

Supporting information

Removal of Alkali and Transition Metal Ions from Water with Hydrophobic Deep Eutectic Solvents

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ESI1: Materials, preparation and metal salt extraction method

Materials for the preparation of the DESs and the extraction of the metal salts

Decanoic acid (DecA) and lidocaine (Lid) were both purchased from Sigma-Aldrich with purities of >98% and >99%, respectively (see Figure S1 for the chemical structures of the components of the DESs). $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was ordered from Alfa Aesar with a purity of >98%. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ were supplied by Boom laboratory with purities of >99% and higher. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl and KCl were purchased from VWR Chemicals with purities of, respectively, >99%, >99.99% and >99.99%. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and LiCl (Merck) had purities >99%, while ZnCl_2 was supplied by Sigma-Aldrich with a purity of >99%.

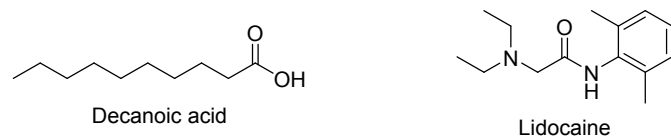


Figure S1: Starting components of the DESs.

Preparation of the DESs

The three DESs were all prepared by the following procedure. DecA (for DecA:Lid (2:1) 89.28 g, DecA:Lid (3:1) 103.20 g and DecA:Lid (4:1) 111.93 g) was weighed in a 250 mL flask and Lid (for DecA:Lid (2:1) 60.72 g, DecA:Lid (3:1) 46.80 g and DecA:Lid (4:1) 38.07 g) was added via a solid funnel or via weighing it off in a weighing boat, after which it was added to the DecA. The flask was closed with a cap and parafilm was wrapped around the cap and the flask to ensure that the DESs were not able to uptake water. Next, the flask was heated to 35 °C in an oil bath until a clear liquid appeared. The inside of the flask was rinsed with the DESs to ensure that all solids were in the liquid phase, after which the DESs were heated again up to 35 °C until a clear homogenous mixture was formed. Before use, the DESs were left overnight at room temperature to investigate if recrystallization occurred.

Mixing of DESs with water

The DESs were mixed with water to examine the amount they would uptake upon contact. Approximately 23 g of DES was mixed with 23 mL of water in centrifuge tubes of 50 mL (CELLSTAR®), which were shaken in an IKA KS 4000 I incubating shaker and centrifuged for 30 min at 12.000 RPM in a Sigma 2-16 KL centrifuge. The top-phase, DES phase, was analyzed for its water content with a Karl-Fischer 899 coulometer titration apparatus. The density of the DES was measured with an Anton-Paar SVM 3000 Stabinger Viscometer and viscosity with a Anton Paar Physica MCR 301 rheometer. The bottom-phase was analyzed for its total organic carbon (TOC).

Metal salt extraction method

Five different stock solutions were prepared. Four stock solutions constituted of a single metal complex, being $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ or KCl and one stock solution was composed of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl, KCl and LiCl. The specific reasons for this are listed below and these numbers correlate to experiment numbers as depicted in Table 1 of the main paper: 1) The stock with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was also used for further research into extraction kinetics and regeneration. 2) For $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ it was checked whether a precipitation would form as was shown in literature for ionic liquids (ILs). 3) $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ showed from initial experiments the formation of a gel like DES phase. 4)

Analysis showed that in some cases the values of sodium and potassium showed similar peaks in analysis with induced coupled plasma (ICP) 5) The stock with a combination of the salts was used to test the versatility and selectivity of the extraction method. The results of experiment 3 led to the exclusion of MnCl_2 from this stock. For all the experiments a concentration of 1.0 g/L of metal ion was used. For experiment 5, the measurement of the chloride concentration after extraction was considered unreliable. The deviations were probably caused by the cumulative variations in distribution coefficients of the alkali cations.

For the extraction first an approximate amount of 10 g of DES was weighed and added to a centrifuge tube (CELLSTAR®) of 50 mL to which 10 mL of metal salt solution was added. The mixture was shaken for 1 h on a Heidolph multireax multivortex shaker with 1800 RPM ($T = 22\text{ }^\circ\text{C}$) and centrifuged for 10 min at 3000 RPM with a Beckmann Coulter centrifuge. The water phase was analyzed with TOC for the amount of organic substance, ion chromatography (IC) for the chlorides and ICP for the metal ions.

Determination of the volumes of the water phase

The volumes of the water phase are determined by the distance between the volume bars, where a ruler is used for the estimation of the height. The volume of the water phase after extraction is then calculated by multiplying the ratio between the two volumes based between the two bars times that volume.

ESI2: Analytical Methodologies

Karl-Fischer

Karl Fischer analysis with an 899 Coulometer (Metrohm Karl Fischer) was used for measuring the water content of the DESs after preparation and after mixing with water.

Density

An Anton Paar SVM 3000 Stabinger Viscometer is used for measuring the density of the developed DESs between 293.15 to 323.15 K at an atmospheric pressure. In the range of 288.15 to 378.15 K the temperature uncertainty is listed as 0.02 K. The absolute uncertainty of the density is approximately $0.5 \text{ kg}\cdot\text{m}^{-3}$.

Viscosity

The viscosity between 293.15 to 323.15 K is measured with an Anton Paar Physica MCR 301 rheometer.

Thermogravimetric analysis (TGA)

A thermogravimetric analyzer, a Perkin Elmer TGA 4000, was used for studying the decomposition temperature of the DESs. The mass of the samples varied from 7 to 13 mg. The precision and the sensitivity of the balance are $\pm 0.01\%$ and $1 \mu\text{g}$. For the heating of the samples a ceramic crucible was used. The conditions for heating were a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ over a temperature range of 30 to 600 °C where a continuous flow of nitrogen, $20 \text{ mL}\cdot\text{min}^{-1}$ with a pressure 0.2 MPa was used.

Nuclear magnetic resonance of the DESs (NMR)

Nuclear Magnetic Resonance was used for recording both hydrogen (^1H) as carbon (^{13}C) NMR spectra. A Bruker 400 automatic NMR was used. The NMR samples were added to a 8" Wilmad NMR tube (outer diameter of 5 mm) and mixed with deuterated chloroform (CDCl_3). The spectra for the ^{13}C NMR were recorded in 1000 scans with a relaxation time of 5 s. The ^1H NMR were recorded with 128 scans and a relaxation time of 2 s. The NMR spectra were used as obtained and analyzed with MestreNova (version 9.1.0-14011) and ChemBiodraw (version 14.0.0.117).

Nuclear magnetic resonance of the water phases after the extraction experiments (NMR)

Undiluted samples of the water phase after extraction were studied using a ^1H NMR water suppressing pulse sequence. The samples were each added to an 8" Wilmad NMR thin-walled tube (outer diameter of 5 mm) and equipped with an 8" Wilmad insert with an inner capacity of $60 \mu\text{l}$, stem height of 50 mm and stem outer diameter of 2 mm filled with D_2O as lock reference. The water peak was suppressed by using a NOESY-presaturation pulse sequence, Bruker 1D noesygppr1d, at the peak maximum of the water peak (WATER program in Bruker TopSpintm).

The spectra were normalized setting the two protons of the $(\text{CH}_3\text{-CH}_2)_2\text{-N-CH}_2\text{-(C=O)-NH-R}$ in lidocaine to 2.00 (carbon 2 in the figures in ESI8, appears around $4.1 > \delta > 4.4 \text{ ppm}$). The ratio between DecA and Lid was calculated by dividing the resulting integral of the CH_3 of DecA (not numbered in the figures in ESI8, appears around $0.7 > \delta > 0.8 \text{ ppm}$) by 3.

Fourier transform infrared (FTIR)

A PerkinElmer Spectrum Two spectrometer equipped with a Spectrum Two UATR (universal attenuated total reflectance) module was used for measuring the Fourier transformed infrared (FTIR) spectra. The measurements were conducted over a wavenumber range of 450-4000 cm^{-1} . For the pure component 4 scans were used, while 16 scans were used for measuring the DESs. Of every sample a background spectrum was recorded, with which a baseline correction was performed with the PerkinElmer Spectrum software (application version 10.03.08.0135, 2012).

Ion chromatography

The chloride concentrations were measured with a Metrohm 761 Compact ion chromatograph (IC). The column in the IC is a Metrohm Metrosep A Supp 5, 150/4.0 mm. The pre-column is a Metrohm Metrosep A Supp 4/5 Guard. The conductivity detector, chemical suppressor from Metrohm, CO₂ suppressor (Metrohm, type 853) are all built into the ion chromatograph.

The reagents of the mobile phase are 3.2 mM sodium carbonate and 1 mM sodium bicarbonate solution in combination with 1% of acetone. The suppressor liquids are 0.5 M H₃PO₄ with 1% acetone and Milli-Q water with 1% of acetone.

The mobile phase has a flow of 0.7 mL/min and the flow of the suppressor solutions have a flow of 0.4 mL/min. The injection volume is 20 µL and the runtime is 20 min. The detection limit is 0.05-0.10 mg/L, while the upper limit is 80 mg/L.

Induced coupled plasma (ICP)

The ICP is a Perkin Elmer from the type Optima 5300 DV with a Perkin Elmer autosampler of type ESI-SC-4 DX fast. The watercooler used for the ICP is the type 6106 P from Polyscience. The internal standard solution is 10 mg/L Yttrium and the rinse solution is 2% nitric acid. The detection limit varies from 25-750 µg/L and the upper limit is 10000 µg/L. The '>' in Table 2 of the main paper means that the values for that metal ion were lower than the detection limit and thus the extraction is actually higher.

Total organic carbon (TOC)

A Shimadzu TOC-L_{CPH} with a ASI-L Autosampler was used for the analysis of the total organic carbon (TOC) in the water phase. The reagents that are used are 2M hydrochloric acid and 25% phosphoric acid. The detection limit is 1.00 mg/L.

ESI3: Densities and viscosities

Table S1 Experimentally determined densities ρ in $\text{g}\cdot\text{cm}^{-3}$ of the studied pure DESs as function of temperature T in K before mixing with water. The corresponding water contents are 731.3 ± 4.2 ppm for DecA:Lid (2:1), 280.1 ± 4.8 ppm for DecA:Lid (3:1) and 242.7 ± 3.2 ppm for DecA:Lid (4:1). The densities are measured in duplicate from the same batch, the experimental reproducibilities were smaller than the reproducibility specifications of the equipment

T/K	$\rho(\text{DecA:Lid (2:1)})/\text{g}\cdot\text{cm}^{-3}$	$\rho(\text{DecA:Lid (3:1)})/\text{g}\cdot\text{cm}^{-3}$	$\rho(\text{DecA:Lid (4:1)})/\text{g}\cdot\text{cm}^{-3}$
293.15	0.9624	0.9540	0.9461
298.15	0.9583	0.9497	0.9419
303.15	0.9540	0.9454	0.9377
308.15	0.9497	0.9411	0.9335
313.15	0.9455	0.9368	0.9293
318.15	0.9412	0.9325	0.9251
323.15	0.9370	0.9282	0.9208

Table S2 Experimentally determined densities ρ in $\text{g}\cdot\text{cm}^{-3}$ of the studied water saturated DESs as function of temperature T in K after mixing with water. The corresponding water contents are 203263.5 ± 3059.1 ppm for DecA:Lid (2:1), 91977.1 ± 119.2 ppm for DecA:Lid (3:1) and 70064.0 ± 312.4 ppm for DecA:Lid (4:1) . The densities are measured in duplicate from the same batch, the experimental reproducibilities were smaller than the reproducibility specifications of the equipment

T/K	$\rho(\text{DecA:Lid (2:1)})/\text{g}\cdot\text{cm}^{-3}$	$\rho(\text{DecA:Lid (3:1)})/\text{g}\cdot\text{cm}^{-3}$	$\rho(\text{DecA:Lid (4:1)})/\text{g}\cdot\text{cm}^{-3}$
293.15	0.9844	0.9655	0.9549
298.15	0.9800	0.9614	0.9510
303.15	0.9739	0.9571	0.9470
308.15	0.9681	0.9527	0.9430
313.15	0.9630	0.9483	0.9390
318.15	0.9582	0.9439	0.9349
323.15	0.9538	0.9396	0.9308

Table S3 Experimentally determined values of the dynamic viscosity η in mPa·s (at a shear rate of 100 1/s) of the studied pure DESs as function of temperature T in K before mixing with water. The corresponding water contents are 731.3 \pm 4.2 ppm for DecA:Lid (2:1), 280.1 \pm 4.8 ppm for DecA:Lid (3:1) and 242.7 \pm 3.2 ppm for DecA:Lid (4:1). The viscosities are measured in duplicate from the same batch. The deviations are precisions

T/K	$\eta(\text{DecA:Lid (2:1)})/\text{mPa}\cdot\text{s}$	$\eta(\text{DecA:Lid (3:1)})/\text{mPa}\cdot\text{s}$	$\eta(\text{DecA:Lid (4:1)})/\text{mPa}\cdot\text{s}$
293.15	352.5 \pm 0.5	302 \pm 2	197.5 \pm 1.5
298.15	237.5 \pm 4.5	208.5 \pm 3.5	142 \pm 2
303.15	160 \pm 3	141.5 \pm 2.5	100.3 \pm 1.7
308.15	111 \pm 2	98.45 \pm 1.55	71.95 \pm 1.05
313.15	78.6 \pm 1.2	70.2 \pm 1.1	52.7 \pm 0.7
318.15	57.15 \pm 0.85	51.1 \pm 0.7	39.35 \pm 0.45
323.15	42.45 \pm 0.55	38.05 \pm 0.45	29.95 \pm 0.35

Table S4 Experimentally determined values of the dynamic viscosity η in mPa·s (at a shear rate of 100 1/s) of the studied water saturated DESs as function of temperature T in K after mixing with water. The corresponding water contents are 203263.5 \pm 3059.1 ppm for DecA:Lid (2:1), 91977.1 \pm 119.2 ppm for DecA:Lid (3:1) and 70064.0 \pm 312.4 ppm for DecA:Lid (4:1). The viscosities are measured in duplicate from the same batch. The deviations are precisions

T/K	$\eta(\text{DecA:Lid (2:1)})/\text{mPa}\cdot\text{s}$	$\eta(\text{DecA:Lid (3:1)})/\text{mPa}\cdot\text{s}$	$\eta(\text{DecA:Lid (4:1)})/\text{mPa}\cdot\text{s}$
293.15	140.0 \pm 1	168.0 \pm 1.0	136.0 \pm 1.0
298.15	106.0 \pm 1	124.5 \pm 1.5	103.0 \pm 1.0
303.15	84.85 \pm 1.05	93.35 \pm 1.15	77.4 \pm 0.9
308.15	65.2 \pm 1.6	71.2 \pm 0.9	59.1 \pm 0.7
313.15	50.8 \pm 0.1	54.4 \pm 0.6	45.6 \pm 0.5
318.15	40.3 \pm 0.6	41.95 \pm 0.45	35.6 \pm 0.3
323.15	31.4 \pm 0.4	32.6 \pm 0.4	28.15 \pm 0.25

ESI4: pH of the water phases

For the standard extractions, given in the paper as Table 1, the pH of the water phase before and after extraction were determined. These are depicted in Table S5 and S6.

