Electronic Supplementary Material (ESI) for Green Chemistry


# SUPPORTING INFORMATION

# Deep Eutectic Solvents as Extraction Media for Azeotropic Mixtures

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**Ternary Liquid-Liquid-Equilibria**

Figures S1 and S2 illustrate the ternary diagram for the DES 1 and DES3, respectively.

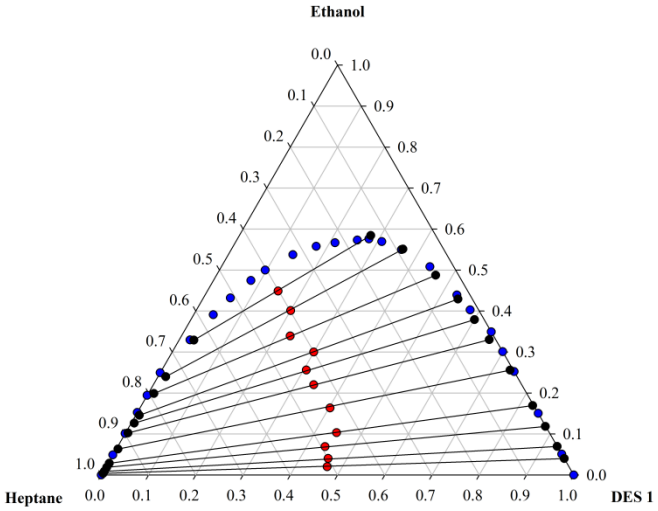


**Figure S1.** Ternary diagram for the system Heptane + Ethanol + DES 1 at 25 ºC. The blue dots represent the binodal, the red dots the experimental starting point of the mixture and the black dots and lines the system tie-lines.

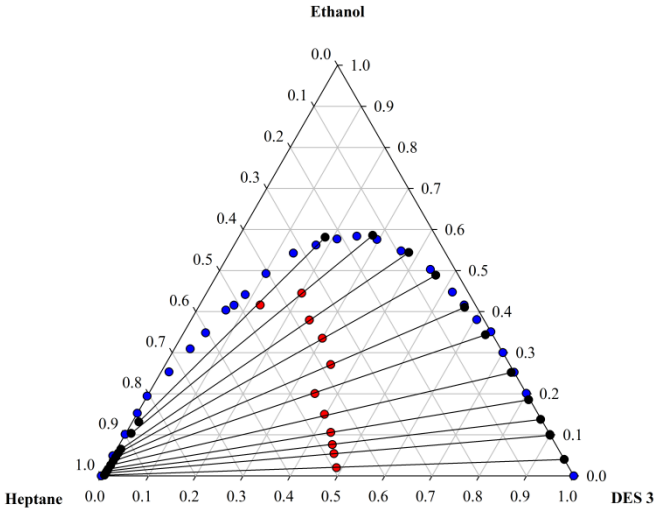

**Figure S2.** Ternary diagram for the system Heptane + Ethanol + DES 3 at 25 ºC. The blue dots represent the binodal, the red dots the experimental starting point of the mixture and the black dots and lines the system tie-lines.

**Distribution Coefficient and Selectivity**

The distribution coefficient and selectivity values of the system with the azeotrope heptane (1) + ethanol (2), as a function of ethanol mass fraction in heptane-rich phase at 25 ºC, are presented in Figures S3 and S4, respectively.

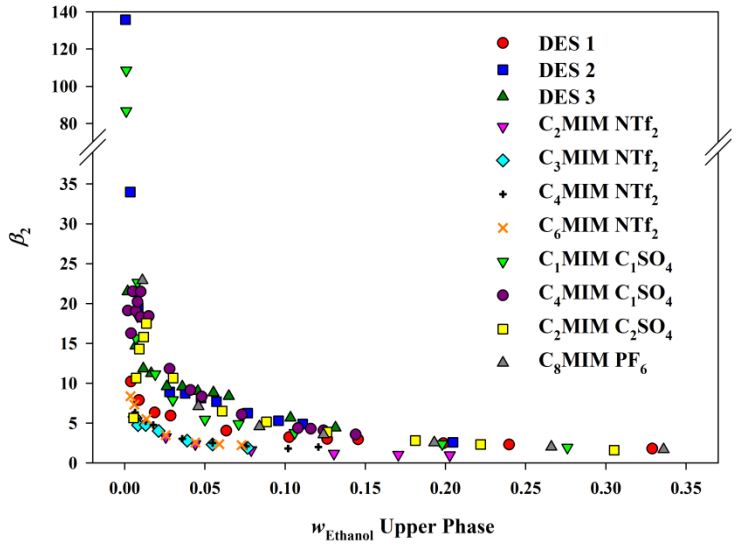


**Figure S3.** Distribution coefficient values, $\beta_2$, of the system with the azeotrope heptane (1) + ethanol (2), as a function of ethanol mass fraction in heptane-rich phase at 25 ºC.[1-5]

