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DOI:
[10.1039/c6cc06105b](10.1039/c6cc06105b)

Document status and date:
Published: 12/08/2016

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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COMMUNICATION

Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents†

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Hydrophobic deep eutectic solvents were used for the first time for the removal of metal ions from non-buffered water. It was shown that the extraction occurs *via* an ion exchange mechanism in which all transition metal ions could be extracted with high distribution coefficients, even for high Co^{2+} concentrations and low DES/water mass ratios. Maximum extraction efficiency could be reached within 5 s and regeneration was possible.

Contamination of water with high metal salt concentrations makes water undrinkable and for some metals (*e.g.* Cd, Pb, As) even traces are highly toxic.[1,2] To avoid this environmental and health issue, the removal of metal salts from water is of major importance. Moreover, their extraction from water can be of interest from an economical perspective, since certain metal salts are getting scarce (*e.g.* Pd, Au, Ag), making them expensive. For these reasons, it is of importance to remove metal salts from an aquatic environment.

A generally accepted and often applied technique for the removal of metal salts from water is liquid–liquid extraction with hydrophobic solvents.[3] Extraction offers advantages over other methods such as the possibility of conducting the removal in a continuous mode, the use of rather easy to operate equipment, simple reactor design, and the need for only small amounts of extractant.[4]

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc06105b

Most investigations into the extraction of metal salts from an aquatic environment have focused on the use of conventional organic water-immiscible solvents such as dodecane, toluene and kerosene. The main disadvantages of these solvents are their toxicity, volatility, and flammability.[5]

More recently, ionic liquids (ILs) have been used for the removal of metal salts from water.[6] ILs are salts composed of a cation and an anion interacting with each other *via* electrostatic forces with a melting temperature lower than 100 °C, typically liquid at room temperature.[7,8] ILs are designer solvents, offering advantages over conventional solvents such as low vapour pressures. However, a major disadvantage of ILs is their extended synthesis and purification. This makes the production of ILs expensive.

Newly developed designer solvents are the so-called deep eutectic solvents (DESs). DESs are composed of two constituents associated with each other *via* hydrogen bonds and presumably van der Waals interactions.[9] These attractive interactions between the different molecules stabilize liquid configurations and hence lower the melting temperature of the mixture with respect to the melting temperature of the pure substances.[9] The first DESs reported were composed of choline chloride and amides.[10] The physicochemical properties of DESs can be tuned *via* selection of the DES' constituents in terms of chemical ratio and nature, molecular structure, and water content. A major advantage of DESs over ILs is their straightforward preparation.

Following the publication of a wide range of hydrophilic DESs, hydrophobic DESs have been developed very recently, which could replace expensive hydrophobic ILs.[11,12] These hydrophobic DESs were tested for the extraction of volatile fatty acids (VFAs) and biomolecules from an aquatic environment.[11,12] Here, the focus is on the use of hydrophobic DESs for the removal of metal salts from an aquatic environment. Studies into the extraction mechanism of hydrophobic ILs indicated that the metal part of the metal salt forms complexes with deprotonated acid groups, while negatively charged chloride interacts with the positively charged ammonium of the IL.[13] Hence, a DES was chosen that consists of decanoic acid and lidocaine since it was

recently shown that approximately 25% of the decanoic acid/lidocaine DES in a 2 : 1 molar ratio was ionized.[14,15]

A hydrophobic DES that could enable the removal of metal salts or metal ions from water is of interest for many industries. For example, in the pulp and paper industry this could involve the removal of transition metals, such as Mn and Fe, from fibre suspensions prior to peroxide bleaching, which could replace the use of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and other acidic environments.[16,17] Moreover, the newly developed DESs could be used for regulating the final metal contents of dissolving pulp and for the removal of metal ions from wood raw material.[16,17] Furthermore, it could be of interest to investigate whether silica and calcium ions could be removed from water and/or from equipment. This is to avoid precipitations inside the equipment. Finally, it could be interesting to determine whether these DESs could be used in ion exchangers.

In this communication, the extraction of different metal chloride salts from water using hydrophobic DESs is investigated for the first time. The pH of the water phases was not changed to improve extraction efficiency as published recently for metal salts in acid solutions.[18] Thus, only metal salt and water were present in the aqueous phase, which has not been investigated before to the best of our knowledge. The investigated hydrophobic DESs consist of decanoic acid (DecA) and lidocaine (Lid) in 2 : 1, 3 : 1 and 4 : 1 molar ratios. The measured distribution coefficients (D) for the ions of the metal salts cobalt chloride ($CoCl_2$), nickel chloride ($NiCl_2$), iron chloride ($FeCl_2$), manganese chloride ($MnCl_2$), zinc chloride ($ZnCl_2$), copper chloride ($CuCl_2$), sodium chloride ($NaCl$), potassium chloride (KCl) and lithium chloride ($LiCl$) is reported. Furthermore, different concentrations and DES/water mass ratios (ϕ_{DES}) are tested for the metal salt $CoCl_2$. Finally, the regeneration of the DESs is investigated.

