

Hydrophobic deep eutectic solvents as water-immiscible extractants

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Hydrophobic Deep Eutectic Solvents: A New Generation of Water-Immiscible Extractants

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Hydrophobic deep eutectic solvents (DESs) are presented for the first time. They consist of decanoic acid and various quaternary ammonium salts. The effect of the alkyl chains on the hydrophobicity and the equilibrium of the two phase DES-water system were investigated. These new DESs were successfully evaluated for the recovery of volatile fatty acids from diluted aqueous solutions.

Introduction

DESs can be defined as mixtures of two or more compounds, a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), that forms a liquid upon mixing with melting points far below that of the individual components, due to self-association.^{1,2} DESs are considered as green solvents sharing the promising solvent characteristics of ILs. Generally, it is assumed that DESs show a low volatility, have a wide liquid range, are water-compatible, non-flammable, non-toxic, biocompatible and biodegradable.^{1,3,4} Their properties can be tuned by the proper selection of the individual components in terms of molecular structure, chemical nature, ratio and water content.^{1,3,4} The major advantages of DESs over ILs are their lower prices and easy preparation. Simply mixing the two solid constituents at moderate temperatures results in a liquid DES, without the need for a solvent or complex purification steps.^{3,5-7} These features make DESs potential alternatives to replace conventional organic solvents as well as ILs.

Due to their hydrogen bonding ability, DESs are generally hydrophilic and thus dissolve rather easily in an aqueous environment. In this work, we present hydrophobic DESs for the first time. To the best of our knowledge, no hydrophobic DESs have been reported yet. This new class of DESs widens its field of applications to include water immiscible solvents. Many processes

could become more effective by using these hydrophobic solvents, due to its aforementioned advantages over ILs and conventional solvents. For example, the removal of products from diluted aqueous systems (e.g. removal of detrimental components from wood and pulp for papermaking purpose, e.g. resins, stickies and inks) could be effectively conducted with these newly developed

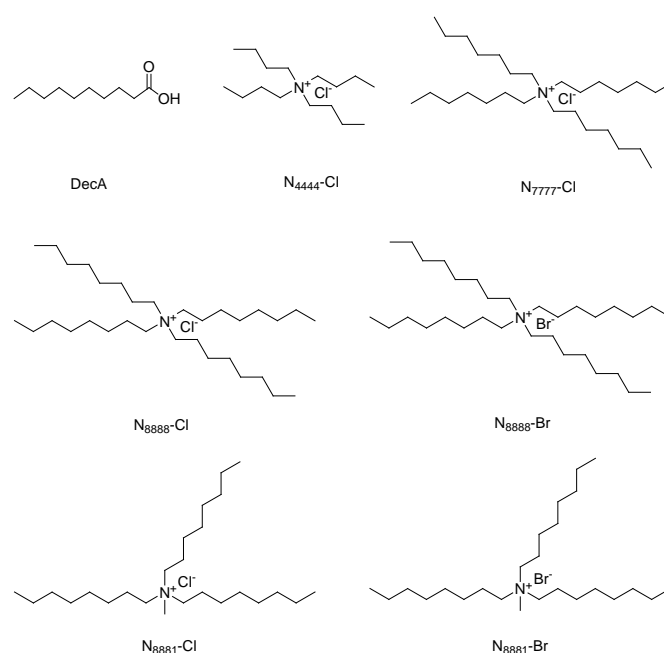


Figure 1: Fatty acid and quaternary ammonium salts used for the preparation of the DESs.

solvents. The ionic character of the HBA of these hydrophobic DESs could offer an advantage in many liquid-liquid extraction processes, as was shown before for ILs.⁸⁻¹²

Here, the first hydrophobic DESs are presented consisting of a fatty acid and a quaternary ammonium salt. DecA is chosen as HBD for its high hydrophobic behaviour in combination with its moderate ability to undergo hydrogen bonding interactions. The solubility of DecA in water is approximately 0.15 mg·g⁻¹ at 20 °C.¹³ As HBAs, 6 quaternary ammonium salts were chosen, namely tetrabutylammonium chloride (N₄₄₄₄-Cl), methyltrioctylammonium chloride (N₈₈₈₁-Cl), tetraheptylammonium chloride (N₇₇₇₇-Cl), tetraoctylammonium chloride (N₈₈₈₈-Cl), methyltrioctylammonium bromide (N₈₈₈₁-Br) and tetraoctylammonium bromide (N₈₈₈₈-Br) (see Figure 1). We will show that the hydrophobic behaviour, and subsequently the leaching of the HBA, depends on the carbon chain length of the quaternary ammonium salt. The water content of the DESs, before and after mixing with water, and all relevant

