing trials

A solvent's overall environmental footprint does not only rely on its intrinsic properties but also on the processes in which it is involved. Life Cycle Analysis (LCA) studies assess environmental impacts of all stages of a product's life from raw material extraction through manufacture, transportation, use and disposal or recycling. Such a comprehensive approach demands expertise, time, a lot of data and is more appropriate for a final assessment of the selected solvent. A more straightforward assessment can be made as a first approach with metrics suggested in Table 3. Intensity-based metrics evaluate the total input (*e.g.* renewably derivable input materials, reagents, solvents, catalysts, energy *etc.*) needed to prepare one

Table 3 Metrics for both solvent and membrane fabrication processes

Criterion	Metric	Simplified metric
Environmental	Renewable intensity = mass renewable derivable material/product mass (kg kg^{-1})	Number of renewably derivable feedstocks
	Process mass intensity = total process mass/product mass (kg kg^{-1})	Number of reactions and separation steps Number of solvents (for membrane fabrication only)
	Energy intensity = process energy/product mass (MJ kg^{-1})	Operational conditions (temperature, pressure) Number of liquid streams to treat Number of solvents per liquid stream
	Use of critical elements	—

unit mass of product.[45,46] Alternatively, counting the number of reactions or noting the operational conditions (temperature, pressure) gives a first indication on the use of resources; numerous reactions under high temperatures and pressures to produce the solvent is likely to be more mass- and energy-intensive than a single-reaction process under ambient conditions. Furthermore, critical elements (rare earth metals, phosphate rock, cobalt…) used in the preparation process need to be indicated. According to the European Union, an element is critical when it is of high economic importance and if there are high supply risks, either due to limited abundance or geo-political issues.[47] Table 3 should also be applied to the membrane fabrication process during stage iii.

In Tables 4 and 5, technical criteria classically encountered in membrane science are listed for polymer solutions and membranes. Effective dissolution of the polymer and additive by the solvent is observed during solubility trials. To cast or spin membranes, the polymer solution must have a viscosity adapted for both appropriate mechanical strength and low-energy pumping. On an industrial scale, temporary shutdowns may require the polymer solution to be stored. The absence of coagulation, gel formation or crystallization can be monitored by turbidity measurements or dynamic light scattering techniques. Once membranes are prepared, their technical performances are to be assessed (Table 5) and compared to the technical specifications of ultrafiltration and its process. For example, ageing trials based on accelerated ageing with the concentration per time of contact parameter ($c \times t$ parameter) indicate to what extent chemicals used during cleaning sequences are compatible with the membrane material.[48] The integrity of membranes can be checked with pressure hold tests or bubble tests.[49]

In what follows, the 3-stage membrane preparation methodology in Table 1 is followed and metrics in Tables 2–5 are applied. HSPs used for solvent shortlisting first need to be explained as well as the experimental setups of membrane preparation and characterization.

3. Hansen solubility parameters (HSPs)

Hansen considers three types of intermolecular interactions for the total cohesion energy (E) of regular solutions:[42]

$$E = E_\mathrm{d} + E_\mathrm{p} + E_\mathrm{h} \tag{1}$$

where E_d is the energy from London dispersion forces, E_p is the energy from dipole–dipole forces (Debye and Keesom) and E_h is the energy from hydrogen-bonding forces. E is equivalent to the latent heat of vaporization, a measure of the strength of attractive forces holding molecules together. During polymer dissolution, these interactions are overcome as the solvent surrounds polymer macromolecules thereby separating them one from another. The partial or Hansen solubility parameters (δ_d, δ_p, δ_h) of a chemical compound are the square root of the quotient of the respective intermolecular energy and the molar volume (V):

$$\delta_\mathrm{d} = \sqrt{\frac{E_\mathrm{d}}{V}}, \delta_\mathrm{p} = \sqrt{\frac{E_\mathrm{p}}{V}}, \delta_\mathrm{h} = \sqrt{\frac{E_\mathrm{h}}{V}} \tag{2}$$

A chemical compound can be represented by a dot in the 3D solubility space ($2\delta_\mathrm{d}$, δ_p, δ_h). Based on experimental solubility data, Hansen defines a solubility volume for a polymer within this 3D space. It is a sphere with centre ($\delta_\mathrm{d\ polymer}$, $\delta_\mathrm{p\ polymer}$, $\delta_\mathrm{h\ polymer}$) and radius R_0. Solvents with HSPs within the solubility sphere dissolve the polymer, whereas those outside do not. For polymer dissolution, the interaction polymer–solvent distance R_a must thus be inferior or equal to R_0:

$$R_\mathrm{a} = \sqrt{4\left(\delta_\mathrm{d\,polymer} - \delta_\mathrm{d\,solvent}\right)^2 + \left(\delta_\mathrm{p\,polymer} - \delta_\mathrm{p\,solvent}\right)^2 + \left(\delta_\mathrm{h\,polymer} - \delta_\mathrm{h\,solvent}\right)^2} \le R_0 \tag{3}$$