Table S5 pH of the water phases before the extraction

Metal complex(es) dissolved in the water phase	pH
CoCl ₂	5.471
FeCl ₂	2.848
MnCl ₂	5.787
CoCl ₂ , NiCl ₂ , ZnCl ₂ , CuCl ₂ , NaCl, KCl, LiCl	4.372

Table S6 pH of the water phases after extraction

After extraction of the following metal complex(es) from the water phase	pH for DecA:Lid (2:1)	pH for DecA:Lid (3:1)	pH for DecA:Lid (4:1)
CoCl ₂	6.306	5.740	5.184
FeCl ₂	6.829	6.324	5.838
MnCl ₂	6.773	6.278	5.792
CoCl ₂ , NiCl ₂ , ZnCl ₂ , CuCl ₂ , NaCl, KCl, LiCl	6.772	6.295	5.806

ESI5: NMR spectra

DecA:Lid (2:1)

Carbon

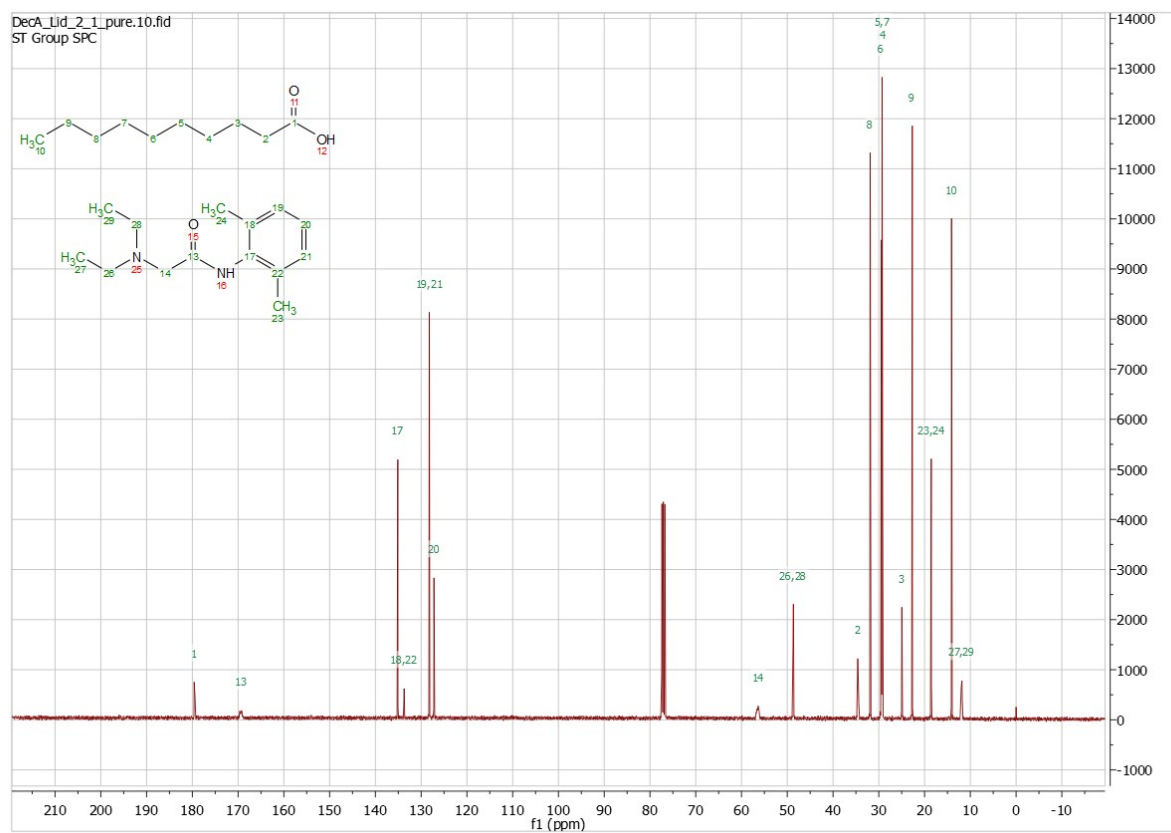


Figure S2 Carbon NMR of the DES DecA:Lid in a 2:1 ratio.

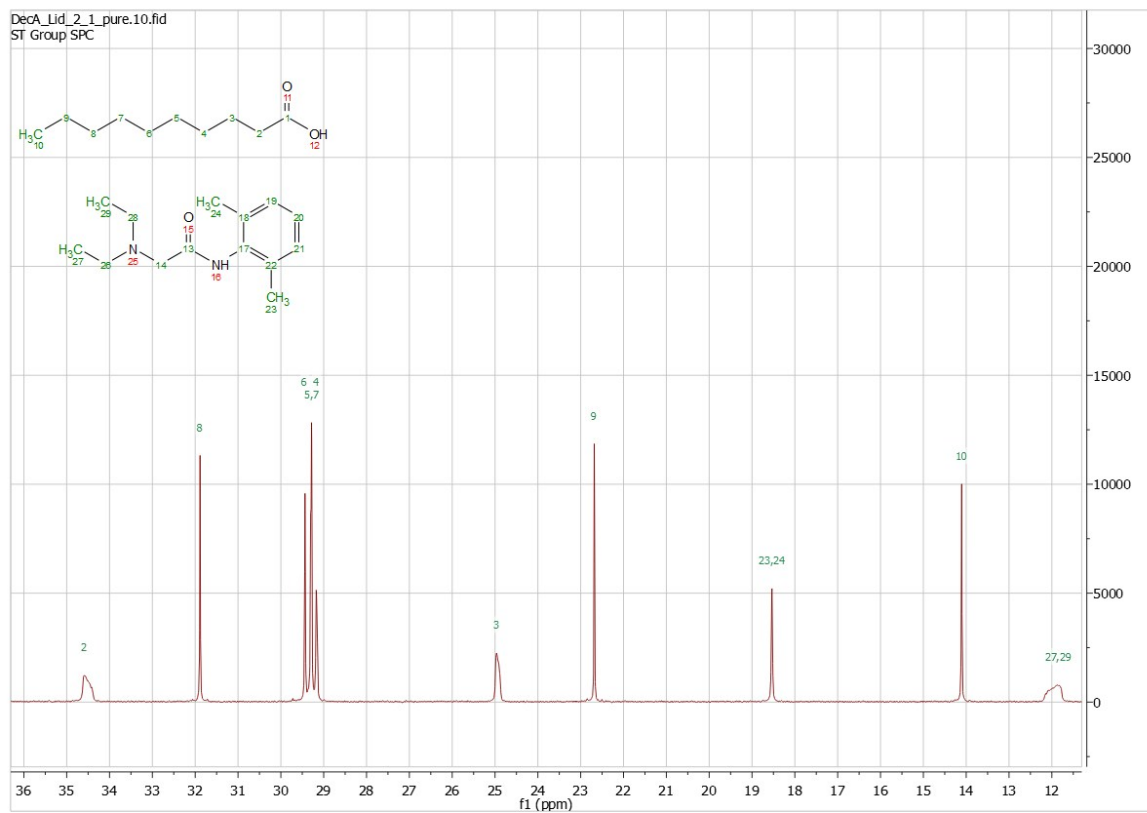


Figure S3 Zoom in of the carbon NMR of the DES DecA:Lid in a 2:1 ratio.

Proton

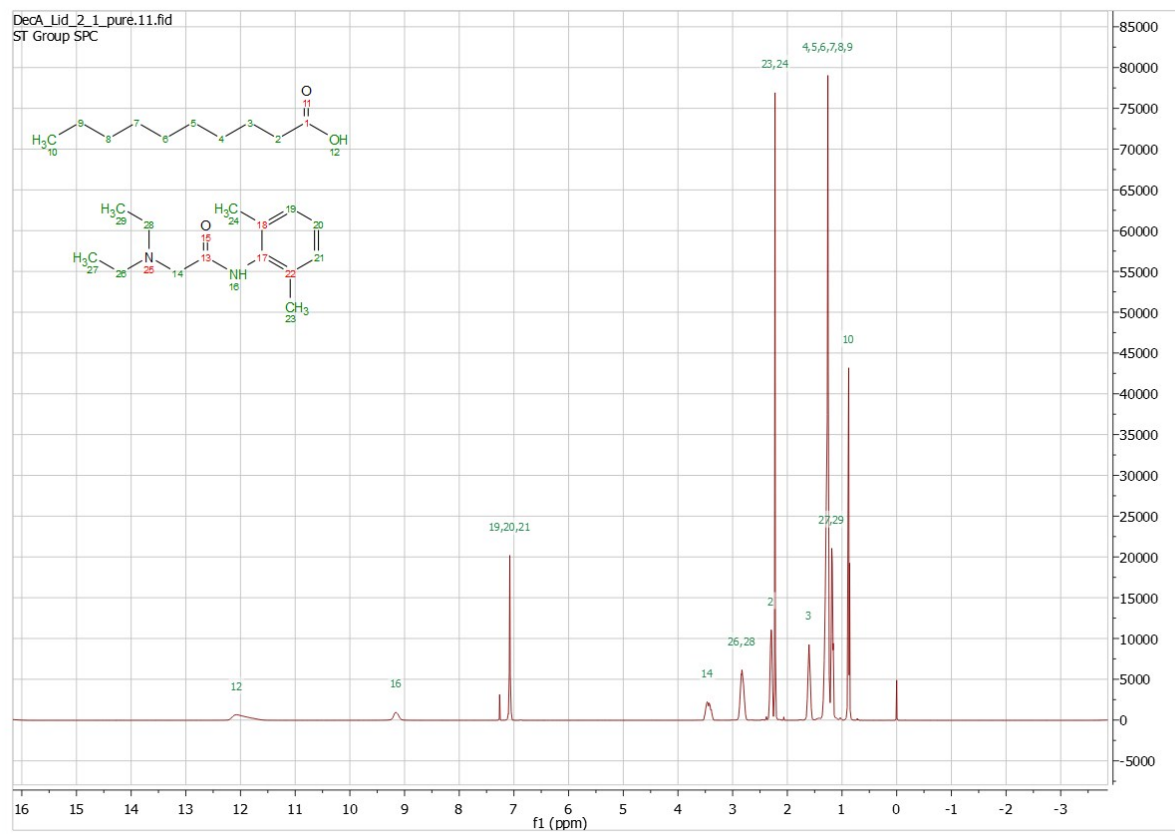


Figure S4 Proton NMR of the DES DecA:Lid in a 2:1 ratio.

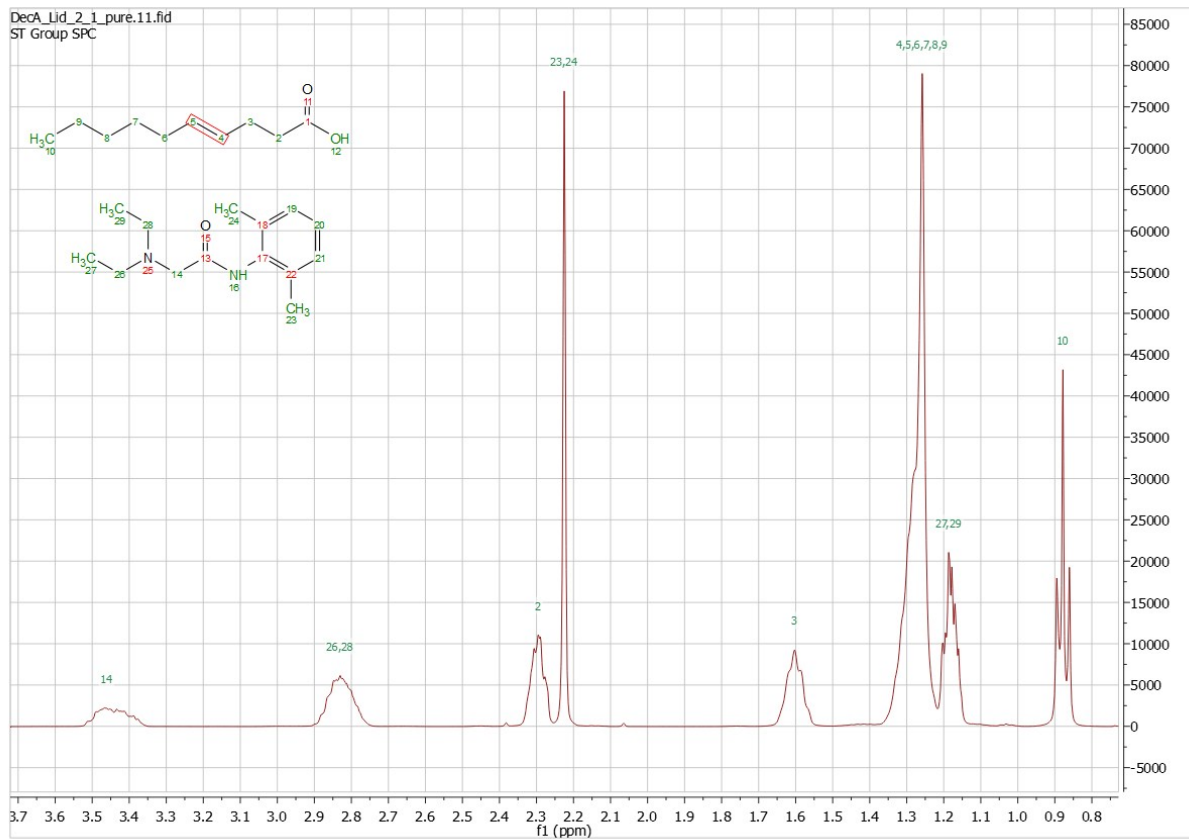


Figure S5 Zoom in of the proton NMR of the DES DecA:Lid in a 2:1 ratio.

