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Editorial introduction into green solvents for development of sustainable chemical processes

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Boelo Schuur is professor Separation Technology at the University of Twente in the Sustainable Process Technology group. With his team he studies separations important for realizing biorefineries and chemistry from wastewater, as well as innovations for existing industrial processes to reduce their carbon footprint. Key in many applications is the use of green solvents.

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Solvents are essential in many processes, including both chemical conversions and (downstream) separations. Solvents facilitate contact between reacting molecules and affect activities of molecules in solution so that desired behavior of the dissolved molecules, the solutes, can be obtained. By manipulating activity of molecules, not only their reactivity can be tailored but also separations can be induced and/or enhanced. Furthermore, innovative use of solvents can offer alternative processing routes for existing processes and new (bio)refining opportunities for entirely new applications such as in biobased production schemes.

Whereas solvents are indispensable for many applications, the use of solvents also intrinsically imposes a risk, as the use of solvents may culminate in residual traces of the solvent in the final product, or by leaching or evaporation, in emissions of the solvent into the environment. To evaluate the sustainability of chemical processes, Human health and care for the environment are key aspects included in the sustainability goals formulated by the United Nations [1] and are typically included in sustainability analyses such as life cycle analyses carried out nowadays.

A growing awareness of the impact on health and environment has resulted in several trends in the use of solvents, aiming at reduced emissions, as well as lowering the impact of emissions:

1) In the first decade of this century ionic liquids (ILs) have appeared as a tremendously wide category of solvents. Depending on application, both hydrophilic ILs and hydrophobic ILs have been implemented across a wide variety of applications. Examples include biorefinery applications, gas purification, catalytic solvents, and fluid separating agents among many others. ILs may be applied pure and as dilutions in both organic diluents and in aqueous systems. In this special issue, various contributions describe ILs in a range of applications.
2) Next to the class of ILs, having been initiated a few years later, deep eutectic systems (DESs) have appeared as a class of solvents. Where the ILs in essence are a single ion pair solvent (although double ILs have been reported as well), DESs are best seen as a composite solvent comprising of multiple molecules attracted to each other by hydrogen bonding. Together they show liquid behavior where their individual melting points are typically much higher. Although salts are often included in DESs, resulting in behavior that to some extent is similar to ILs, due to the nature of the hydrogen bonding composite solvents, DESs are intrinsically different as they can be applied in varying ratios where the stoichiometry of cations and anions in ILs is strictly bound

by charge neutrality. Natural DESs (NADESs) are a class of DESs formed by combination of species obtained directly from nature and offer a class of biobased solvents.

3) Next to NADES and more classical biobased solvents such as ethanol and lactic acid, new classes of biobased solvents have appeared in the scientific literature, with examples as 2-methyl tetrahydrofuran, guaiacol and dihydrolevoglucosenone (cyrene), produced from lignocellulosic biomass. In some contributions in this themed issue, biobased (also called biosourced) solvents are mentioned as an upcoming new class.
4) A very important challenge for the scientific community is to limit the rise in CO_2 concentration in the atmosphere. Among the mitigating solutions, conversion of CO_2 into green solvents has been proposed. Among the contributions in this special issue on Green Solvents, one paper is specifically dealing with cyclic carbonates produced from CO_2.
5) For separations involving solvents to be operated in a sustainable fashion, it is key that they are operated reversibly and that means that the solvent can be regenerated efficiently. The reversibility is a key to overall operating expenses and alternative driving forces for solvent and sorbent regeneration is a young field with a high interest. The contribution from Hatton and co-workers in this issue discusses electrochemical driving forces as alternative for thermal regeneration.

Having mentioned five trending categories of innovative solvents, and expressing the wide range of application areas is covered with these trends, it is a great pleasure for us to briefly introduce the eleven contributions in this issue and how each contributes to the inclusive view on the state of the art in green solvents that this issue aims to present.

Chang Geun Yoo and co-authors focus in their work on utilization of biomass, and how DESs can contribute in two roles, functioning both as a catalyst in the delignification and as a solvent in fractionation. As special subcategory DESs they consider renewable DESs, also called NADES. With respect to the catalytic activity, it was stressed that in the absence of acid functionality, such as in glycol + choline chloride DES mixtures, no significant delignification activity was found, while for fluid properties, the use of glycol was beneficial. Also, conversion of carbohydrates to produce compounds such as furfural and 5-hydroxy methyl furfural was reviewed. Overall, it was concluded that highly interesting pathways exist, but still much is unknown regarding the exact mechanisms of the reactions catalyzed by DESs.

Mara Freire and co-authors in their contribution on aqueous biphasic systems (ABS) describe how traditional application areas such as aqueous two-phase partitioning for downstream fractionation in biotechnological production systems have developed during the recent years and continue to develop towards industrial large-scale applications, but also how ABS find more and more innovative application windows. The new opportunities indicated include sample pretreatment and biodiagnostics, 3D printing and micropatterning.