In other words, the relative energy difference (RED) must be inferior or equal to 1:

$$\mathrm{RED} = \frac{R_\mathrm{a}}{R_0} \le 1 \tag{4}$$

Different HSP values for CA are available in Hansen's User's Handbook[50] (Table 6): each set of (δ_d, δ_p, δ_h) values hold true for a given industrial polymer. Differences in HSP values may be explained by the specificities of each industrial polymer (*i.e.* degree of acetyl substitution, molecular weight, type and percent of impurities…). This information is unfortunately not detailed in the references, as shown in the second column of Table 6.

Polymer HSP values can be determined experimentally by carrying out solubility tests with solvents having known HSPs. However, the polymer solubility sphere radius R_0 depends on the solubility criteria predefined by the experimenter. Depending on the targeted application, it can range from a low degree of polymer swelling to complete dissolution in given operating conditions.

4. Experimental

4.1. Materials

CTA (Eastman CA-436-80S, 43.6% acetyl content) was kindly supplied by ABC Membranes (France). CDA (average M_n ~

Table 6 HSPs for CA in Hansen's User's Handbook[50]

Name as found in User's Handbook	Supplier	δ_d (MPa)$^{1/2}$	δ_p (MPa)$^{1/2}$	δ_h (MPa)$^{1/2}$	R_0 (MPa)$^{1/2}$
Cellidora A, Bayer	Bayer	18.2	12.4	10.8	7.4
Cellulose acetate	N/A[a]	16.9	16.3	3.7	13.7
Cellulose acetate	N/A[a]	18.3	16.5	11.9	8.8
Cellulose acetate	N/A[a]	14.9	7.1	11.1	12.4

[a] Non available data.

30 000 Da, 39.8% acetyl content) and LiCl (≥99%) were purchased from Sigma-Aldrich (USA). All three chemicals were desiccated at 120 °C during 15 minutes before use. Methyl lactate (99%) was obtained from J&K Scientific (China), ethyl lactate (≥98%) kindly supplied by Galactic S.A. (Belgium) and triethyl phosphate (synthesis grade) purchased from Merck (USA). Dimethyl carbonate (≥99%), ethyl levulinate (≥99%), gamma-valerolactone (≥99%) and methyl levulinate (≥98.0%) were purchased from Sigma-Aldrich. Polyethylene glycol (PEG, 200 kDa), sodium bisulfite and glycerol (laboratory reagent grade) were purchased from Sigma-Aldrich, Acros Organics (Belgium) and VWR International (USA), respectively. Ultra-pure water (T = 23 ± 2 °C) with a resistivity of 18 MΩ cm was produced by a PURELAB Maxima unit (ELGA, UK).

4.2. Solubility trials

The HSPs of CDA and CTA were determined with the software HSPiP 5.0.[50,51] based on the results of solubility trials (soluble or insoluble). The latter were carried out at 25 °C with a 12 wt% polymer solution under mechanical agitation for one week to achieve the solubility equilibrium. 21 well-defined solvents were chosen so as to cover a large area of the 3D solubility space. Blends of two miscible solvents were used to better define the sphere boundary. Solubility was visually qualified seeking clear solution; insoluble or swell polymer were classified as non soluble.

The same protocol was followed to test shortlisted alternative solvents for polymer dissolution. For LiCl dissolution trials, 1.2 wt% of the additive was blended with each alternative solvent.

4.3. Flat sheet membrane preparation

Polymer solutions were prepared with CDA as polymer and LiCl as additive. Either ethyl lactate or methyl lactate was used as solvent. LiCl was first dissolved in one solvent at 80 °C during 1 h. The polymer was added gradually to the solvent-additive solutions during 24 h. The solutions were mechanically stirred at 300 rpm and kept at 80 °C during another 24 h for homogenization. The polymer solutions were cast on a glass plate at 80, 70 or 60 °C using a Gardner knife with a gap of 200 μm and finally immersed in a coagulation bath (15 v/v% methyl lactate or glycerol in ultra-pure water) at 25 °C for 1 h. The subsequent flat sheet membranes were placed in an ultra-pure water bath for 3 h. The water was renewed every hour to remove any residual solvent and additive. Flat sheet membranes were then stored in 10 g L^{-1} sodium bisulfite solutions.