DecA:Lid (3:1)

Carbon

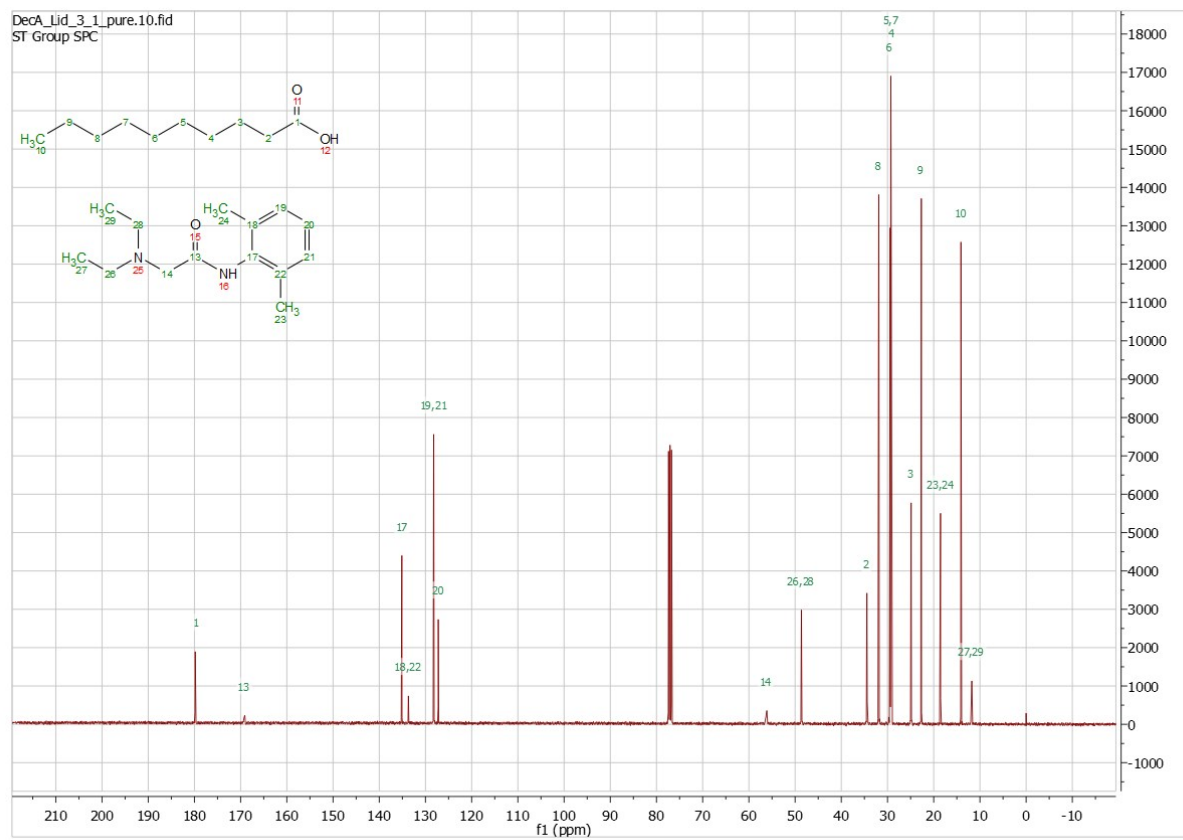


Figure S6 Carbon NMR of the DES DecA:Lid in a 3:1 ratio.

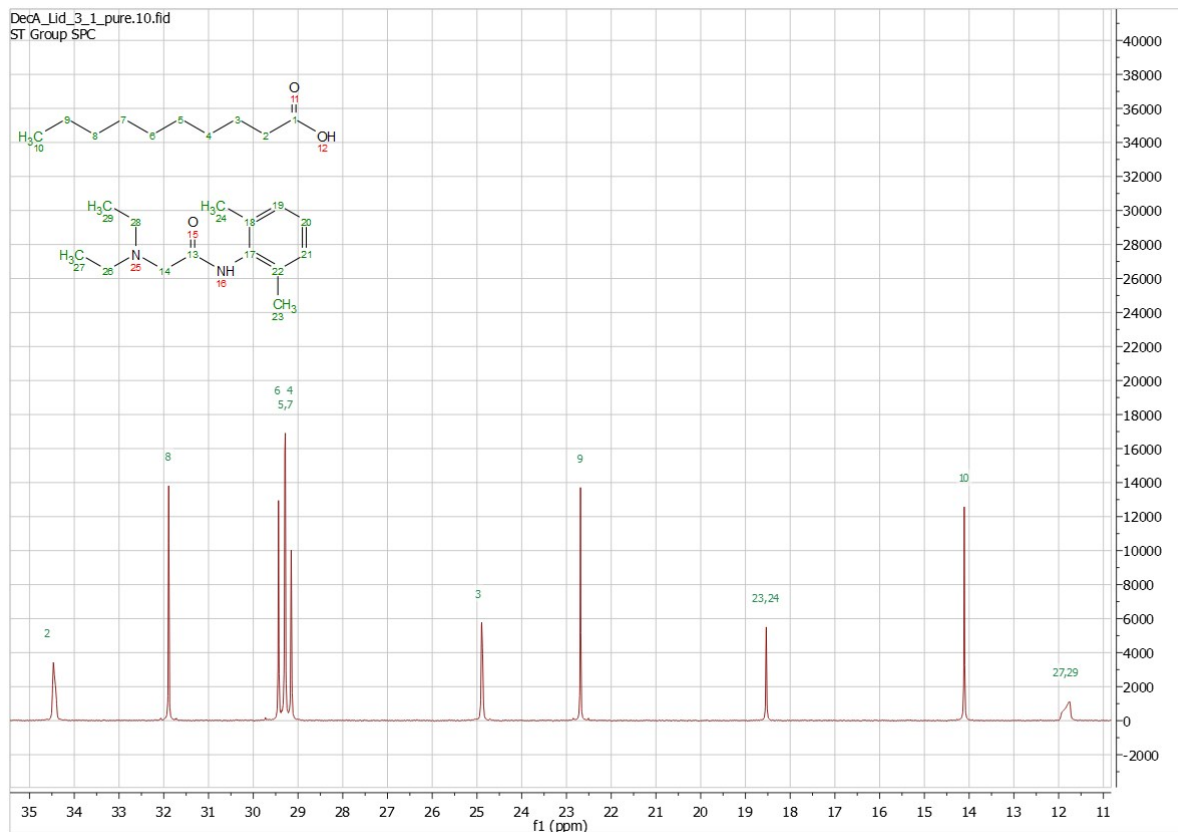


Figure S7 Zoom in of the carbon NMR of the DES DecA:Lid in a 3:1 ratio.

Proton

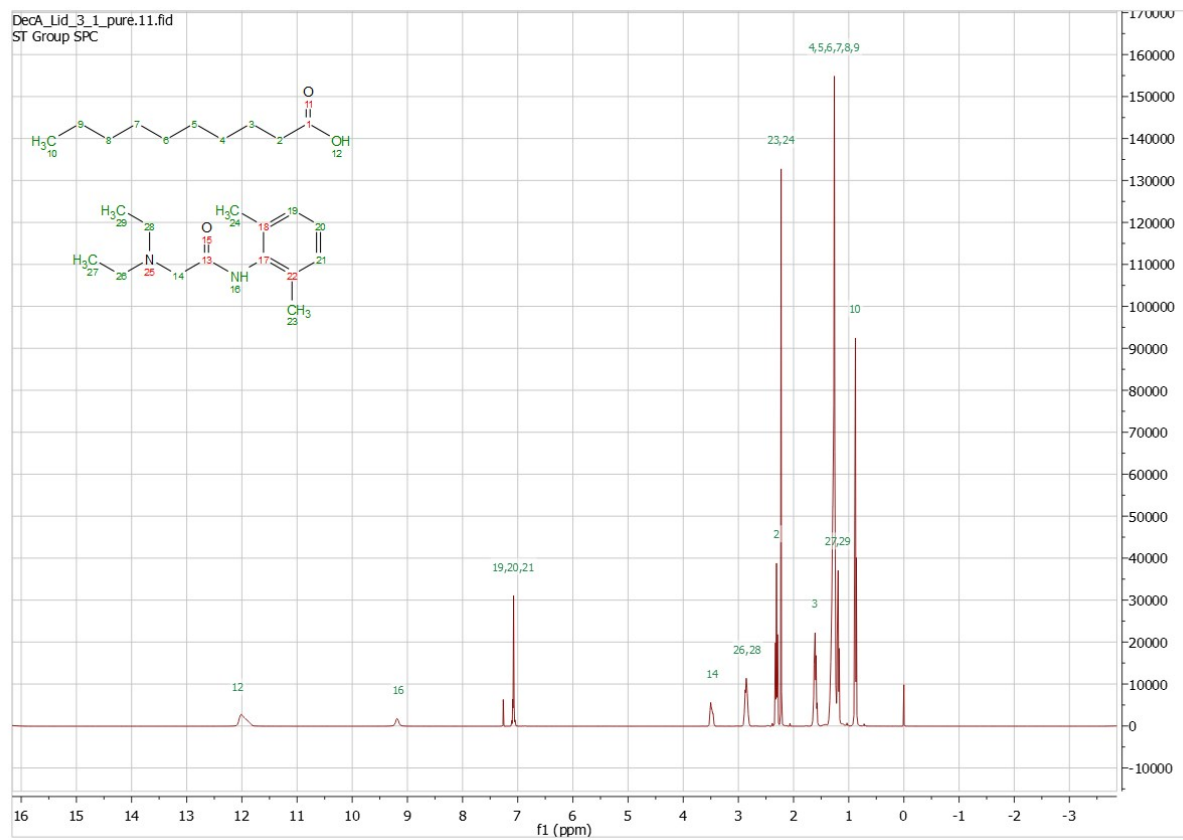


Figure S8 Proton NMR of the DES DecA:Lid in a 3:1 ratio.

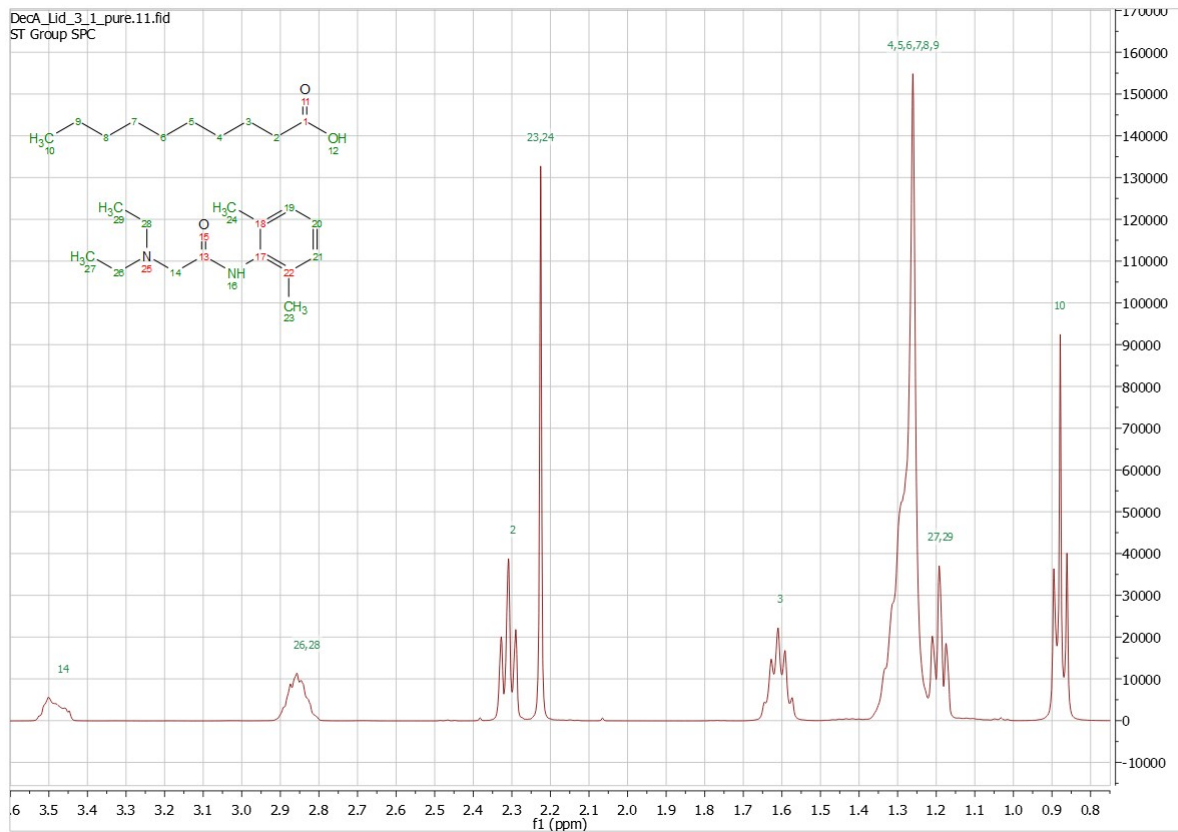


Figure S9 Zoom in of the proton NMR of the DES DecA:Lid in a 3:1 ratio.