Various physicochemical properties (water contents, densities, and viscosities before and after mixing) and NMR, FTIR, and TGA spectra were measured. More information on these properties and the preparation of the DESs, the mixing of DESs with water and the extractions can be found in ESI,† S1–S7. The water contents of the DESs show an increment after mixing with water. The densities also increased after mixing with water, while the viscosities decreased. The degradation temperatures varied between 182.5 and 192.4 °C, which show that these DESs are rather thermally stabile. The concentration of the organic substance (DES) in the water phase after mixing with water was 7.9–16.1 mg per g of water. NMR analysis of the pure DESs showed that no chemical reaction occurred between the constituents of the DES and FTIR analysis demonstrated that the DESs were partially deprotonated.

The distribution coefficients of the metal ions over the water and hydrophobic DES phases were determined using five separate experiments and are presented in Table 1. For all experiments reported in Table 1 an initial concentration of 1.0 g L^{-1} metal ion was used. The measured D values were calculated based on analysis of the water phase using the equation:

$$D = \frac{C_{\text{ion},0}^{\text{aq}} - C_{\text{ion},1}^{\text{aq}} \cdot \left(\dfrac{V_1^{\text{aq}}}{V_0^{\text{aq}}}\right)}{C_{\text{ion},0}^{\text{aq}}}$$

Table 1 Distribution coefficients (D) of metal cations and chloride anions over the hydrophobic DESs and water phases. For $D \to 0$, the ion remains in the aqueous phase, while the ion is completely extracted into the DES when $D \to 1$. For the explanation of the different experiments also see the ESI S1. The pH values of the aqueous phase before and after extraction can be found in Tables S5 and S6 of the ESI

		DecA : Lid (2 : 1)	DecA : Lid (3 : 1)	DecA : Lid (4 : 1)
Exp. 1	Co	>0.996 ± 0.001	>0.996 ± 0.001	0.983 ± 0.002
	Cl	0.113 ± 0.002	0.078 ± 0.008	0.101 ± 0.059
Exp. 2	Fe	>0.992 ± 0.001	>0.991 ± 0.001	>0.991 ± 0.001
	Cl	0.197 ± 0.003	0.080 ± 0.001	0.113 ± 0.007
Exp. 3	Mn	>0.992 ± 0.001	>0.991 ± 0.001	0.983 ± 0.004
	Cl	0.086 ± 0.002	0.081 ± 0.027	0.065 ± 0.011
Exp. 4	K	0.457 ± 0.001	0.397 ± 0.011	0.457 ± 0.001
	Cl	0.141 ± 0.001	0.078 ± 0.031	0.072 ± 0.001
Exp. 5	Co	0.990 ± 0.001	0.946 ± 0.012	0.777 ± 0.008
	Ni	>0.996 ± 0.001	0.983 ± 0.001	0.880 ± 0.004
	Zn	>0.995 ± 0.001	>0.995 ± 0.001	>0.995 ± 0.001
	Cu	>0.996 ± 0.001	>0.996 ± 0.001	>0.996 ± 0.001
	Na	0.195 ± 0.001	0.140 ± 0.009	0.127 ± 0.040
	K	0.211 ± 0.028	0.161 ± 0.018	0.134 ± 0.005
	Li	0.266 ± 0.015	0.166 ± 0.001	0.128 ± 0.036

satisfying $0 \leq D \leq 1$. In this formula $C_{\text{ion},0}^{\text{aq}}$ and $C_{\text{ion},1}^{\text{aq}}$ are the ion concentrations before (0) extraction and after (1) extraction, while V_0^{aq} and V_1^{aq} are the volumes of the aqueous phase before and after extraction. This volume correction was needed because some of the water was transferred to the DES phase during contact.

As shown in Table 1, most metal cations are extracted with high efficiencies ($D \to 1$). The experiments with only single metal salts in the water phase all show high D for the cationic metal ions, except for K^+, which can be explained by the preference of fatty acids to bind with transition metals and not with alkali metals.[19] Two observations should be mentioned.