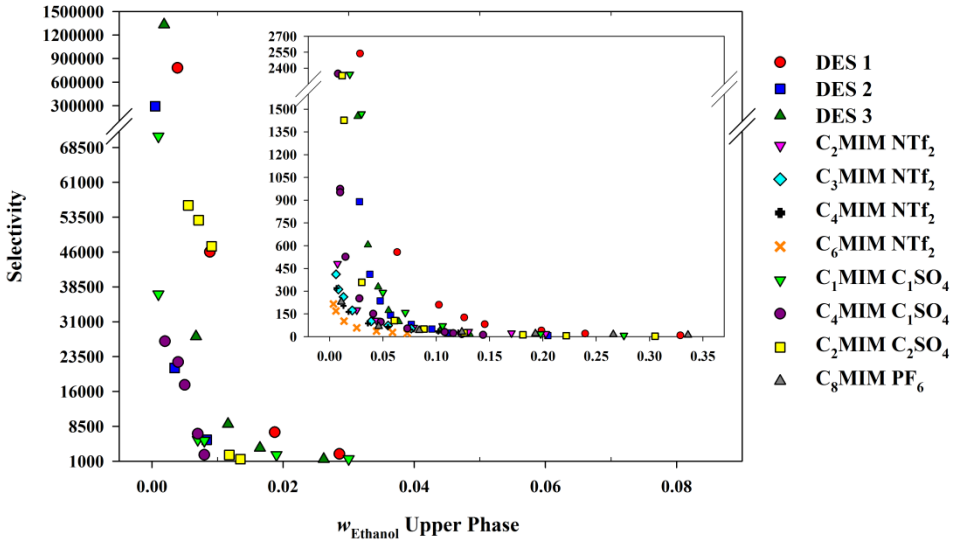


**Figure S4.** Selectivity, *S*, of the system with the azeotrope heptane (1) + ethanol (2), as a function of ethanol mass fraction in heptane-rich phase at 25 ºC.[1-5]

**NMR studies**

The $^1$H spectra of DES 1, DES 2 and DES 3 are depicted in Figures S5, S6 and S7, respectively. All the experiments were carried out on a Bruker AVANCE 400 spectrometer operated at room temperature with 16 scans for $^1$H NMR, using oxide deuterium as solvent. The chemical shifts of the spectra are listed in Table S1.

**Table S1.** $^{1}$H NMR chemical shifts for the DES used in this work.

| | DES 1 | DES 2 | DES 3 |
|---|---|---|---|
| 1 | 3.98 | 3.98 | 3.98 |
| 2 | 3.44 | 3.44 | 3.45 |
| 3, 4, 5 | 3.12 | 3.12 | 3.13 |
| 6, 6’ | 3.55-3.59 | – | 3.58 |
| 7, 7’ | 3.70 | 2.79 | 3.58 |
| 8, 8’ | 3.44-3.49 | 2.52 | – |
| 10, 10’ | – | 2.15 | – |

