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Editorial

Advances in Deep Eutectic Solvents: New Green Solvents

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This Special Issue, entitled "Advances in deep eutectic solvents: New green solvents", was organized to collect original research articles on the latest developments in the new green solvents, deep eutectic solvents (DESs), and their applications.

DESs are composed of hydrogen-bond donors (HBAs) and hydrogen-bond acceptors (HBDs), and have similar properties to ionic liquids (ILs), for instance, low vapor pressure, high thermostability, structural tunability and high solubilities for many solutes. Compared to ILs, DESs are cheap, biodegradable, low-toxic and easy to prepare by mixing an HBD and an HBA. Therefore, DESs are considered to be newly green solvents. In the past decades, DESs are receiving more and more attention. Due to their unique properties, DESs have the potential to replace the traditional organic solvents for use in the separation of mixtures [1], absorption [2], metal extraction [3], catalytic reaction [4], biomass and biomaterial preparation [5], material synthesis [6], electrochemistry [7], and so on. In this Special Issue, seven articles were selected. These articles consist of one review paper and six original research papers, and discuss these topics in more detail. The contents of this Special Issue are briefly presented below.

The separation of benzene and cyclohexane azeotrope is one of the most challenging tasks in the chemical industry due to their close boiling points. There are two ways to separate benzene and cyclohexane mixtures: liquid–liquid extraction and extractive distillation. For the liquid–liquid extraction of benzene and cyclohexane mixtures, McGaughy and Reza [8] measured the liquid–liquid equilibrium (LLE) of benzene, cyclohexane and DESs. The selected HBAs included tetrabutylammonium bromide ($N_{4444}Br$), tetrahexylammonium bromide ($N_{6666}Br$), choline chloride (ChCl), and methyltriphenylphosphonium bromide (METPB), and the HBDs included ethylene glycol (EG) and glycerol (Gly). COSMO-RS was used to predict the LLE data with adjustments to reflect DES-specific interactions. The results showed that the COSMO-RS model predictions for the LLE of EG-based DES were very accurate with root-mean-square deviations (RMSD) below 1% for both $N_{4444}Br$:EG and METPB:EG DESs. Moreover, mass transfer kinetics were determined experimentally for the DESs and the results were fit to a first-order kinetics model. METPB:Gly DES had the highest mass transfer coefficient at 0.180 min^{-1}.

In the article reported by Hua et al. [9], three DESs were used as solvents for the separation of benzene and cyclohexane via extractive distillation. Tetrabutylammonium bromide:levulinic acid (1:2) DES showed the best entrainment results. Vapor-liquid equilibrium (VLE) measurements at atmospheric pressure revealed that the DES could break the mixture azeotrope with relative volatility up to 4.763. The FT-IR study indicated that there are hydrogen bonding and π–π interactions between levulinic acid and benzene, which could be responsible for the entrainer to break the azeotrope.

For the application of DESs in the extractive distillation of benzene and cyclohexane mixtures, Bai et al. [10] measured the density and viscosity of DESs at temperatures from 293.2 to 353.2 K and atmospheric pressures. The authors measured the VLE data of the ternary system (benzene + cyclohexane + DESs), and then used three thermodynamic

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models, NRTL, WILSON and UNIQUAC, to predicate VLE. The results indicated that the NTRL model was suitable for predicting the VLE of the separation system containing DESs.

DESs are also used to prepare catalysts for chemical reactions. Faizan et al. [11] prepared DESs from ChCl as a HBA, and mono-, bi- and tri-metallic salts of niobium, molybdenum and zircon as HBDs. The DESs were used to prepare vanadium phosphorus oxide (VPO) catalysts for the selective oxidation of *n*-butane to maleic anhydride in a fixed-bed reactor. A large conversion of *n*-butane and high selectivity to maleic anhydride were obtained using the developed DES catalysts. Compared to an unpromoted VPO catalyst, the DES-derived catalyst led to an increase of 7.8% in the mass yield of maleic anhydride and an increase of 16% in *n*-butane conversion.

Sulfur dioxide (SO_2), nitric oxide (NO) and carbon dioxide (CO_2) are acidic gases, mainly released from the combustion of fossil fuel. DESs were broadly investigated for the capture of these acidic gases. In the review article [12], Wang et al. summarized timely non-functionalized and functionalized DESs, including binary and ternary DESs, for capturing SO_2, CO_2 and NO from simulated flue gases. New strategies to improve the absorption capacity of acidic gasses were introduced. A third component was introduced to DESs to decrease their viscosity and improve their CO_2-absorption capacity. DESs synthesized with halogen salt HBAs and functionalized HBDs were used to improve the absorption of SO_2 and NO and decrease the viscosities after absorption, due to the physicochemical interaction between gases and DESs. The mechanism of the absorption and the ways to enhance the absorption capacity, as well as the challenges in capturing SO_2, CO_2 and NO from flue gases, were discussed.

Finally, Maniam and Paul [13] preliminarily assessed the "greenness" of halide-free ILs using an approach of multi-criteria decision analysis. DESs have similar properties to ILs, so the approach can be used to determine the "greenness" of DESs, especially the halide-free DESs.

In conclusion, this Special Issue aimed to arrange the major topics related to DESs, their properties, and their current advances, including the separation of mixtures, metal extraction, absorption, and chemical reactions. Lastly, the Guest Editors would like to thank the Editorial Board of *Processes*, the reviewers, and the authors who contributed to this Special Issue. All authors have read and agreed to the published version of the manuscript.

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