4.4. Membrane and polymer solution characterizations

4.4.1. Viscosity measurement. The viscosity of polymer solutions were measured using a rheometer (Physica MCR 301, Anton Paar, Austria) equipped with a rotational cylinder measuring system.

4.4.2. Pure water permeability. Ultra-pure water permeability (L_p, L h^{-1} m^{-2} bar^{-1}) at 20 °C was measured using a dead-end set-up (Amicon cell)[52] and determined as the slope of the following equation:

$$J_{20°C} = L_{p,20°C}\text{TMP} \tag{5}$$

where $J_{20°C}$ is the permeate flux at 20 °C (L h^{-1} m^{-2}) and TMP is the applied transmembrane pressure (bar). The effective membrane surface was 1.52 × 10^{-3} m^2. Before sampling, the permeate flux was left to stabilize 15 min at 1 bar.

4.4.3. PEG rejection. A 200 kDa PEG solution of 1 g L^{-1} was filtered with the same set-up as for pure water permeability. The stirring speed was 300 rpm and the four applied TMPs were 0.2, 0.4, 0.6 and 0.8 bar.

Retentate and permeate PEG samples were analyzed with a total organic carbon analyzer (TOC-L CSH, Shimadzu, Japan). The observed PEG retention R_{obs} is calculated by equation:

$$R_{\text{obs}} = 1 - \frac{C_p}{C_r} \tag{6}$$

where C_p and C_r are the concentrations of the permeate and retentate solutions, respectively. The retentate solutions are sampled at the membrane surface.

The membrane retention coefficient R_m is obtained by extrapolation of R_{obs} at zero flux:[53]

$$\ln\left(\frac{1 - R_{\text{obs}}}{R_{\text{obs}}}\right) = \ln\left(\frac{1 - R_m}{R_m}\right) + \frac{J}{k_{\text{BL}}} \tag{7}$$

where J is the flux density (m^3 m^{-2} s^{-1}) and k_{BL} is the mass transfer coefficient in the boundary layer (m s^{-1}).

4.4.4. Scanning electron microscope (SEM). Membrane samples were cryofractured in liquid nitrogen and sputter coated with gold (Emitech K550X, Quorum Technologies Ltd, UK). Cross-sectional images obtained using a Phenom XL scanning electron microscope (Phenom World, The Netherlands) provide information on the structure of the prepared membranes.

5. Results and discussion

5.1. Alternative solvent shortlisting

CTA's δ_d and δ_p determined based on the results of solubility trials are similar to those of Cellidora A, Bayer (see Tables 6 and 7). δ_h is however 2.4 MPa$^{1/2}$ lower than Bayer's polymer, indicating a lower hydroxyl content. The determined solubility radius R_0 of CTA is 2.5 times smaller than that of Cellidora A, possibly due to a more restrictive applied solubility criteria, *i.e.* complete dissolution of 12 wt% polymer at 25 °C. Solvents among Hansen's database and from the literature[51,54,55] have been shortlisted for their dissolution potential and water solubility (see Table 7). In particular, a selection criteria of RED smaller than 3.0 was applied to solvents. This arbitrary threshold was deemed necessary to keep time for experimentation within reasonable limits. It was furthermore observed that water solubility did not constitute a discriminatory factor for solvent shortlisting. In the 3D Hansen solubility space, CTA

Table 7 HSPs and REDs of alternative solvents

Alternative solvent	δ_d (MPa)$^{1/2}$	δ_p (MPa)$^{1/2}$	δ_h (MPa)$^{1/2}$	R_0 (MPa)$^{1/2}$	RED (CTA)	RED (CDA)
CTA[a]	18.2	11.4	8.4	3.0	—	—
CDA[a]	16.2	9.9	8.1	4.9	—	—
Dimethyl carbonate[b]	15.5	8.6	9.7	—	2.1	0.5
Ethyl lactate[b]	16.0	7.6	12.5	—	2.4	1.0
Ethyl levulinate[b]	16.5	7.8	6.8	—	1.7	0.5
Gamma-valerolactone[b]	16.9	11.5	6.3	—	1.1	0.6
Methyl lactate[b]	16.9	8.3	16.1	—	2.9	1.7
Methyl levulinate[b]	16.7	8.5	7.5	—	1.4	0.4
Triethyl phosphate[b]	16.7	11.4	9.2	—	1.0	0.4

[a] Determined experimentally in this study. [b] Source HSPiP software database.[51]

is situated in a little dense area with few solvents, giving no RED of shortlisted solvents lower than 1.