DecA:Lid (4:1)

Carbon

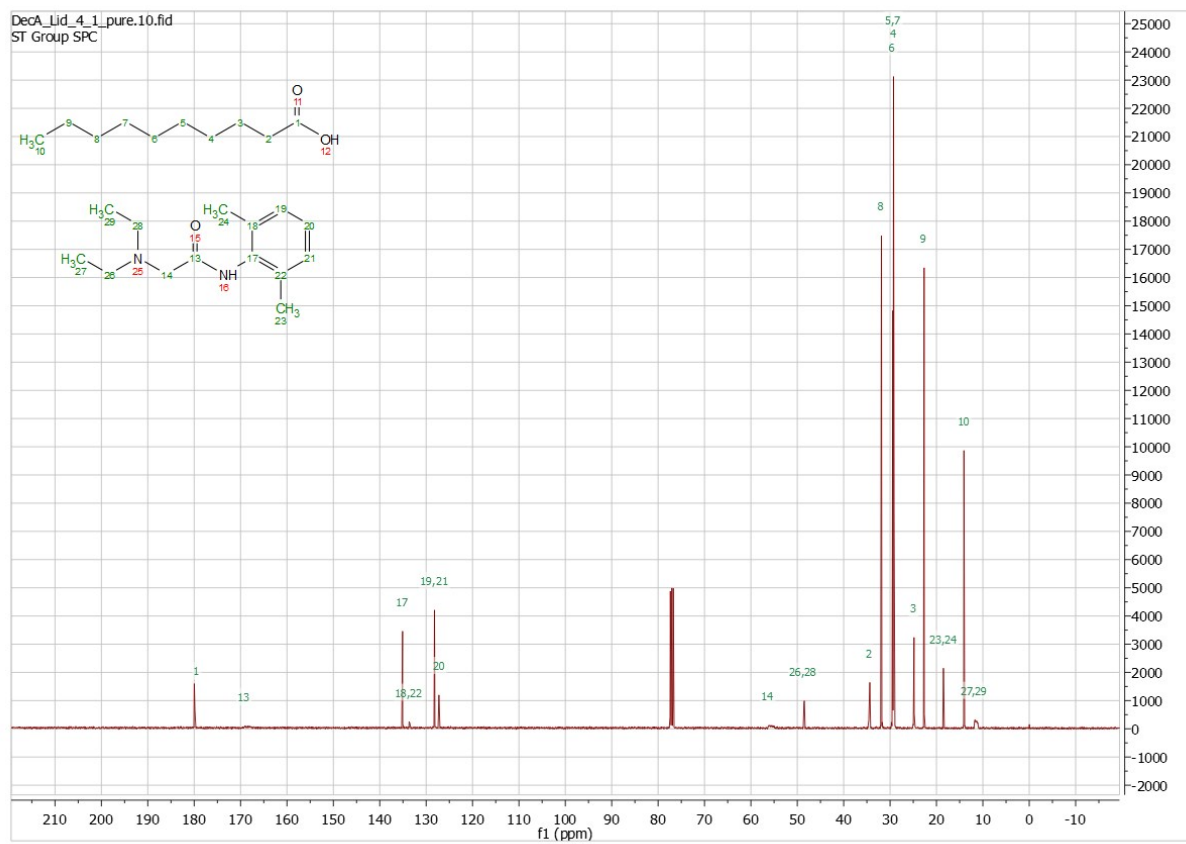


Figure S10 Carbon NMR of the DES DecA:Lid in a 4:1 ratio.

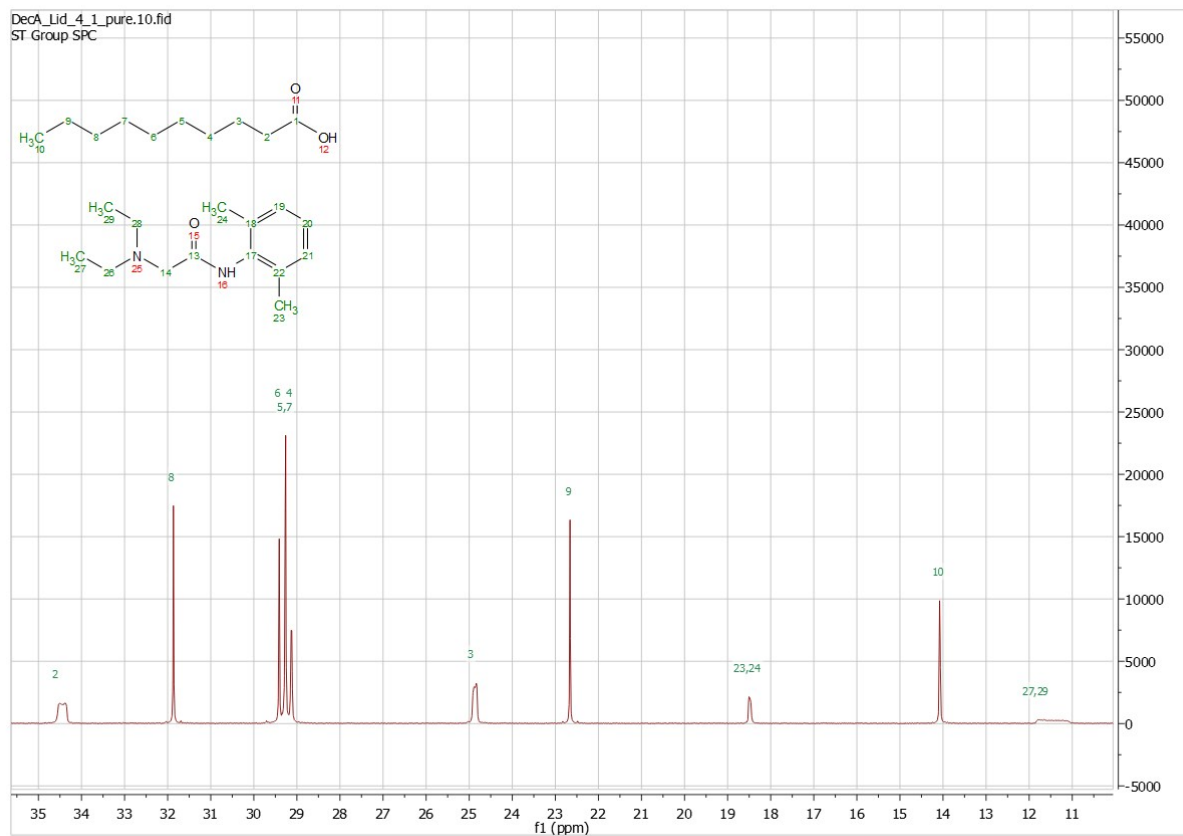


Figure S11 Zoom in of the carbon NMR of the DES DecA:Lid in a 4:1 ratio.

Proton

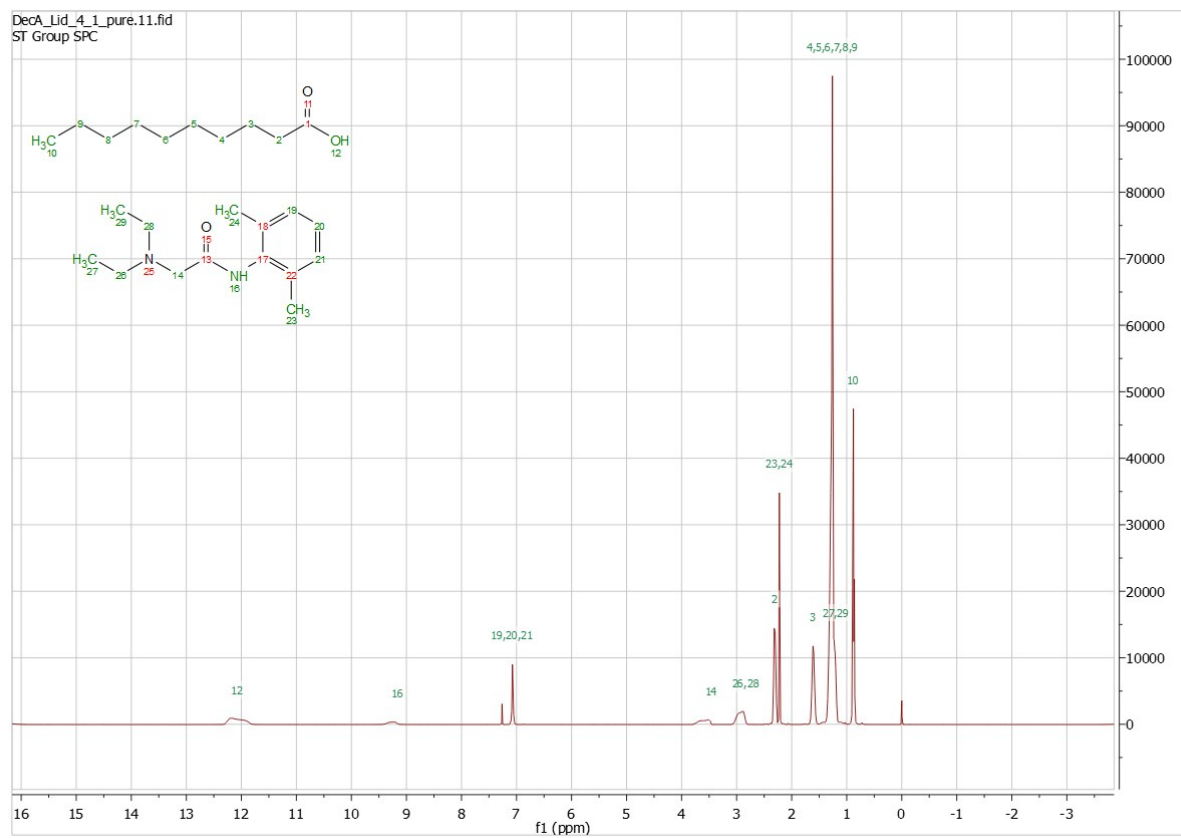


Figure S12 Proton NMR of the DES DecA:Lid in a 4:1 ratio.

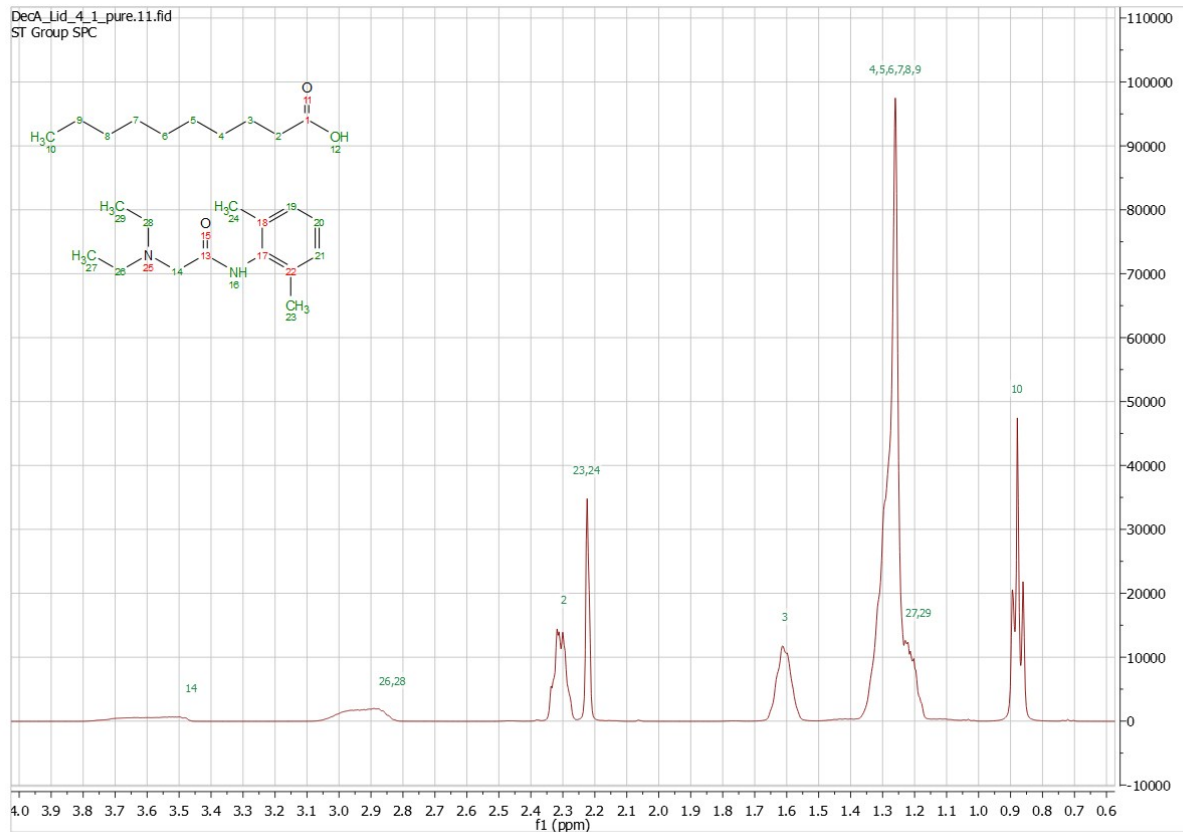


Figure S13 Zoom in of the proton NMR of the DES DecA:Lid in a 4:1 ratio.