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Table 1 Physicochemical properties of the prepared deep eutectic solvents (DESs). Both density (ρ) and viscosity (η) data are measured at 25 °C. The water contents correspond to the DES before and after mixing with water. C_{salt} represents the concentration of salt in the water-rich phase after mixing the DES with water

DESs	ρ [kg·m ⁻³]	η [mPa·s]	T_m [°C]	T_d [°C]	$W_{\text{before,H}_2\text{O}}$ [ppm]	$W_{\text{after,H}_2\text{O}}$ [ppm]	C_{salt} [mg·salt/g·water]	$m_{\text{salt,leached}}/m_{\text{salt,DES}}$ [g·g ⁻¹]
DecA:N ₄₄₄₄ -Cl (2:1)	916.8	265.26	-11.95	194.64	8140	69380	155.21	0.3475
DecA:N ₈₈₈₁ -Cl (2:1)	896.4	783.41	-0.05	199.26	2580	62220	16.19	0.0300
DecA:N ₇₇₇₇ -Cl (2:1)	890.7	172.87	-16.65	199.22	7740	23387	13.09	0.0232
DecA:N ₈₈₈₈ -Cl (2:1)	888.9	472.58	1.95	207.66	4640	17849	11.44	0.0193
DecA:N ₈₈₈₁ -Br (2:1)	942.2	576.53	8.95	186.16	3225	42433	13.08	0.0231
DecA:N ₈₈₈₈ -Br (2:1)	929.8	636.36	8.95	192.09	920	20049	14.23	0.0523

physicochemical properties will be presented. Finally, the studied DESs will be evaluated as extractants for volatile fatty acids (VFAs) from diluted aqueous solutions. The obtained extraction efficiencies will be compared with trioctylamine (TOA) as extracting agent.

Results and discussion

The first experiment conducted was the preparation of the DES DecA:N₄₄₄₄-Cl in a 2:1 molar ratio (detailed methods can be found in ESI1). This DES was mixed with water in a mass ratio of about 1:1 (1 gram DES with 1 gram water) as shown in Figure 2. Analysis of the DES phase after mixing with water showed an increase of the water content in the DES phase from approximately 8140 ppm to 69380 ppm (analysis details in ESI2). Furthermore, ion chromatography (IC) proves that around 34.8 % ($m_{\text{salt,leached}}/m_{\text{salt,DES}}$) of the N₄₄₄₄-Cl leached to the water phase, a phenomena that occurs due to the high solubility of N₄₄₄₄-Cl in water (see ESI3). The leaching is confirmed with ¹H-NMR spectroscopy of the top (DES-rich) phase, as is presented in ESI4. N₄₄₄₄-Cl peaks exhibit a similar decrease in intensity after the DES is mixed with water. Considering the obtained results for the DES prepared with N₄₄₄₄-Cl, quaternary ammonium salts with higher hydrophobicity were investigated.

The research continued with the quaternary ammonium salt N₈₈₈₁-Cl as HBA, since it was hypothesised that this quaternary ammonium salt was more hydrophobic due to its longer carbon chains. For N₈₈₈₁-Cl it was shown that only 3.0 % leached to the water phase. This is more than one order of magnitude smaller than the leaching of N₄₄₄₄-Cl. The water content of the DES prepared with N₈₈₈₁-Cl was 2580 ppm. Despite the fact that this is lower than the initial water content of DecA:N₄₄₄₄-Cl (2:1), the water contents of the DES phase after mixing with water are similar. This could be explained by the methyl group on the quaternary ammonium salt N₈₈₈₁-Cl, inducing less steric hindrance for the water to have contact with the charged groups.

Since these results were not satisfactory enough, it was decided to shift the investigation to quaternary ammonium salts with four



Figure 2: (left) pure DES DecA:N₄₄₄₄-Cl (2:1) and (right) DecA:N₄₄₄₄-Cl (2:1) after mixing with water.

alkyl chain lengths of 7 or 8 carbon atoms. These DESs were expected to be more hydrophobic due to the longer alkyl chains and the symmetry of the cation. This is related to the enhancement of the steric hindrance avoiding the accessibility of water to the charged core of the salt.

The DESs DecA:N₇₇₇₇-Cl (2:1) and DecA:N₈₈₈₈-Cl (2:1) showed, after preparation, water contents of 7740 and 4640 ppm. Interestingly, the water contents of the DESs prepared with N₇₇₇₇-Cl and N₈₈₈₈-Cl were higher in comparison to those in the DES prepared using N₈₈₈₁-Cl as HBA. A plausible explanation that could be given for the higher water contents is the fact that water is an impurity of the quaternary ammonium salts (purities of N₈₈₈₁-Cl, N₇₇₇₇-Cl, N₈₈₈₈-Cl and are respectively 97%, 95% and 98% and are not specified). Additionally, hygroscopicity of the salts can play a role, although its contribution is not clear.