Other parameters, found in Table 8, are based on available data. NMP being a common solvent is included in Table 8 for comparison reasons. Recent attention has been given to solvents under development such as gamma-valerolactone and methyl levulinate. This could have encouraged certain researchers to work on the characterization of the solvents and might partly explain why information on physico-chemical properties can be found. On the other hand, the scarcity of data in European Chemicals Agency's databases is indicative of a general information gap.[56] For example, data on toxicity and environmental fate of these solvents remains limited and do not allow complete comparisons between solvents to be drawn.

Although no solvent has known mutagenic, carcinogenic or reprotoxic properties, 4 solvents have associated health hazard statements under the GHS. Triethyl phosphate is harmful if swallowed (H302). Ethyl lactate, methyl lactate and gamma-valerolactone may cause serious eye irritation or damage (H318 and H319). The two alkyl lactates may also cause respiratory irritation (H335). It calls for appropriate engineering and administrative controls and the use of personal protective equipment to maintain worker safety. This also holds true for volatility and flammability issues. With initial boiling points lower than 250 °C at 1 bar, the 7 shortlisted solvents are all defined as volatile organic compounds according to the European Directive 2004/42/CE. Three solvents have flammability hazard statements: ethyl and methyl lactate (H226) and dimethyl carbonate (H225). Low flash points, especially that of dimethyl carbonate, make scaling-up a more cumbersome process. Explosion-proof equipment is recommended and inert gas may be used in a fully closed vessel for polymer solution preparation to reduce oxygen content. Adequate ventilation in the surrounding environment minimizes the formation of flammable atmosphere by keeping solvent vapours below the lower explosion limit. At first glance, the flammability hazard has substituted the reprotoxicity hazard of common solvents (NMP, DMA, DMF). It can also be argued that high risks linked to flammable solvents are mainly limited to heating during polymer solution preparation, whereas those of reprotoxic solvents are temperature-independent and can therefore be problematic throughout the solvents' life cycle. As for environmental criteria, the shortlisted solvents have bioconcentration factors lower than 500 and logarithms of the octanol–water partition coefficient lower than 4, indicating low levels of bioaccumulation potential. No ecotoxicity is revealed. Triethyl phosphate is the only non-readily biodegradable solvent, indicating the absence of rapid and ultimate degradation in most environments including biological sewage treatment plants. Optimized aerobic conditions are necessary to potentially biodegrade it. Given its high boiling point, recovery from liquid waste streams by distillation is expected to be energy-intensive. For alkyl lactates and alkyl levulinates, hydrolysis is a feasible degradation pathway. However, rapid conversion into their respective acids requires special use and storage to avoid contact with water.

The fabrication processes of the shortlisted solvents have been investigated (see Table 9) and hotspots pointed out. Dimethyl carbonate and triethyl phosphate are the two non-biosourced solvents of the list. The main commercial production pathway for dimethyl carbonate is the oxidative carbonylation of methanol with typical reaction conditions equal to 120 °C and 27 bar.[57] Currently, no renewably derivable feestock is used but methanol could be obtained from biomass. Low values of intensity-based metrics reflect the low number of reactions and purification steps needed. Garcia-Herrero[57] estimates process mass intensity, excluding water, and energy intensity to be equal to 1.61 kg and 22.7 MJ per kg dimethyl carbonate, respectively. Energy consumption is mainly accounted for by the use of steam in separation steps. Extensive recovery of non-reacted input material and catalysts lowers waste intensity to 0.31 kg kg^{-1} dimethyl carbonate. Triethyl phosphate production process from phosphorus oxychloride and ethanol takes place in milder conditions (10–30 °C, 0.08–0.15 bar).[58] Nonetheless, the key issue is the use of phosphate rock as feedstock. It is converted to white phosphorus, which is then used to make triethyl phosphate through intermediates phosphorus trichloride and phosphorus oxychloride. Phosphate rock is identified as a critical raw material by the European Union: production is limited to three main countries, substitution is impossible and no current recycling is done.[47] Some researchers suggest that affordable phosphorus reserves may be depleted in 50–100

Table 8 Metrics for the solvent applied to 7 shortlisted alternative solvents and NMP