ESI6: TGA thermograms

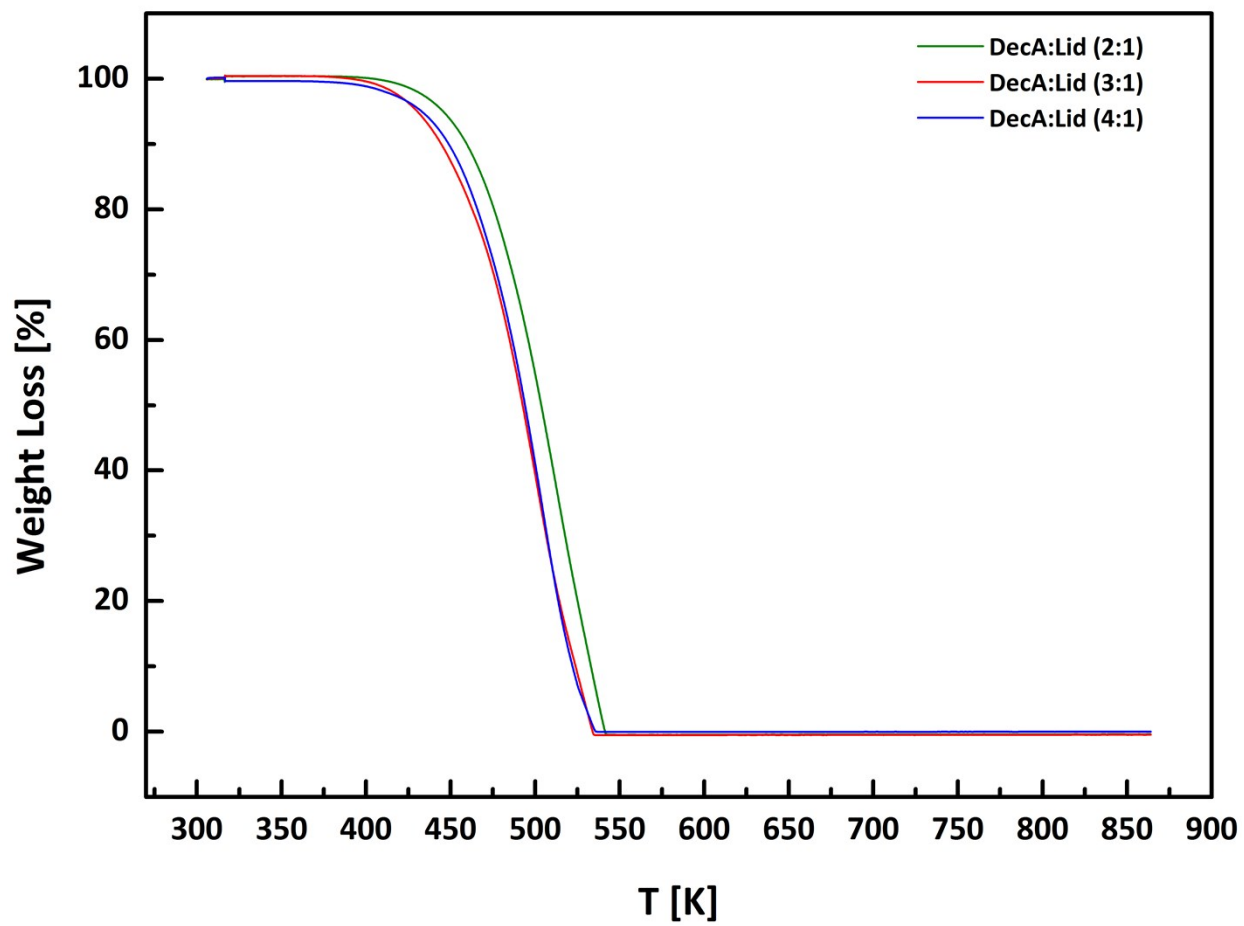


Figure S14 TGA Thermograms for the tested DESs. On the x-axis the temperature in Kelvin is depicted, while the weight loss in percentages is depicted on the y-axis.

ESI7: FTIR spectra

DecA:Lid (2:1)

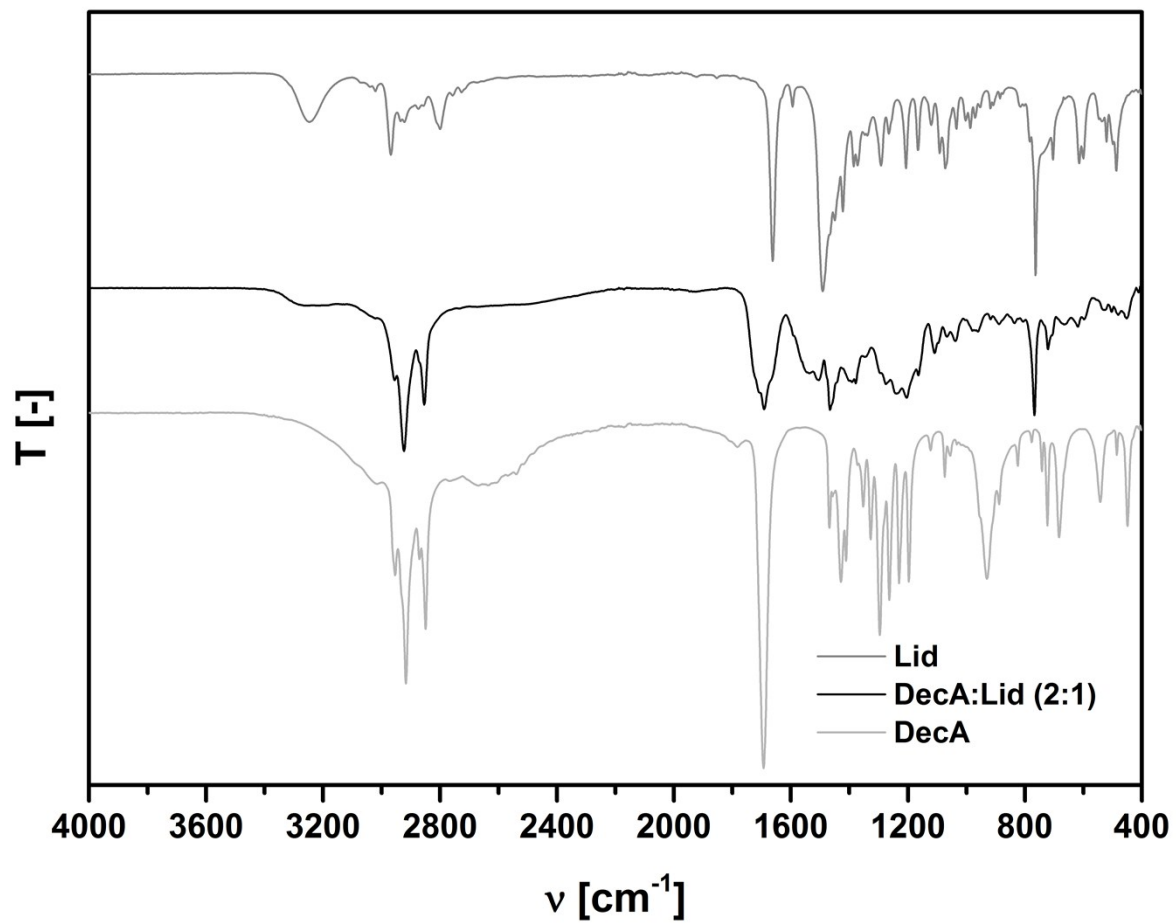


Figure S15 FTIR spectra of DecA, Lid and the DES DecA:Lid in a 2:1 ratio. On the x-axis the wavenumber in reciprocal centimeters is given, while on the y-axis the transmittance is depicted.

DecA:Lid (3:1)

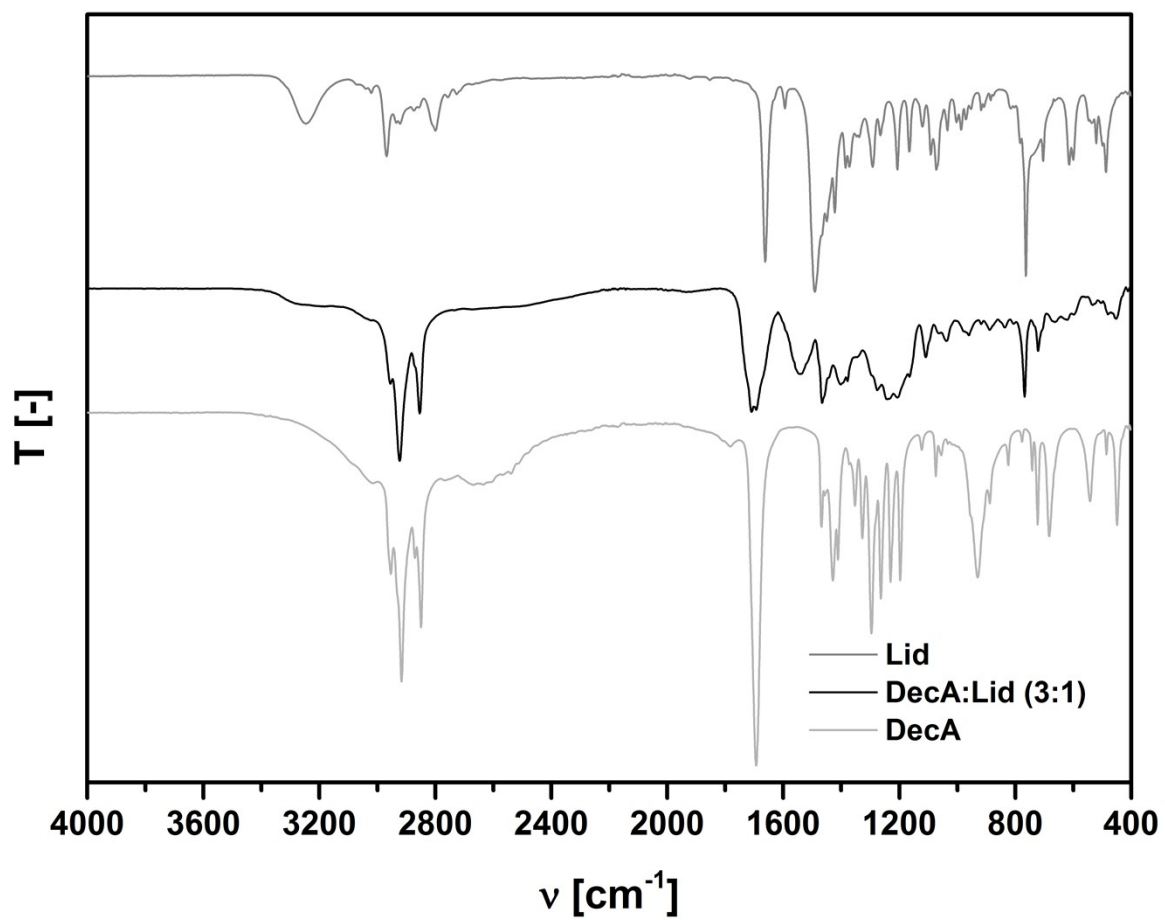


Figure S16 FTIR spectra of DecA, Lid and the DES DecA:Lid in a 3:1 ratio. On the x-axis the wavenumber in reciprocal centimeters is given, while on the y-axis the transmittance is depicted.

DecA:Lid (4:1)

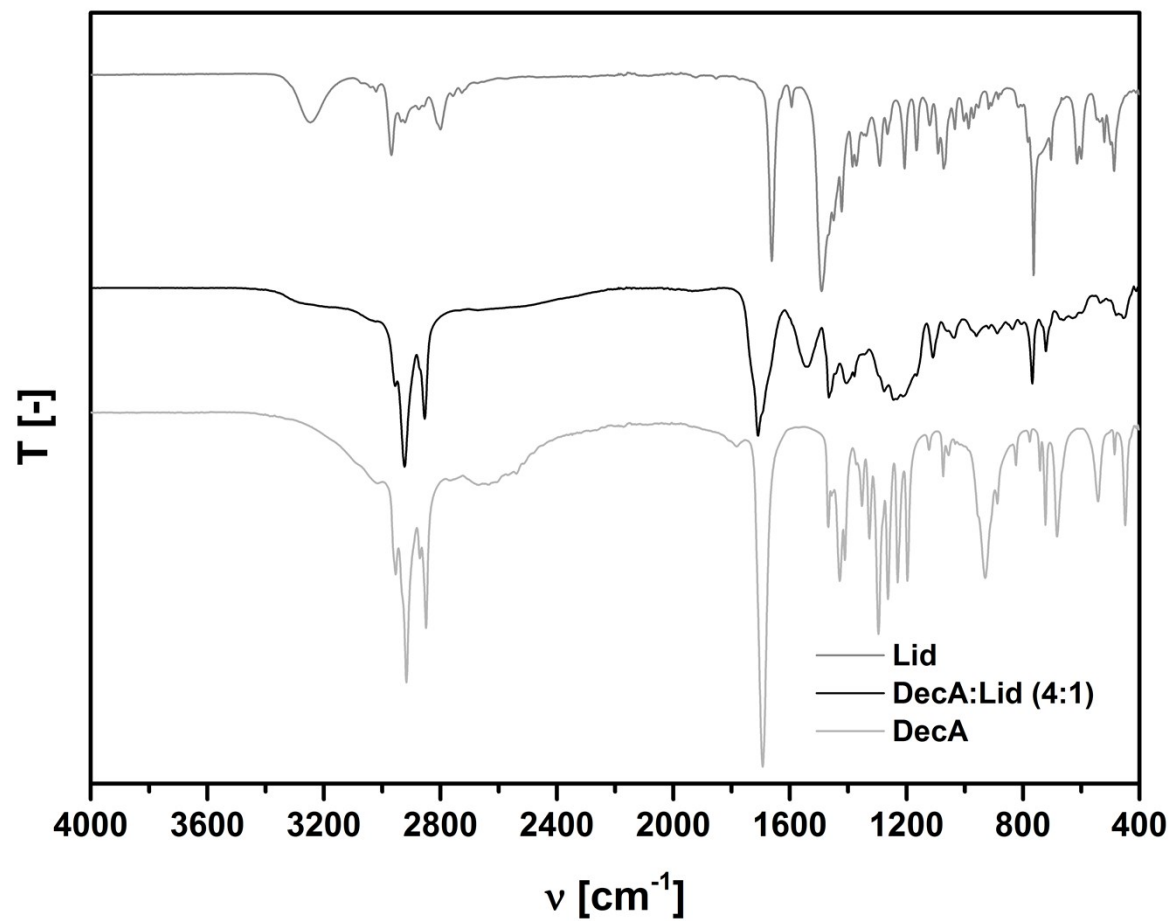


Figure S17 FTIR spectra of DecA, Lid and the DES DecA:Lid in a 4:1 ratio. On the x-axis the wavenumber in reciprocal centimeters is given, while on the y-axis the transmittance is depicted.