Dooli Kim and Suzana P. Nunes describe how common solvents for membrane production such as N-methylpyrrolidone (NMP) and N,N-dimethyl formamide (DMF) are substances of high environmental concern and that significant research on various classes of solvents for their replacement is being undertaken. A few classes have gained small but identifiable momentum in the past years (DESs and biosourced solvents), while ILs continue to receive most attention as green solvents for membrane production. From their overview, it is clear that although sustainable alternatives seem available, each solvent has its advantages and drawbacks and it is suggested that legislation may help phasing out toxic solvents.

Suojiang Zhang and co-workers describe how indoor pollutants form a threat to laboratory safety, and how IL-based adsorbents can be used to adsorb gases that are toxic and/or hazardous when exceeding explosive limits. In their overview, they present several solid carriers such as activated carbon and silica in combination with a variety of ILs. A series of metal-containing ILs are shown to have high capacities for several gases. However, combined capacities when multiple gases are concerned simultaneously, still form a point of concern.

Berlyn R. Mellein, Aaron M. Scurto and Mark B. Shiflett also describe gas separations with ILs, and their work mainly focuses on methods to describe liquid phase solubilities of gases. Both theoretical aspects and experimental techniques are reviewed, and it may be concluded that this area of science is very lively and a variety of thermodynamic equations, being either predictive or descriptive are in use and are being further developed. For upscaling operations, it is of key importance that good correlations and sound understanding of gas solubilities in ILs is available.

María González-Miquel and Ismael Díaz contribute to this collection with a perspective on solvent selection tools making use of modeling and simulation. In their overview, they present current multiobjective solvent-selection protocols making use of simulation tools for property estimation. Especially the combination of models at different levels is seen as a key development, which may be extended further. Essential in the predictive power of quantum chemical-based models is whether or not associating behavior such as in ILs is included properly. As editor, we interpret this as a highly important conclusion and warn new scientists in the field that such simulation tools are not solutions that always work. It is key that scientists working with model predictors make sure their input into the model software is correctly describing the chemistry in the actual situation.

Masahiro Goto and co-workers describe how enzymatic reactions can be facilitated by ILs. Key aspects to which ILs contribute include stable solubilization of substrates that are only sparsely soluble in water and in traditional organic solvents. This offers opportunities for higher rates and good yields. Immobilization of the enzymes can further facilitate the recyclability of the enzymes in the system, making them stable in the IL phase. The authors indicate that further research on exact pathways and kinetics are important.

Esteban Quijada-Maldonado and Julio Romero contribute to this special issue with a review on rare earth element extractions using green solvents. Traditionally, metal extractions have been heavily reliant on kerosene as the diluent. However, recently, more scientific attention has been given to ILs as a safer and less environmentally demanding alternative. Due to the growing request to recycle rare earths from consumer electronics, new developments are essential to allow the recycling to be done in a sustainable fashion. In their review, Quijada-Maldonado and Romero emphasize that ILs offer great options for lanthanide extraction, but also that fractionation of adjacent rare earths remains challenging.

Paolo P. Pescarmona's review evaluates recent development in the field of cyclic carbonates as solvents. Synthesizing these solvents using epoxides and CO_2 from the atmosphere is a direct approach that may help reduce the atmospheric CO_2 level. Pescarmona notes that the world market for cyclic carbonates is markedly lower than the emission levels of CO_2, but this interesting approach can be considered as one of many individual measures that in concert may be significant in reducing the rise of atmospheric CO_2 concentrations. Next to a discussion on a growing number of application areas for cyclic carbonates, a highly interesting list of notes for good practice towards catalytic synthesis is provided.

Mega Kar and Cristina Pozo-Gonzalo describe developments in the field of nonaqueous zinc batteries. Zinc batteries have great potential to repeatedly store and discharge electric energy, an essential element in the energy transition. Where the price of zinc-based rechargeable batteries is potentially at least one order of magnitude lower than that of lithium ion batteries, offering a highly exciting outlook towards much reduced costs for electrically powering cars and appliances in households, aqueous electrolytes offer limited stability and Kar and Pozo-Gonzalo review nonaqueous electrolyte alternatives. They conclude that concentrated salts and ionic liquids offer safe alternatives, but there are still challenges ahead.

Alan T. Hatton and co-workers address in their review CO_2 capture with redox-responsive sorbents and mediators. Traditional solvents for CO_2 capture rely on thermal energy to release the CO_2 from the solvent during the regeneration stage in the process. In their review, Hatton et al. discuss electrochemical pH swings as option for changing the thermodynamic equilibrium speciation of CO_2. Furthermore, electrochemical switching of organic solvents and of sorbents are highly interesting topics covered, and even carbon dioxide reduction integrated in a synergistic process with the capture have been demonstrated, and further breakthroughs in this area are anticipated.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Reference

1. Transforming our world: the 2030 agenda for sustainable development at https://sustainabledevelopment.un.org/post2015/transformingourworld.