Parameter	Metric	NMP[56,70]	Dimethyl carbonate[56,71]	Ethyl lactate[56,72]	Ethyl levulinate[56,73–75]	Gamma-valerolactone[56,73,76–78]
Solvency	Relative energy difference with CTA[a]	0.5	2.1	2.4	1.7	1.1
	Solubility in water	Miscible; 1 kg L^{-1} at 20 °C	114.7–138.2 g L^{-1} at 20–25 °C and pH 6	Miscible	12.6 g L^{-1}	Miscible
Stability	Thermal decomposition	No data	No data	No data	No data	>600 °C, appropriate catalyst necessary
	Hydrolysis	No data	Half-life 5 days at 50 °C	Half-life 72 days at pH 7 and 7 days at pH 8	6.0% after 5 days at 40 °C	>28 days at 60 °C
Volatility	Vapour pressure	0.039 kPa at 20 °C	5.3–7.6 kPa at 20–25 °C	0.51–0.87 kPa at 20–25 °C	0.011 kPa at 25 °C	0.65 kPa at 25 °C
	Boiling point	202–204 °C	89.7–91 °C	154 °C	206 °C	207 °C
Inflammability	Flash point	91 °C	14–19 °C H225 (highly flammable liquid and vapour)	46–54 °C H226 (flammable liquid and vapour)	90 °C	81 °C
Other physical hazard	Explosiveness, self-reactivity, pyrophoricity, oxidizing, corrosivity	None	None	None	None	No data
Acute toxicity	Acute toxicity estimate values	None	None	None	None	None
Specific target organ toxicity	Single and repeated exposure tests	None	None	None	None	No data
Aspiration hazard or irritation	Aspiration hazard, skin corrosion or irritation, serious eye damage or eye irritation, respiratory or skin sensitization	H315 (causes skin irritation) H319 (causes serious eye irritation) H335 (may cause respiratory irritation)	None	H335 (may cause respiratory irritation) H318 (causes serious eye damage)	None	H319 (causes serious eye irration)
Carcinogenic, mutagenic, reprotoxic	Germ cell mutagenicity tests Carcinogenicity tests Reprotoxicity tests	H360D (may damage the unborn child)	None	None	None	No data
Biodegradability	Ready biodegradability	Readily biodegradable	Readily biodegradable	Readily biodegradable	No data	No data
Bioaccumulation	Bioconcentration factor	Estimated 3	0.23–0.354 at 20–25 °C pH 6.5–7.4	3	Estimated 1.26	−0.272
	Logarithm octanol–water partition coefficient	−0.46 at 25 °C	Estimated 3.2	0.31	0.38	Estimated 1.00
Ecotoxicity	Acute aquatic toxicity Chronic aquatic toxicity	None	None	None	None	No data

Parameter	Metric	Methyl lactate[56,79,80]	Methyl levulinate[73–75]	Triethylphosphate[56,81]
Solvency	Relative energy difference with CTA[a]	2.9	1.4	1.0
	Solubility in water	Miscible	Miscible	500 g L^{-1} at 25 °C
Stability	Thermal decomposition	No data	No data	No data
	Hydrolysis	Half-lives estimated 68, 6.8 and 0.68 days at pH values of 7, 8 and 9, respectively	7.9% after 5 days at 40 °C	Half-life 5.5 years
Volatility	Vapour pressure	0.340 kPa at 20 °C	0.446 kPa at 60 °C	0.0523 kPa at 25 °C
	Boiling point	144 °C	193–195 °C	215.5 °C

Table 8 *(Contd.)*

Parameter	Metric	Methyl lactate[56,79,80]	Methyl levulinate[73–75]	Triethylphosphate[56,81]
Inflammability	Flash point	58 °C H226 (flammable liquid and vapour)	72 °C	115 °C
Other physical hazard	Explosiveness, self-reactivity, pyrophoricity, oxidizing, corrosivity	None	No data	None
Acute toxicity	Acute toxicity estimate values	None	No data	H302 (harmful if swallowed)
Specific target organ toxicity	Single and repeated exposure tests	None	No data	None
Aspiration hazard or irritation	Aspiration hazard, skin corrosion or irritation, serious eye damage or eye irritation, respiratory or skin sensitization	H335 (may cause respiratory irritation) H319 (serious eye irritation)	No data	None
Carcinogenic, mutagenic, reprotoxic	Germ cell mutagenicity tests Carcinogenicity tests Reprotoxicity tests	None	No data	None
Biodegradability	Ready biodegradability	Readily biodegradable	No data	Inherently biodegradable
Bioaccumulation	Bioconcentration factor Logarithm octanol–water partition coefficient	−0.2 Estimated −0.67	Estimated 1.00 −0.17	<1.3 1.11
Ecotoxicity	Acute aquatic toxicity Chronic aquatic toxicity	None	No data	None

[a] Source HSPiP software database.[51]

Table 9 Metrics for the solvent fabrication processes of the 7 shortlisted alternative solvents