ESI8: NMR spectra of the water phase after the extraction experiments

Water phase after extraction of 0.5 g/L Co²⁺ with DecA:Lid (2:1)

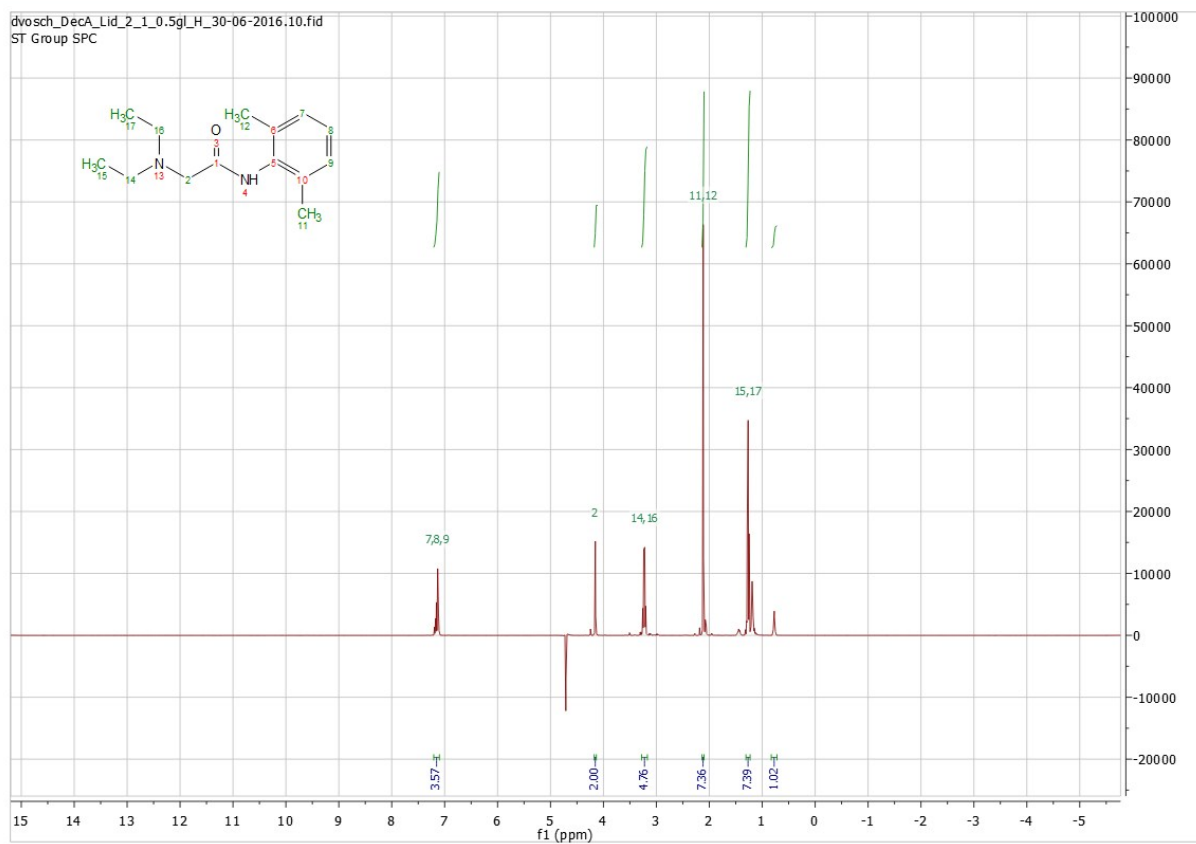
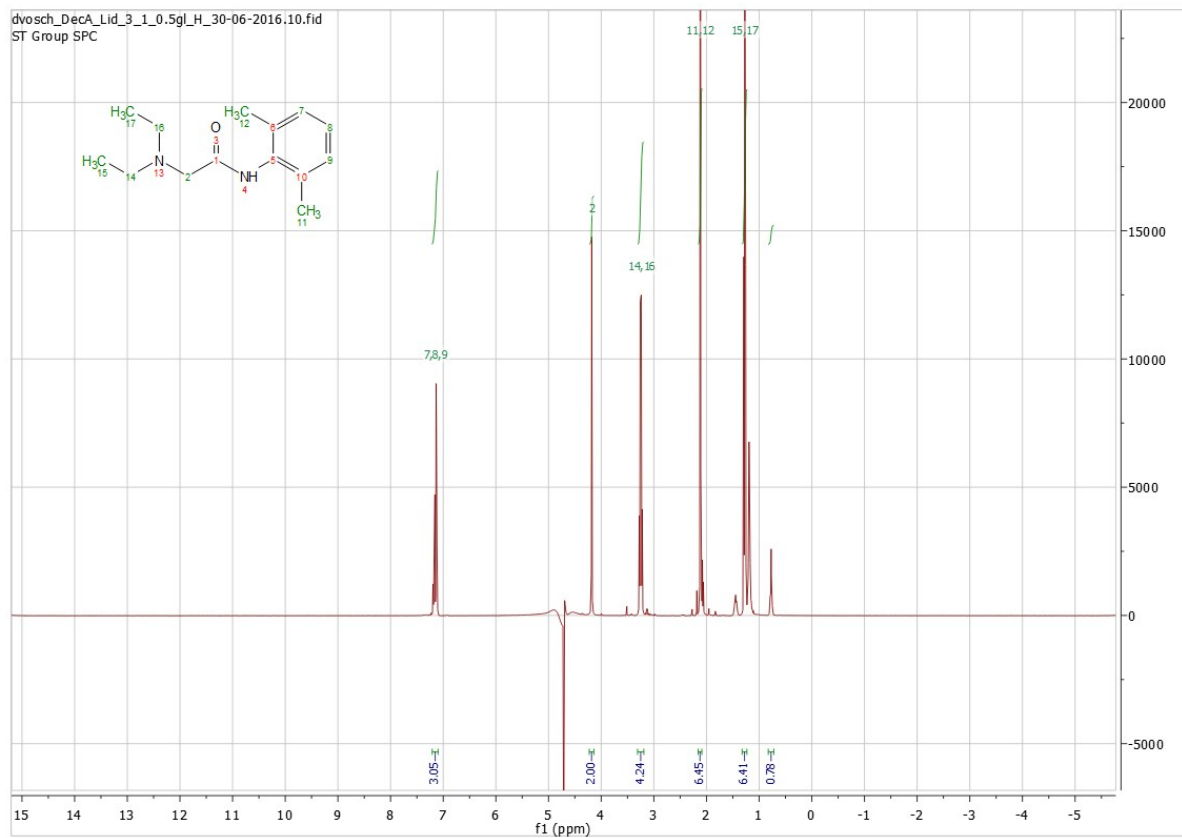


Figure S18 NMR spectrum of the water phase (water peak suppressed) after the extraction of 0.5 g/L Co²⁺ with DecA:Lid (2:1).

DecA:Lid (3:1) after extraction of 0.5 g/L Co²⁺



Fig

ure S19 NMR spectrum of the water phase (water peak suppressed) after the extraction of 0.5 g/L Co²⁺ with DecA:Lid (3:1).

DecA:Lid (4:1) after extraction of 0.5 g/L Co²⁺

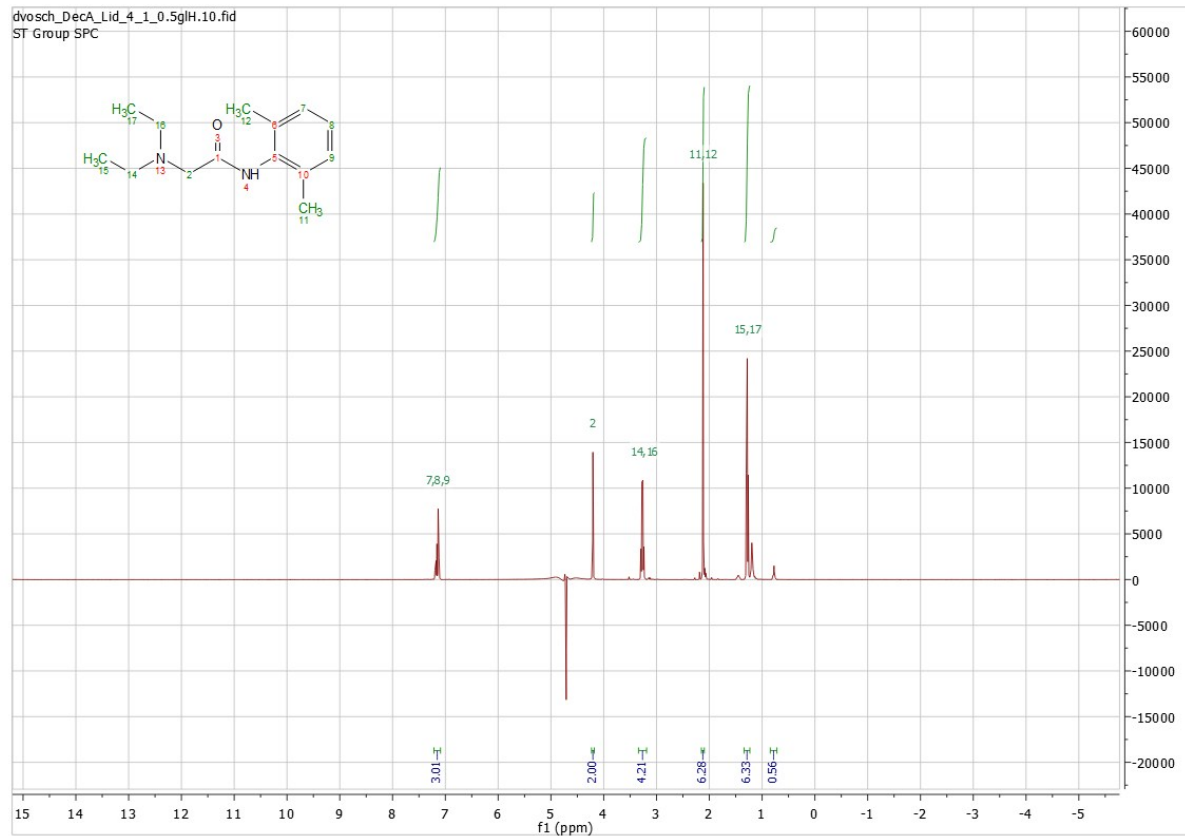
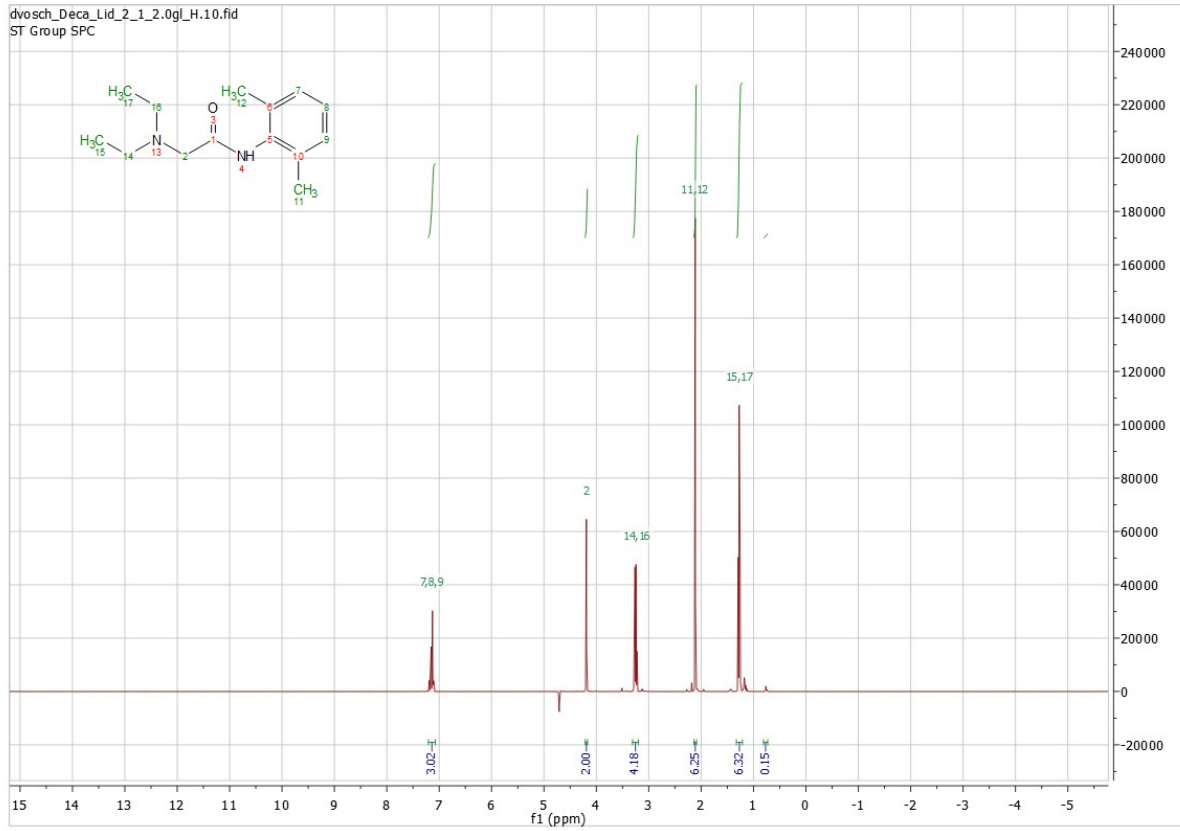


Figure S20 NMR spectrum of the water phase (water peak suppressed) after the extraction of 0.5 g/L Co²⁺ with DecA:Lid (4:1).

DecA:Lid (2:1) after extraction of 2.0 g/L Co²⁺



Fig

ure S21 NMR spectrum of the water phase (water peak suppressed) after the extraction of 2.0 g/L Co²⁺ with DecA:Lid (2:1).