After mixing the hydrophobic DESs with water, the top layer contains more water than before. DecA:N₇₇₇₇-Cl (2:1) has a higher water content compared to DecA:N₈₈₈₈-Cl. This was expected, since the carbon chains of N₇₇₇₇-Cl are shorter than those of the octyl based quaternary ammonium salt. The same trend is observed for the leaching, for longer alkyl chains of the HBA less salt is transferred to the water-rich phase. Besides a decrease of salt anion concentration in the bottom (water-rich) phase, only a slight reduction of the HBA was detected in the top phase for salts other than N₄₄₄₄-Cl (ESI4). This is probably related to the hydrophobicity of the DES, which increases with increasing alkyl chain length. A change in anion from chloride to bromide for the DESs prepared with the quaternary ammonium salts N₈₈₈₁ and N₈₈₈₈, showed no clear correlation.

Table 1 presents the physicochemical properties (densities, dynamic viscosities, decomposition temperatures, melting points and water contents) of the newly prepared hydrophobic DESs. Experimental details are available as ESI5 to ESI7.

From the analysis of the physicochemical properties the following was observed: the densities at 25 °C are within the range of 889 to 942 kg·m⁻³, which is considerably lower than found for most hydrophilic DESs and water.⁴ The low densities of these DESs can be explained by the low densities of both constituents used to prepare the DES. The viscosities are moderate, varying between 173 to 783 mPa·s at 25 °C. The large differences can be associated with the strength of interaction between the HBD and HBA. Furthermore, the following trends are observed: (i) the longer the alkyl chain length, the higher the viscosity, and (ii) salts containing a bromide anion have higher viscosities compared to those containing a

chloride anion. This is in agreement with the trend observed for ILs.^{14,15} The decomposition temperatures are rather high, which allows the use of the DESs at elevated temperatures. In combination with the low melting points, this results in a wide thermal operating window. In contrast to an earlier reported DecA based DES, no deprotonation of the acid could be observed for either of the solvents presented here. The C=O stretch shows a single sharp peak for pure DecA, which is broadened, but maintained for all quaternary ammonium salt based DESs (see ES18). This could be justified by the fact that, the ammonium cation of the HBA is unable to be protonated in contrast to the amide of lidocaine.¹⁶

The prepared hydrophobic DESs were evaluated for the extraction of VFAs (acetic, propionic and butyric acid) from diluted aqueous solutions. Amine-based extractants (e.g., TOA) are conventionally used for the extraction of carboxylic acids.¹⁷ Usually, these long-chain aliphatic amines are dissolved in water-immiscible diluents, such as octanol, in order to increase their extracting power. Yang and co-workers¹⁸ explored the effect of pH on the extraction of acetic, propionic and butyric acid using a tertiary amine (Alamine 336) and a quaternary amine (Aliquat 336). The studied amines had been used as single extractants and were also dissolved in two water-immiscible organic solvents (kerosene and 2-octanol). It was found that Aliquat 336 has the capability of extracting both dissociated and undissociated forms of the acids, whereas Alamine 336 only extracts the dissociated form of the acids. In this work, pure TOA was used as extractant in order to compare with the newly prepared hydrophobic DESs. The extraction efficiencies of the DESs and of the pure TOA for each VFA are listed in Table 2. The extraction efficiencies, E , were calculated from the VFA concentration in the water-rich phase before, $C_{VFA,0}^{aq}$, and after the extraction, $C_{VFA,1}^{aq}$:

$$\text{Extraction efficiency : } E [\%] = \frac{C_{VFA,0}^{aq} - C_{VFA,1}^{aq}}{C_{VFA,0}^{aq}} \times 100\% \quad (1)$$

Table 2 Extraction efficiencies of acetic, propionic and butyric acid from diluted aqueous solutions with the reported DESs and triethylamine (TOA)

DESs ^a	E [%]		
	Acetic Acid	Propionic Acid	Butyric Acid
DecA:N ₈₈₈₁ -Cl (2:1)	38.0	70.5	89.8
DecA:N ₇₇₇₇ -Cl (2:1)	32.0	76.5 ^b	91.5 ^b
DecA:N ₈₈₈₈ -Cl (2:1)	25.0 ^b	52.7	81.3
DecA:N ₈₈₈₁ -Br (2:1)	29.7	63.4	83.1
DecA:N ₈₈₈₈ -Br (2:1)	30.6	65.9	87.4
TOA	18.6	45.9	73.5

^a DecA:N₄₄₄₄-Cl was not further investigated due to the high leaching of the salt.

^b The top phase (DES phase) was turbid.