Metric	Simplified metric	Dimethyl carbonate[57]	Ethyl lactate[60,62]	Ethyl levulinate[64]	Gamma-valerolactone[64,67,68,70]	Methyl lactate[61,62]	Methyl levulinate[64]	Triethyl phosphate[47,58]
Renewable intensity	Number of renewably derivable feedstocks	0	1 (lactic acid)	1 (levulinic acid)	1 (either levulinic acid or ethyl levulinate)	1 (lactic acid)	1 (levulinic acid)	0
Process mass intensity	Number of reactions and separation steps	1.61 kg kg^{-1}, 4 reactions	5 reactions, calcium sulphate separation (1 kg kg^{-1} of lactic acid)	5 reactions	Min. 3 reactions	5 reactions, calcium sulphate separation (1 kg kg^{-1} of lactic acid)	5 reactions	Min. 4 reactions
Energy intensity	Operational conditions	22.7 MJ kg^{-1}, 120 °C, 27 bar	50–100 °C, 1 bar	100–230 °C, 1 bar	140–380 °C, 30–55 bar	50–100 °C, 1 bar	100–230 °C, 1 bar	10–30 °C, 0.08–0.15 bar
Use of critical elements	—	None	None	None	None	None	None	Phosphate rock

years.[59] In response to the use of finite resources and their potential depletion, interest at the international level has been given to renewable resources. Carbohydrates from sugar-based biomass and lignocellulose biomass can be converted to building blocks and platform chemicals such as lactic acid and levulinic acid for further chemical synthesis. Ethyl lactate and methyl lactate can both be recovered by distillation after catalyzed esterification of lactic acid with ethanol and methanol, respectively.[60,61] Reaction conditions are mild (50–100 °C, 1 bar) but equilibrium limitations specific to esterifications need to be overcome.[60] Constable *et al.*[37] consider that esterification reactions have average reaction mass efficiencies of 67% and mass intensities of 11.4 kg kg^{-1} ester. The reaction mass efficiency is defined as the percentage of the mass of the reactants that remain in the product.[37] The total number of chemical steps in the synthesis of both lactate esters are predominantly due to lactic acid synthesis. In the conventional process, lactic acid recovery and purification from fermentation broths require complex separation steps.[62] One separation step involves calcium sulphate, of which one kilogram needs to be disposed of for every kilogram of lactic acid produced.[62] Advances in electrodialysis technolgies seek to eliminate this salt waste.[63] The production of ethyl and methyl levulinate also involves a final esterification step. Several reaction pathways are being investigated, among which synthesis from levulinic acid and furfuryl alcohol.[64] Levulinic acid can be obtained by acid-catalyzed hydrolysis of carbohydrates at 100–250 °C with a relatively high yield.[65,66] Isolating and purifying it is however more complicated.[65] Gamma-valerolactone can be obtained by hydrogenation from either levulinic acid or ethyl levulinate with high temperatures and pressures of H_2 and a metal catalyst.[64,67,68] On average, hydrogenation reactions have reaction mass efficiencies of 74% and mass intensities of 18.6 kg kg^{-1}.[61] Jessop[15] considers gamma-valerolactone can be obtained by only 4 steps. Interestingly, Zhang[69] reports on recent advances made in obtaining gamma-valerolactone from a one-pot-conversion of carbohydrates such as fructose with 3 main reactions. The most striking conclusion to emerge from the analysis of the solvents' fabrication processes is that data on intensity-based metrics is lacking, making it tedious to compare them in a comprehensive manner.

5.2. Solubility trials with shortlisted solvents

None of the 7 shortlisted alternative solvents was found to have a solvency power high enough to totally dissolve CTA. Triethyl phosphate only partially dissolved CTA. Blends of alternative solvents were tested and gave similar negative results. These results agree with the REDs greater or equal to 1 (see Table 7). In the literature, difficulties have also been encountered to find suitable alternative solvents for CTA. It has for example been found that a lower polymer concentration (*i.e.* 10 wt%) was necessary for gamma-valerolactone to dissolve CTA.[83] Overall, our solubility trials pinpoint a scientific barrier linked to the limited number of alternative solvents with appropriate solvency power. Ongoing research in green chemistry offers promising insights into new solvents, in particular those produced from biobased platform chemicals. An example is dihydrolevoglucosenone (Cyrene), a molecule derived from cellulose in a two-step process and currently under development.[82] Its HSPs make it a promising alternative for dipolar aprotic solvents and a potential solvent for CTA in the near future (RED equal to 0.7).