DecA:Lid (3:1) after extraction of 2.0 g/L Co²⁺

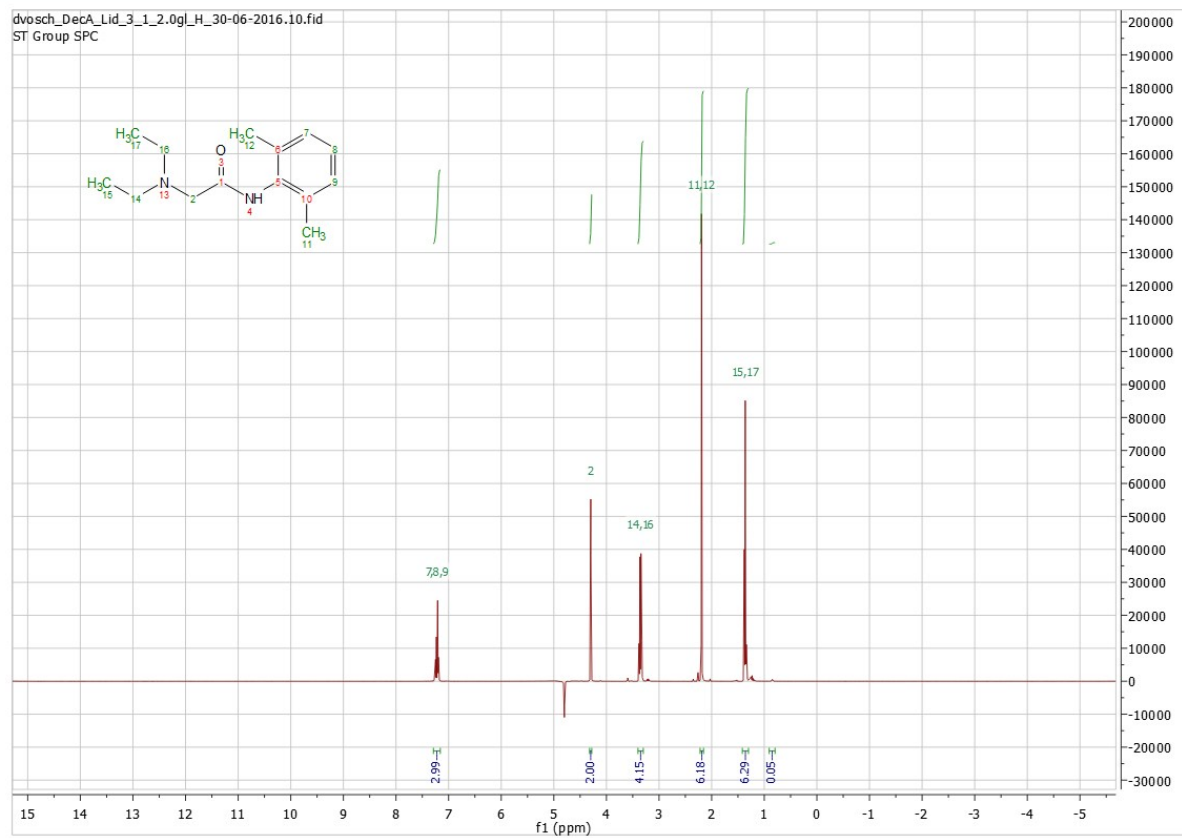


Figure S22 NMR spectrum of the water phase (water peak suppressed) after the extraction of 2.0 g/L Co²⁺ with DecA:Lid (3:1).

DecA:Lid (4:1) after extraction of 2.0 g/L Co²⁺

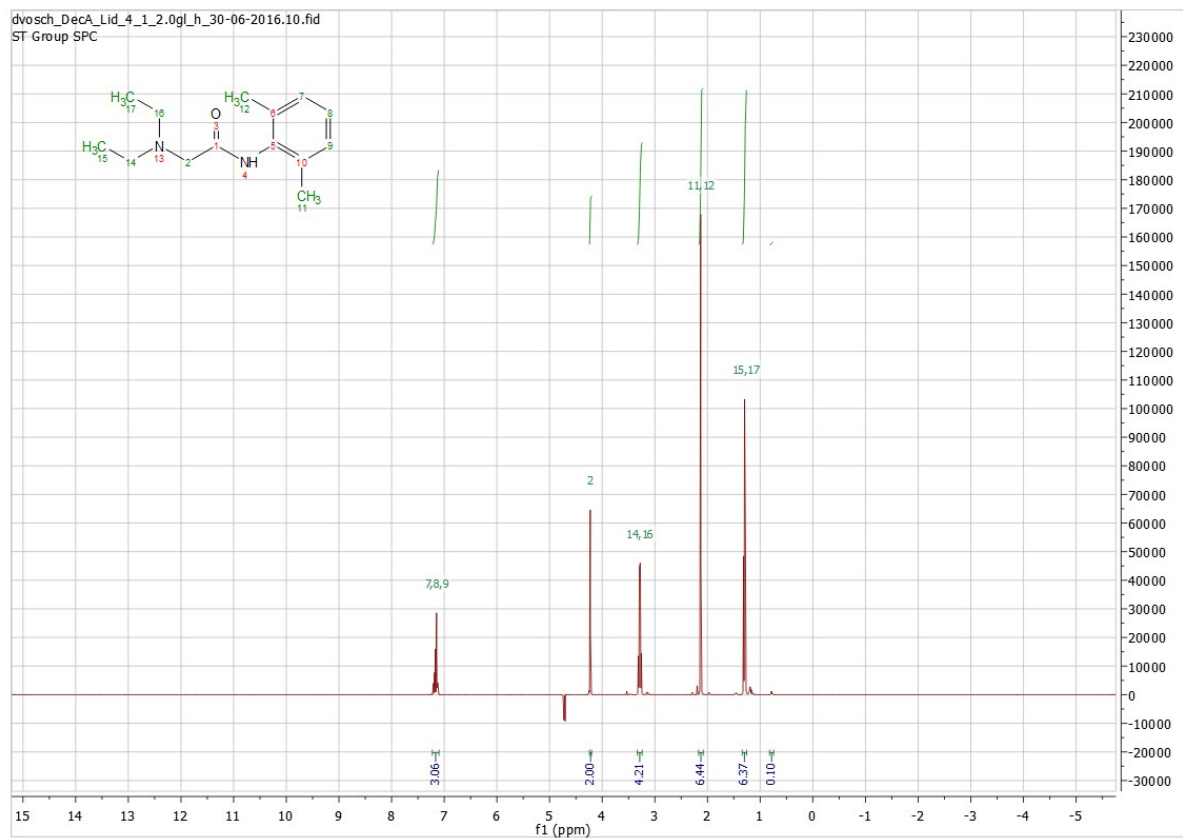


Figure S23 NMR spectrum of the water phase (water peak suppressed) after the extraction of 2.0 g/L Co²⁺ with DecA:Lid (4:1).

DecA:Lid (2:1) after extraction of 4.0 g/L Co²⁺

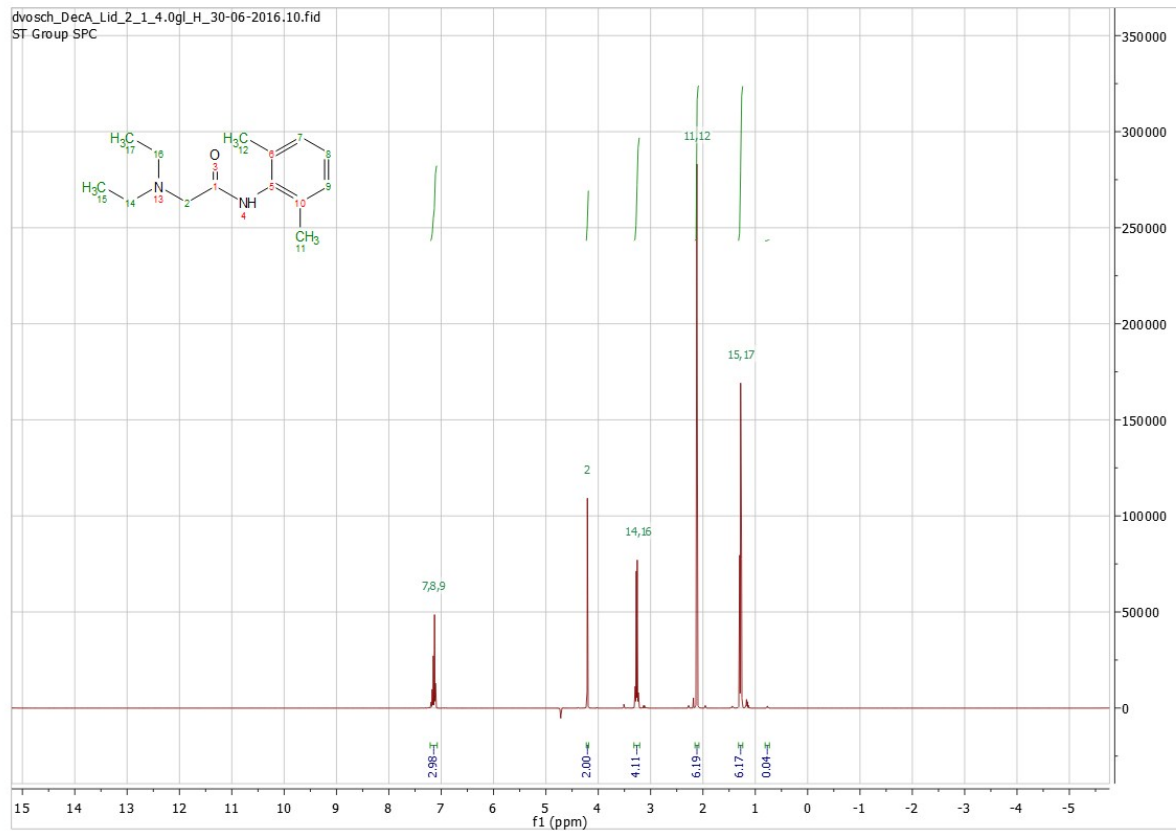


Figure S24 NMR spectrum of the water phase (water peak suppressed) after the extraction of 4.0 g/L Co²⁺ with DecA:Lid (2:1).

DecA:Lid (3:1) after extraction of 4.0 g/L Co²⁺

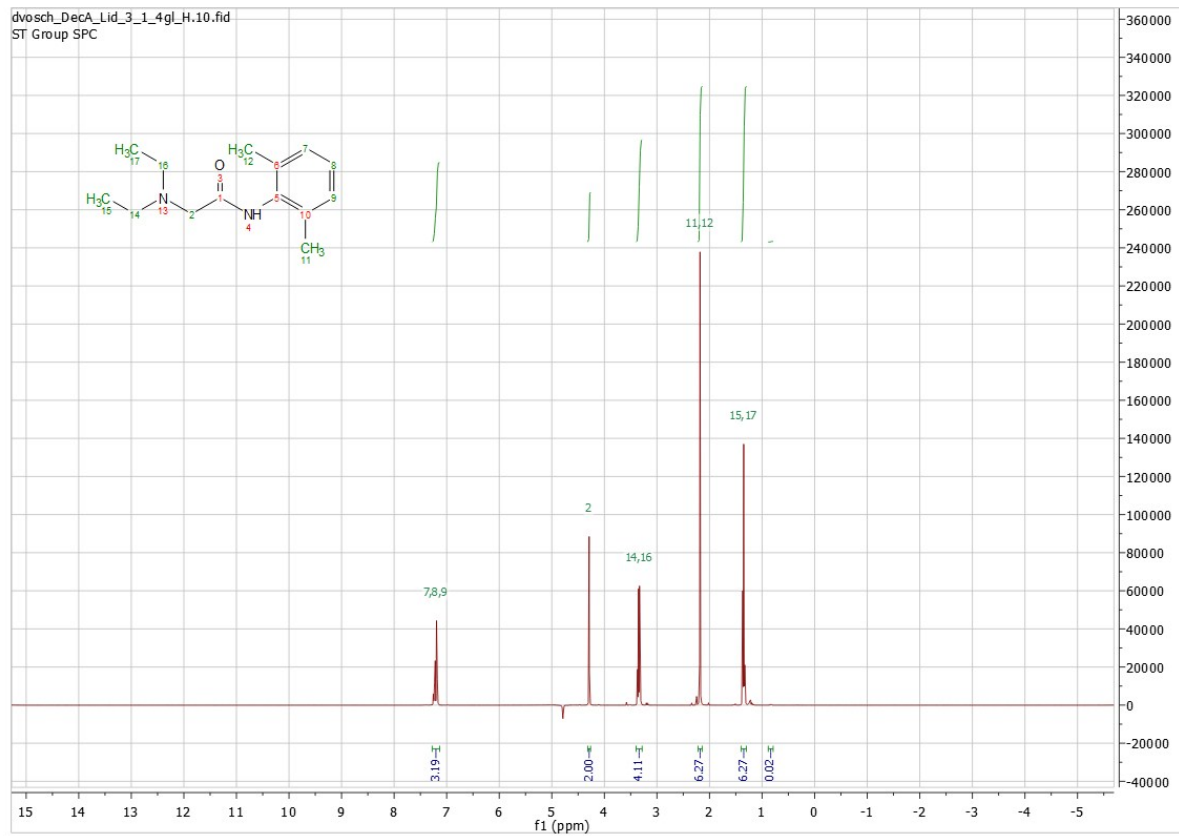


Figure S25 NMR spectrum of the water phase (water peak suppressed) after the extraction of 4.0 g/L Co²⁺ with DecA:Lid (3:1).