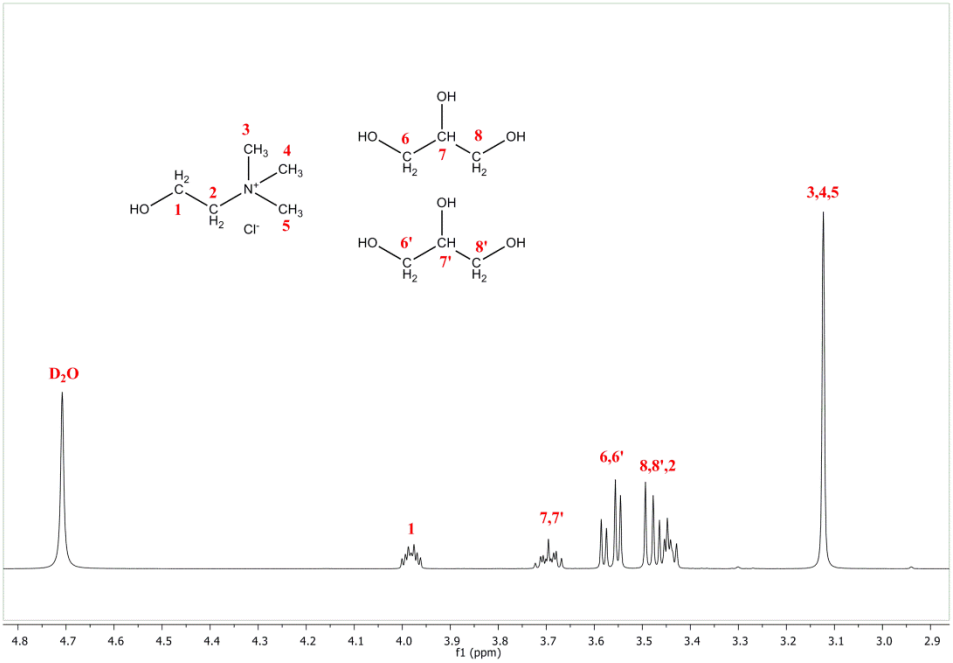


**Figure S5.** $^{1}$H NMR spectrum of DES 1 in deuterium oxide at 25 ºC. The structure and numbering of the DES is also depicted.

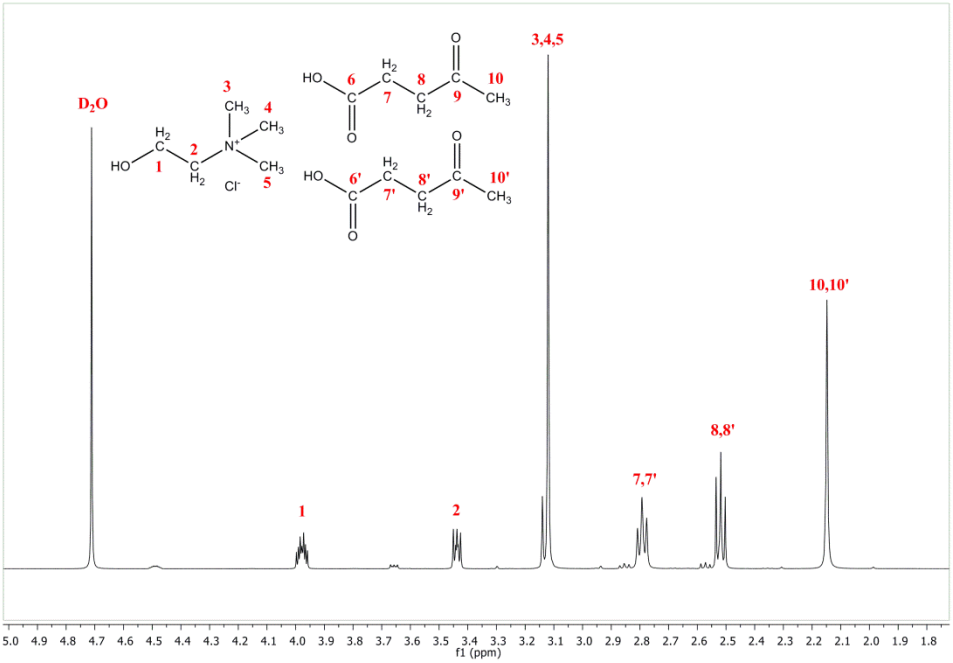


**Figure S6.** $^{1}$H NMR spectrum of DES 2 in deuterium oxide at 25 ºC. The structure and numbering of the DES is also depicted.