CDA was tested as an alternative polymer to CTA. Its lower degree of substitution makes it easier to solubilize by common solvents.[84] REDs of the shortlisted alternative solvents are lower for CDA than for CTA and are lower or equal to 1.0, with the exception of methyl lactate (see Table 7). All 7 solvents, including methyl lactate, totally dissolved CDA in the solubility trials. Limitations in the conventional hypothesis in determining RED values may explain why the value for methyl lactate – CDA is greater than 1.0 whereas CDA is found to be soluble in methyl lactate. The hypothesis is that a sphere describes the solubility volume of a given polymer. Limitations have been observed in the literature[85] and certain authors suggest that an ellipsoid may better fit data than a sphere.[86] Wiśniewski *et al.*[87] further acknowledge that solubility volumes are generally unsymmetrical.

In additional solubility trials, only ethyl and methyl lactate dissolved LiCl. Further testing was thus carried out with the two alkyl lactates. Although out of the scope of this work, this selection by no means disqualifies the other 5 solvents for membrane preparation, especially if a different additive were to be used.

Homogeneous ternary mixtures (CDA : LiCl : solvent) with weight compositions equal to 12 : 1 : 87 and 15 : 3 : 82 were obtained for both alkyl lactates. Furthermore, the viscosity range (1.2–4.9 Pa s) allowed to cast flat sheet membranes and is also appropriate for hollow fibre casting. As for the stability of the polymer solution, no gel formation nor crystallization has been visually observed. Quantitative characterization could be particularly relevant during the scaling-up process from flat sheet membrane to hollow fibre preparation.

5.3. Membrane performance and characterization

Permeabilities of flat sheet membranes prepared in different coagulation baths are detailed in Table 10. The addition of glycerol or the solvent to the aqueous coagulation bath is expected to lower the membrane formation rate and decrease the formation of finger cavities so as to avoid having membranes with lower rejection to micro-solutes as compared to membranes prepared with water as sole non-solvent.[9] Results show that membranes prepared with ethyl lactate have very

Table 10 Permeability values (L h^{-1} m^{-2} bar^{-1}) of CDA flat sheet membranes prepared with 82 wt% ethyl lactate or methyl lactate and 3 wt% LiCl at 80 °C

	Coagulation bath composition	
Alternative solvent	15 v/v% solvent in water	15 v/v% glycerol in water
Ethyl lactate	0	15
Methyl lactate	202	92

Table 11 Permeability and retention values of CDA flat sheet membranes prepared with 82 wt% methyl lactate and 3 wt% LiCl at different casting temperatures and coagulated in a 15 v/v% methyl lactate bath

Casting temperature (°C)	Permeability ($L\ h^{-1}\ m^{-2}\ bar^{-1}$)	PEG retention (%)
60	49	94
70	357	93
80	188	91

low pure water permeabilities (0 and 15 $L\ h^{-1}\ m^{-2}\ bar^{-1}$), which are irrelevant for ultrafiltration applications. Further screening trials at different casting temperatures have thus been carried out on the most permeable membrane, *i.e.* methyl lactate as solvent in both the polymer solution and coagulation bath. Values in Table 11 show that casting temperature, which directly impacts on energy intensity, has a significant effect on permeability and less so for PEG retention. Permeability values of membranes prepared with methyl lactate are comparable to those found in the literature for ultrafiltration membranes.[88] Retention rates of 200 kDa PEG above 90% suggest membrane pore diameters below 48 nm. Indeed, the calculated hydrodynamic radius of the tracer as described by Meireles *et al.*[89] equals 24 nm. The sponge substructure containing finger-like pores near the skin layer as shown in Fig. 1 is furthermore consistent with the description by Strathmann *et al.*[90] of low pressure ultrafiltration membranes. Flat sheet membrane preparation in this work shows promising technical results. Although out of the scope of this work, hollow fibre preparation can be considered in a further step with complete characterization (selectivity, mechanical and chemical resistance) as indicated in Table 5.

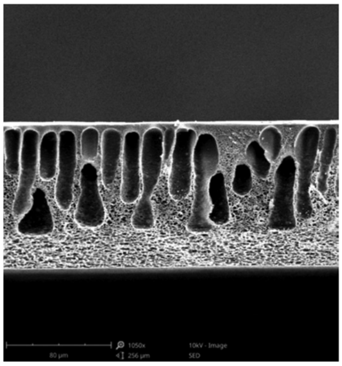

Fig. 1 Cross-sectional morphology of CDA flat sheet membrane prepared at 80 °C.