Some small precipitations were observed in the water phase after extraction of Fe^{2+}, which can be explained by the fact that it precipitates at higher pH.[13] After extraction of Mn^{2+} the DES phase formed a gel/solid like phase, which is most likely caused by the interaction of the manganese cation with one of the constituents of the DES. For K^+, the reported hydrophobic DESs show a decrease in D with an increase of the decanoic acid to lidocaine ratio. This might be caused by the increase of hydrophobicity with an increase of decanoic acid in the DES. The experiment in which a combination of metal ions is extracted, experiment 5, shows high D for all transition metal ions, although the D values of Ni and Co decrease with an increase of the decanoic acid to lidocaine ratio. Furthermore, it can be observed that the extraction of the alkali metal ions in such a mixture of metal ions is rather low. This was already expected from the literature on the extraction of metal salts with ILs.[13,19] Fig. 1 shows that with an increase in the concentration of the metal ion Co^{2+}, D decreases. The higher the decanoic acid to lidocaine ratio, the higher the decrease in D.

For the chloride ions it was found that the D is small, which was not expected from previous research into the extraction
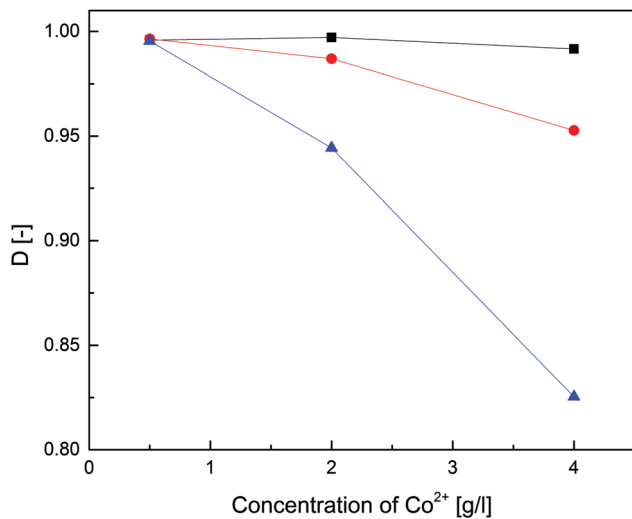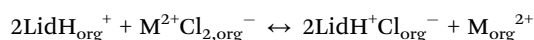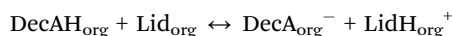
Fig. 1 Distribution coefficient (D) with increasing initial concentration of Co^{2+} in the water phase. ■ = DecA : Lid (2 : 1), ● = DecA : Lid (3 : 1) and ▲ = DecA : Lid (4 : 1). The lines are added for clarification purposes.
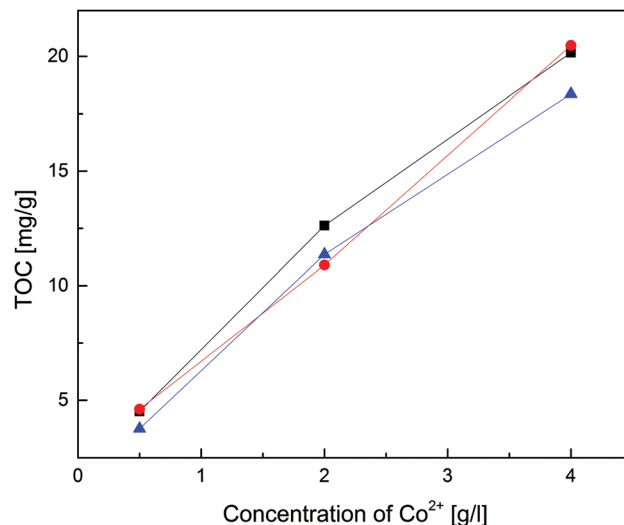

Fig. 2 TOC values with increasing initial concentration of Co^{2+} in the water phase. ■ = DecA : Lid (2 : 1), ● = DecA : Lid (3 : 1) and ▲ = DecA : Lid (4 : 1). The lines are added for clarification purposes.

mechanism of metal salts with similar fatty acid based ILs.[6,13] The low distribution coefficient of the DESs for the extraction of chloride ions may be explained by the interaction of the protonated lidocaine with chloride anions. Most likely, lidocaine hydrochloride is formed, which has a higher water solubility in comparison to lidocaine itself ($50 \ mg \ mL^{-1}$ for lidocaine chloride vs. $0.41 \ mg \ mL^{-1}$ for lidocaine). Thus, upon extraction of the metal ion into the DES phase, protonated lidocaine is transferred simultaneously to the water phase (forming lidocaine hydrochloride), which is an ion exchange process:

$$DecAH_{org} + Lid_{org} \leftrightarrow DecA_{org}^- + LidH_{org}^+$$

$$2LidH_{org}^+ + M^{2+}Cl_{2,org}^- \leftrightarrow 2LidH^+Cl_{org}^- + M_{org}^{2+}$$