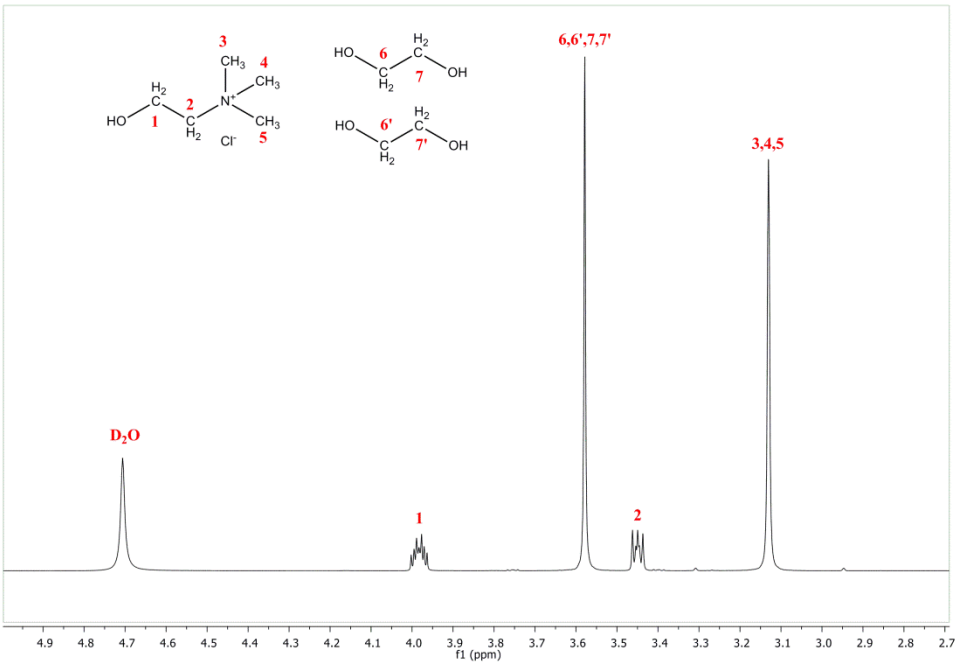


**Figure S7.** $^{1}$H NMR spectrum of DES 3 in deuterium oxide at 25 ºC. The structure and numbering of the DES is also depicted.

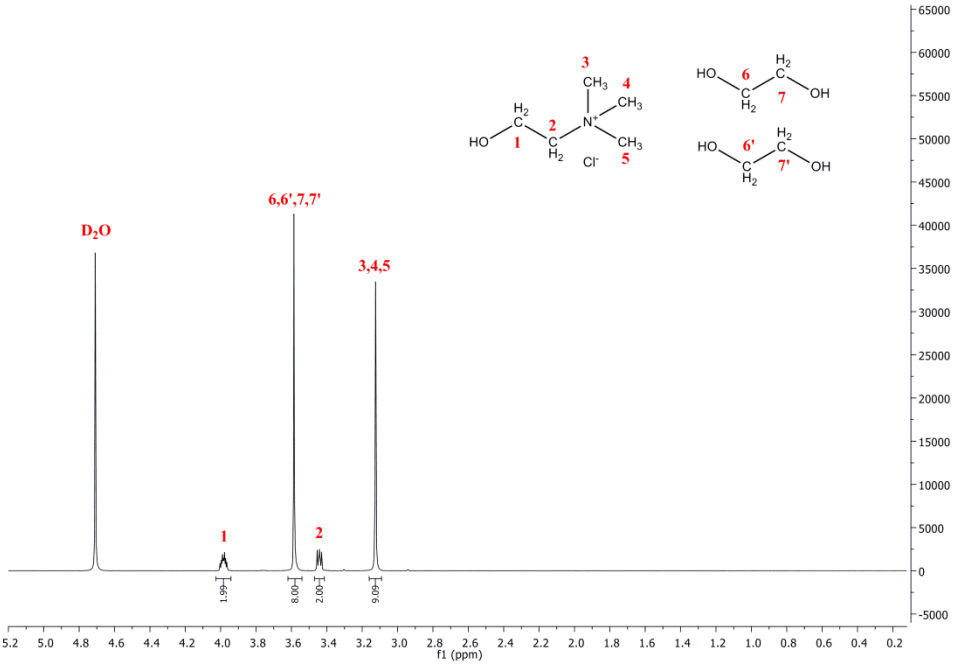


**Figure S8.** [1]H NMR spectrum of recovered DES 3 (after evaporation of heptane and ethanol) in deuterium oxide at 25 ºC. The structure and numbering of the DES is also depicted.

## References

1 A. B Pereiro and A. Rodríguez, *Ind. Eng. Chem. Res.*, 2009, **48**, 1579–1585.
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