The studied hydrophobic DESs show higher extraction efficiencies for the VFAs compared to TOA. The chemical/structural nature of these DESs favours the extraction of VFAs, due to the hydrogen bonding ability in combination with the ionic character of the salt. This results in higher extraction efficiencies than the ones obtained with TOA. Additionally, these new solvents could have the capability of extracting both dissociated and undissociated forms of

the acid, broadening the application of hydrophobic DESs for different pH environments. This is in agreement with the previously mentioned behaviour of Aliquat 336 and Alamine 336.¹⁸ When hydrophobic DESs are used as extractants, the extraction efficiency increases with the alkyl chain length of the VFA, due to the increase of the dispersive interactions between the used solvents and the VFAs (as expected). The highest extraction efficiencies for all the VFAs were found when using DecA:N₈₈₈₁-Cl (2:1) (asymmetric ammonium) as solvent. This can be related with the lower steric hindrance effect of the alkyl chains, which increases the accessibility not only of the VFAs but also of the water. This is in agreement with the lower hydrophobicity of this DES. By changing the N₈₈₈₁-Cl for a symmetric salt (such as N₈₈₈₈-Cl and N₇₇₇₇-Cl), the extraction efficiencies decrease with the increase of the alkyl chain of the salt, due to the higher contribution of the steric hindrance. Exceptional cases were found for the extraction of propionic and butyric acid using DecA:N₇₇₇₇-Cl (2:1), where higher extraction efficiencies are observed compared to the ones obtained using DecA:N₈₈₈₁-Cl (2:1) as extracting agent. This can be explained by the fact that the DES phase was still turbid, even after 90 min of centrifuging.

Conclusions

For the first time hydrophobic DESs are developed by combining DecA as HBD and quaternary ammonium salts as HBA. The high hydrophobicity can be concluded from the low water contents after mixing with water (~1.8 wt%) and the low leaching of the quaternary ammonium salts (~1.9 wt%). Generally, water content and salt leaching decrease with increasing carbon chain length. The extraction efficiencies increase with increasing chain length, and thus hydrophobicity, of the VFAs. The extraction efficiencies of the VFAs showed that the innovative hydrophobic DESs perform better in all cases than the conventional extraction medium TOA. This can be explained by the nature of these innovative solvents.

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References

1. Q. Zhang, K. De Oliveira Vigier, S. Royer, and F. Jérôme, *Chemical Society reviews*, 2012, **41**, 7108–46.
2. A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, and R. K. Rasheed, *Journal of the American Chemical Society*, 2004, **126**, 9142–7.
3. E. L. Smith, A. P. Abbott, and K. S. Ryder, *Chemical reviews*, 2014, **114**, 11060–82.
4. M. Francisco, A. van den Bruinhorst, and M. C. Kroon, *Angewandte Chemie (International ed. in English)*, 2013, **52**, 3074–85.
5. Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, and Y. H. Choi, *Analytica chimica acta*, 2013, **766**, 61–8.
6. C. Ruß and B. König, *Green Chemistry*, 2012, **14**, 2969–2982.
7. H. Zhao and G. A. Baker, *Journal of Chemical Technology & Biotechnology*, 2013, **88**, 3–12.
8. D. Parmentier, S. J. Metz, and M. C. Kroon, *Green Chemistry*, 2013, **15**, 205–209.
9. A. Berthod, M. J. Ruiz-Angel, and S. Carda-Broch, *J Chromatogr A*, 2008, **1184**, 6–18.
10. G. Tian, in *Green Solvents II*, Springer, 2012, pp. 119–153.
11. N. R. Rodriguez, B. S. Molina, and M. C. Kroon, *Fluid Phase Equilibria*, 2015, **394**, 71–82.
12. C. Li, D. Li, S. Zou, Z. Li, J. Yin, A. Wang, Y. Cui, Z. Yao, and Q. Zhao, *Green Chemistry*, 2013, **15**, 2793–2799.
13. A. Ralston and C. Hoerr, *The Journal of Organic Chemistry*, 1942, **7**, 546–555.
14. M. A. Rocha, C. M. Neves, M. G. Freire, O. Russina, A. Triolo, J. A. Coutinho, and L. M. Santos, *The Journal of Physical Chemistry B*, 2013, **117**, 10889–10897.
15. D. Rooney, J. Jacquemin, and R. Gardas, in *Ionic Liquids*, Springer, 2010, pp. 185–212.
16. P. J. Griffin, T. Cosby, A. P. Holt, R. S. Benson, and J. R. Sangoro, *The Journal of Physical Chemistry B*, 2014, **118**, 9378–9385.
17. V. S. Kislik, *Solvent extraction: classical and novel approaches*, Elsevier, 2011.
18. S. T. Yang, S. A. White, and S. T. Hsu, *Industrial & engineering chemistry research*, 1991, **30**, 1335–1342.