5.4. Metrics applied to the membrane fabrication process using methyl lactate

The metrics in Table 12 give a brief overview of improvements and remaining challenges in using methyl lactate as alternative solvent during membrane fabrication. As reference (see Table 12), hollow fibres prepared with CTA 20 wt%, LiCl 2 wt% and NMP as solvent are taken. Spinning of the reference membrane takes place at 80 °C and the bore liquid is a glycerol–water blend. The bore liquid in inner skin hollow fibre preparation can be assimilated to the coagulation bath in flat sheet membrane preparation, as carried out in this work. Industrial compositions and process conditions remain confidential but are not expected to significantly differ from the ones mentionned above. Compared to the reference, three improvements in the membrane preparation process with methyl lactate exist:

(i) increased number of renewably derivable feedstocks: the renewably intensity increases from 1.0 to 4.9 kg kg^{-1} since NMP is petrochemical-based, whereas methyl lactate can be obtained by fermentation of carbohydrates,

(ii) reduced number of solvents: methyl lactate is used both in the polymer solution and coagulation bath, instead of having two distinct solvents,

(iii) reduced number of compounds per liquid stream: coagulation and rinsing waste streams each contain 3 (water, methyl lactate and LiCl) instead of 4 compounds (water, NMP, glycerol and LiCl), which simplifies waste management.

Challenges remain to improve environmental and technical performances. Current process mass intensity of membranes prepared with CDA 15 wt% equals 6.7 kg kg^{-1}, whereas that of industrial membranes taken as reference equals 5.0 kg kg^{-1}. Increasing the polymer's weight percentage in the polymer solution will reduce mass intensity but also lead to less permeable sponge-structured membranes. The skin layer where the polymer first coagulates is expected to have an increased strength linked to higher polymer concentration and a lower ten-

Table 12 Metrics applied to the membrane fabrication process of CDA flat sheet membranes

Metric	Simplified metric	Reference membrane[a]	CDA flat sheet membrane
Renewable intensity		1.0 kg kg^{-1}	4.9 kg kg^{-1}
	Number of renewably derivable feedstocks	1 (CTA)	2 (CDA, methyl lactate)
Process mass intensity		5.0 kg kg^{-1}	6.7 kg kg^{-1}
	Number of reactions and separation steps	1 phase separation step	1 phase separation step
	Number of solvents	3 (NMP, water, glycerol)	2 (methyl lactate, water)
Energy intensity	Operational conditions	80 °C, 1 bar	60–80 °C, 1 bar
	Number of liquid streams to treat	2 (coagulation, rinsing)	2 (coagulation, rinsing)
	Number of solvents per liquid stream	4 (water, NMP, glycerol, LiCl)	3 (water, methyl lactate, LiCl)
Use of critical elements	—	None	None

[a] Polymer solution composition: CTA 20 wt%, LiCl 2 wt% and NMP as solvent. Spining temperature: 80 °C. Bore liquid: glycerol–water blend.

dency to rupture and initiate fingers.[90] Energy and solvent intensity can also be further optimized by fine tuning casting temperature and coagulation bath composition, respectively. One might question to what extent intensity-based metrics can be optimized. The ideal NIPS process consists of a bio-sourced polymer as unique input: process mass intensity equal to 1 kg kg^{-1} and energy intensity equal to 0 MJ kg^{-1}. This entails no heating, no solvent and, by extension, no phase inversion. In reality, the polymer weight percentage encountered in the literature is rarely above 35 wt% due to viscosity increase of the polymer solution.[91] The lowest process mass intensity obtained would be 2.9 kg kg^{-1}. If all inputs were derived from renewable feedstocks, renewable intensity would also equal 2.9 kg kg^{-1}. No indication is however provided about the technical feasibility of obtaining performant membranes with such values. Trade-offs between use of resources and membrane properties are inevitable.

6. Concluding remarks

Measuring sustainability performance is a prerequisite for improving it and supports researchers in their endeavour to develop greener membranes and associated processes. The metric-based approach as developed in this study is a first step to rationalize sustainable membrane preparation. Hotspots and hazards other than solvent reprotoxicity have been pointed out and technical feasibility assessed.

Ultrafiltration CDA membranes have been prepared with methyl lactate, a non-toxic but flammable solvent. Although other solvents labelled as green by the scientific community have been studied, the field of chemistry has yet to propose a vast choice of alternative solvents with high solvency power for membrane applications. Extensive information on the environmental fate and toxicity of these newly commercialized solvents could help make better-informed decisions.

As for membrane science, accurate tools for predicting the impact of process parameters on membrane properties could simplify the integration of EHS criteria.

Discriminating solvents early in the screening stage remains inconclusive. For complete comparison, technical feasibility is to be considered alongside LCA, socio-economic and risk analysis. The three analysis require to anticipate scale-up by providing information specific to the design and production site in addition to data collected during our metric-based approach. In other words, the underlying vision advocated is to embed ecodesign practices into membrane science.

Conflicts of interest

There are no conflicts to declare.

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