This hypothesis was tested by varying the initial concentration of the metal ion to investigate if the concentration of the total organic carbon (TOC) in the water phase increased with an increasing amount of Co^{2+}. The change in TOC values with initial Co^{2+} concentration, as shown in Fig. 2, supports that most likely Co^{2+} is exchanged with the positively charged lidocaine. To strengthen this assumption, NMR analysis was performed on the water phases after extraction (see the ESI,† S8, for the NMR spectra). Table S7 of the ESI,† S8, clearly shows that with an increase of extracted metal ions the amount of lidocaine relative to the amount of decanoic acid in the aqueous phase becomes higher, indicating that indeed an ion exchange mechanism occurs. A small amount of decanoic acid will always dissolve in the water phase due to its limited water solubility (an amount that does not increase with an increase in the amount of metal ions that are extracted), which explains the relatively high amount of decanoic acid compared to lidocaine for the extraction of $0.5 \ g \ L^{-1} \ Co^{2+}$.

ϕ_{DES}, which is defined as the DES/water mass ratio, is varied in order to examine its influence on the D of Co^{2+} (Fig. 3). The results

show that even for low ϕ_{DES} ($\phi_{DES} < 0.1$), D values of 0.796 and higher can be achieved. Moreover, it was found that high D for Co^{2+} as reported here could be achieved within 5 s for all the 3 DES ratios (ESI,† S9).

Finally, it was investigated whether regeneration of the DES could be achieved. Sodium oxalate ($0.1 \ M \ Na_2C_2O_4$) was used for the regeneration of the DES, since previous research into ILs showed that this was an efficient stripping solution.[20,21] This solution was shaken with an equal weight of DES for 1 h. Analysis of the water phase shows that D becomes approximately 0.85–0.90 for the regeneration of Co^{2+} into the water phase (see also Table 2). After regeneration with the DESs, it was verified whether Co^{2+} extraction for the water phase was still feasible, even though the DES cannot be reused infinitely
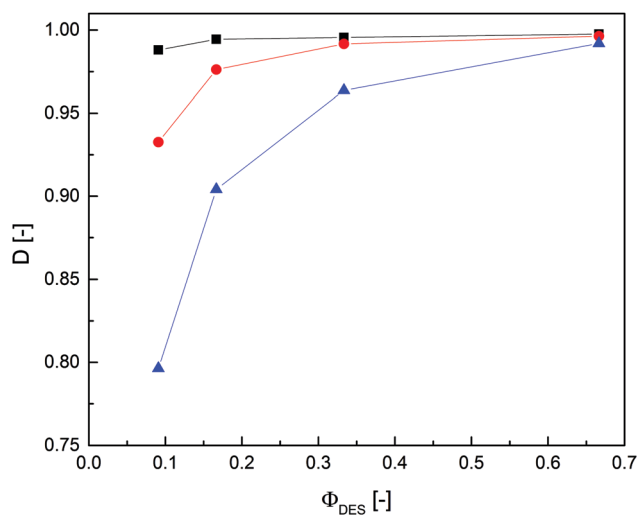

Fig. 3 Distribution coefficient (D) with increasing DES/water mass ratios. ■ = DecA : Lid (2 : 1), ● = DecA : Lid (3 : 1) and ▲ = DecA : Lid (4 : 1). The lines are added for clarification purposes.

Table 2 Distribution coefficients (D) for the extraction and regeneration of Co^{2+} for the DESs

		DecA:Lid (2:1)	DecA:Lid (3:1)	DecA:Lid (4:1)
Extraction	Co^{2+}	>0.996	>0.996	0.983
Regeneration	Co^{2+}	0.848	0.867	0.899
Extraction after regeneration	Co^{2+}	0.706	0.994	0.995

due to leakage to the water phase. The results show that for the 3:1 and 4:1 ratios of decanoic acid to lidocaine extraction was still possible with high D. It is noted that the water phase now became turbid after extraction, even after centrifugation. The most plausible explanation for this is a slight increase in the density of the DES. For the 2:1 ratio of decanoic acid to lidocaine the D was only 0.706 after regeneration and it is noted that the volume of the DES phase decreased for the extraction after regeneration.

The ability of the hydrophobic DESs to extract metal ions is compared with another class of innovative designer solvents, *i.e.* ILs, based on fatty acids and quaternary ammonium salts.[6,13] Experiments without pH control of the water phase showed metal ion extraction lower than in our case, while they extracted more chloride ions.[6] This can be explained by the difference in the extraction mechanism, which is full metal salt extraction in the case of the ILs.[22] When for ILs the pH of the water phase is adjusted, similar metal ion removal could be achieved as with the DESs.[13]

To conclude, it is shown for the first time that metal ion extraction from a non-buffered aquatic environment is possible with hydrophobic DESs. An ion exchange process occurs, in which the positively charged metal ion is most likely exchanged with the partially positively charged lidocaine. This claim is supported by an increase of the TOC value upon increasing the metal salt concentration and NMR spectra. These analyses show that only a small amount of decanoic acid is present in the water phase after extraction. All transition metal ions could be removed with high values for the distribution coefficient, as well in a pure metal salt solution as in a mixed metal salt solution. Even at low ϕ_{DES}, D values for Co^{2+} were close to unity. A time experiment shows that within 5 s the same D can be achieved as after shaking for 1 h. Finally, it was proven that regeneration with a $Na_2C_2O_4$ solution is possible. However, efficient reuse is only possible for the DES with a higher decanoic to lidocaine ratio (3:1 and 4:1).

Overall, this communication shows the potential of the use of hydrophobic DESs for the removal of metal ions from an aquatic environment. Further research can be directed into two routes. One route can aim at finding other cheaper and greener constituents that can act as ion exchange constituents. Probably, the most preferable route is finding a constituent that is able to be protonated without becoming hydrophilic when taking up a chloride anion and so conduct a complete metal salt extraction.

Notes and references

1 P. Madoni and M. G. Romeo, *Environ. Pollut.*, 2006, **141**, 1–7.
2 T. Martin and D. Holdich, *Water Res.*, 1986, **20**, 1137–1147.
3 J. Rydberg, *Solvent extraction principles and practice, revised and expanded*, CRC Press, 2004.
4 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657–1665.
5 M. L. Dietz, *Sep. Sci. Technol.*, 2006, **41**, 2047–2063.
6 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.
7 J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.
8 P. Wasserscheid and T. Welton, *Ionic liquids in synthesis*, Wiley Online Library, 2008, vol. 1.
9 M. Francisco, A. van den Bruinhorst and M. C. Kroon, *Angew. Chem., Int. Ed.*, 2013, **52**, 3074–3085.
10 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70–71.
11 D. J. G. P. van Osch, L. F. Zubeir, A. van den Bruinhorst, M. A. A. Rocha and M. C. Kroon, *Green Chem.*, 2015, **17**, 4518–4521.
12 B. D. Ribeiro, C. Florindo, L. C. Iff, M. A. Coelho and I. M. Marrucho, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2469–2477.
13 D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans and M. C. Kroon, *Ind. Eng. Chem. Res.*, 2015, **54**, 5149–5158.
14 P. J. Griffin, T. Cosby, A. P. Holt, R. S. Benson and J. R. Sangoro, *J. Phys. Chem. B*, 2014, **118**, 9378–9385.
15 K. Bica, J. Shamshina, W. L. Hough, D. R. MacFarlane and R. D. Rogers, *Chem. Commun.*, 2011, **47**, 2267–2269.
16 R. Susilo, R. Chandraghatgi and P. Englezos, *Pulp Pap. Can.*, 2005, **106**, 47–50.
17 E. Norkus, J. Vaičiūnienė and T. Vuorinen, *Carbohydr. Polym.*, 2006, **66**, 316–320.
18 E. E. Tereshatov, M. Yu. Boltoeva and C. M. Folden, *Green Chem.*, 2016, **18**, 4616–4622.
19 J. Preston, *Hydrometallurgy*, 1985, **14**, 171–188.
20 D. Parmentier, S. Paradis, S. J. Metz, S. K. Wiedmer and M. C. Kroon, *Chem. Eng. Res. Des.*, 2016, **109**, 553–560.
21 D. Parmentier, Y. A. Valia, S. J. Metz, O. S. Burheim and M. C. Kroon, *Hydrometallurgy*, 2015, **158**, 56–60.
22 D. Parmentier, T. Vander Hoogerstraete, D. Banerjee, Y. A. Valia, S. J. Metz, K. Binnemans and M. C. Kroon, *Dalton Trans.*, 2016, **45**, 9661–9668.