DecA:Lid (4:1) after extraction of 4.0 g/L Co²⁺

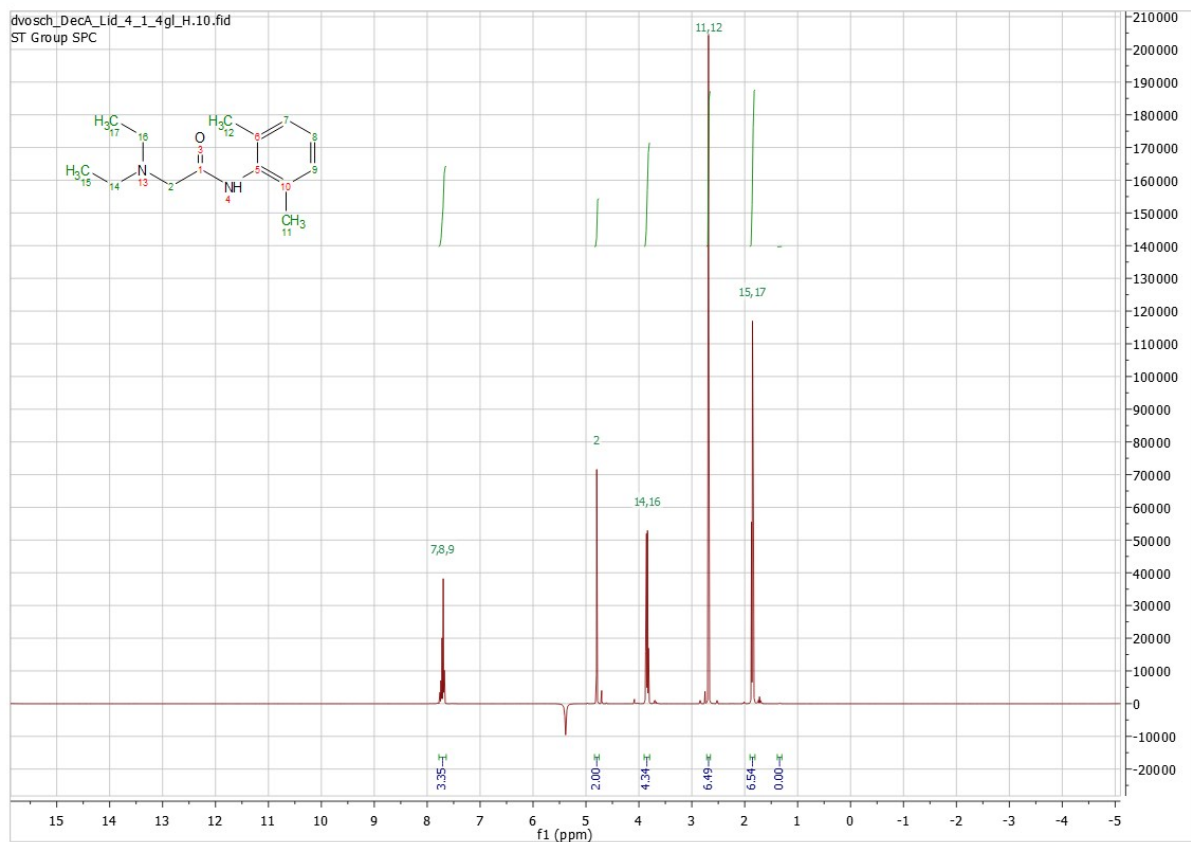


Figure S26 NMR spectrum of the water phase (water peak suppressed) after the extraction of 4.0 g/L Co²⁺ with DecA:Lid (4:1).

Table S7 Mole ratio of Lid:DecA for all the water phases measured.

Name	Mole ratio of Lid:DecA
Water phase after extraction of 0.5 g/L Co ²⁺ with DecA:Lid (2:1)	1 : 0.34
Water phase after extraction of 0.5 g/L Co ²⁺ with DecA:Lid (3:1)	1 : 0.26
Water phase after extraction of 0.5 g/L Co ²⁺ with DecA:Lid (4:1)	1 : 0.19
Water phase after extraction of 2.0 g/L Co ²⁺ with DecA:Lid (2:1)	1 : 0.05
Water phase after extraction of 2.0 g/L Co ²⁺ with DecA:Lid (3:1)	1 : 0.02
Water phase after extraction of 2.0 g/L Co ²⁺ with DecA:Lid (4:1)	1 : 0.03
Water phase after extraction of 4.0 g/L Co ²⁺ with DecA:Lid (2:1)	1 : 0.01
Water phase after extraction of 4.0 g/L Co ²⁺ with DecA:Lid (3:1)	1 : 0.01
Water phase after extraction of 4.0 g/L Co ²⁺ with DecA:Lid (4:1)	1 : 0.00

ESI9: Time experiment

A time experiment was conducted to investigate how fast the extraction of the metal ion Co^{2+} to the water phase proceeds. As Figure S27 shows, equal extraction can be achieved after approximately 5 in comparison to the distribution coefficients measured after 1 h.

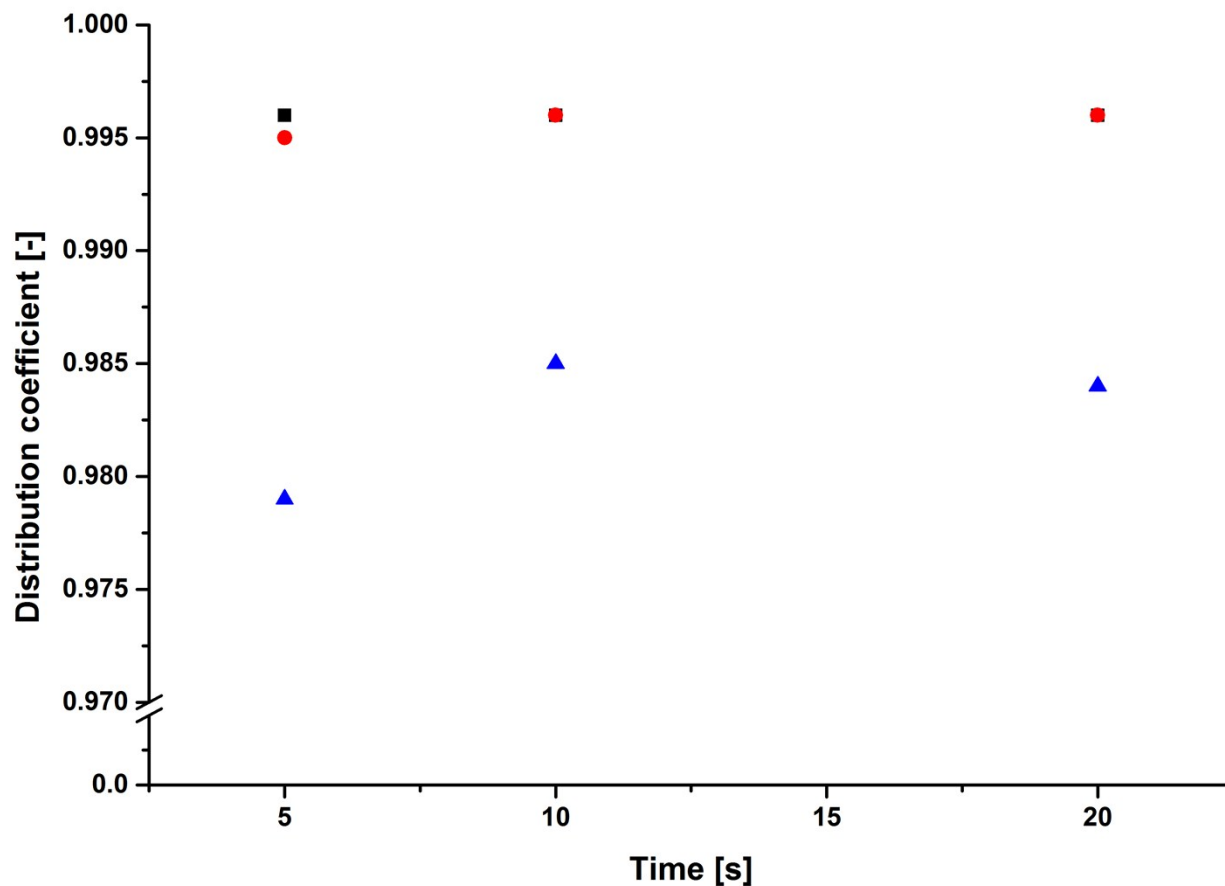


Figure S27 Distribution coefficient of Co^{2+} over the time. ■ = DecA:Lid (2:1), ● = DecA:Lid (3:1) and ▲ = DecA:Lid (4:1).

ESI10: Photo of the DES and water phases after extraction

Extraction of 1.0 g/l Co^{2+} from water with a 1:1 DES to water ratio

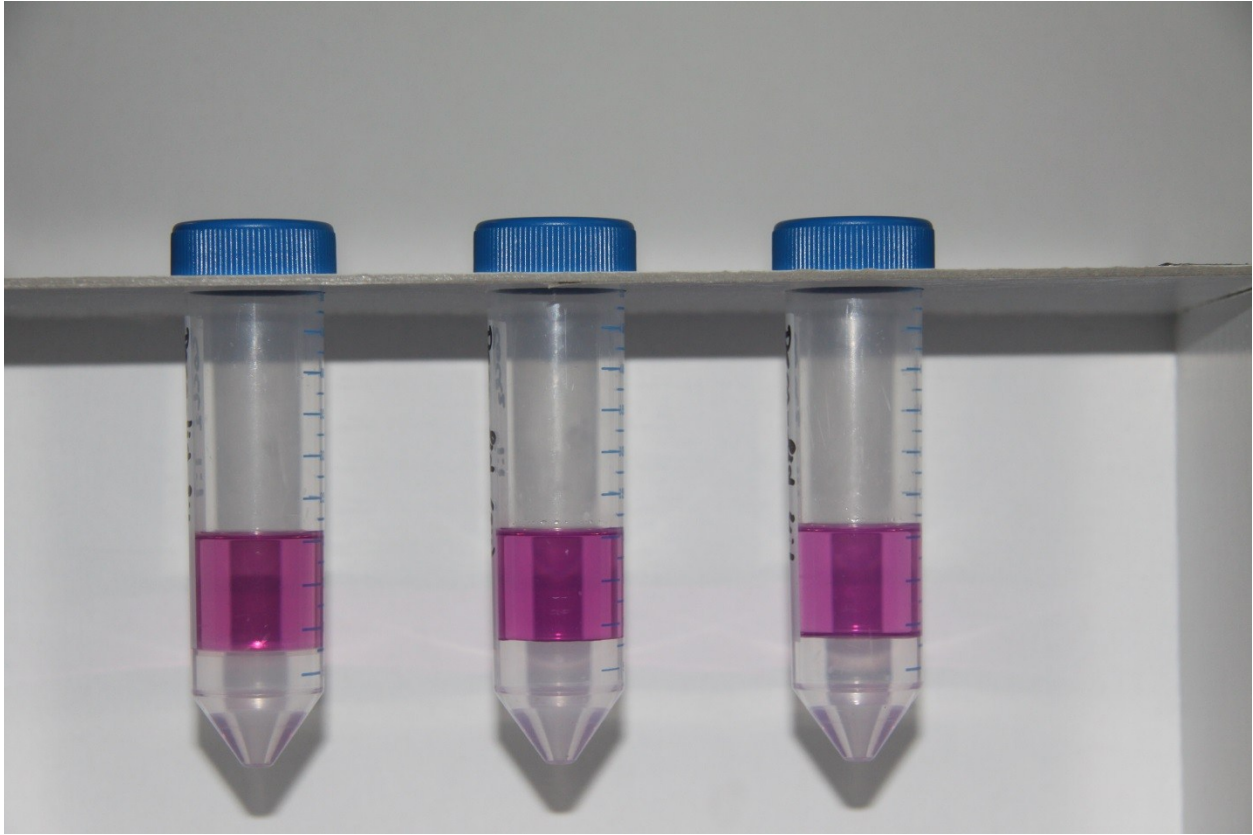


Figure S28 Photo after the extraction of 1.0 g/l Co^{2+} from an aquatic environment, where approximately 10 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l Fe²⁺ from water with a 1:1 DES to water ratio

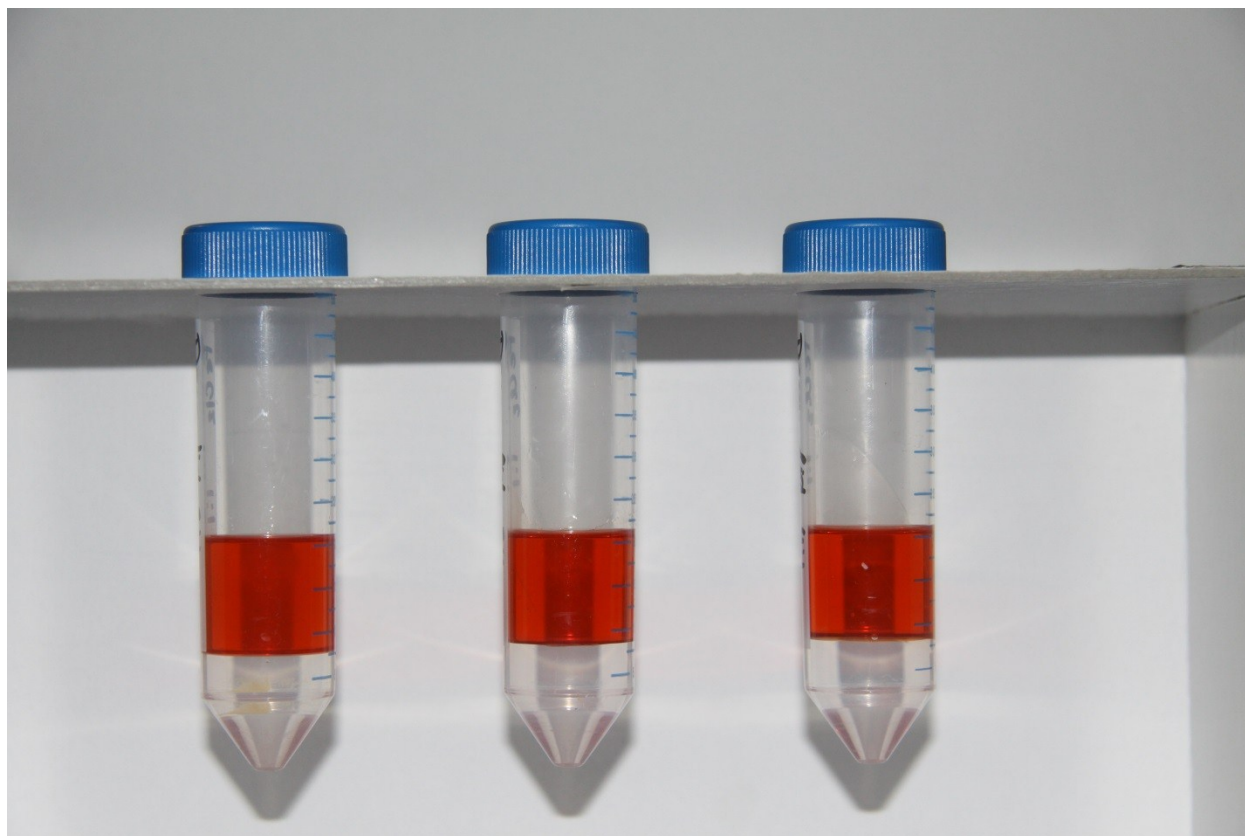


Figure S29 Photo after the extraction of 1.0 g/l Fe²⁺ from an aquatic environment, where approximately 10 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l Mn^{2+} from water with a 1:1 DES to water ratio

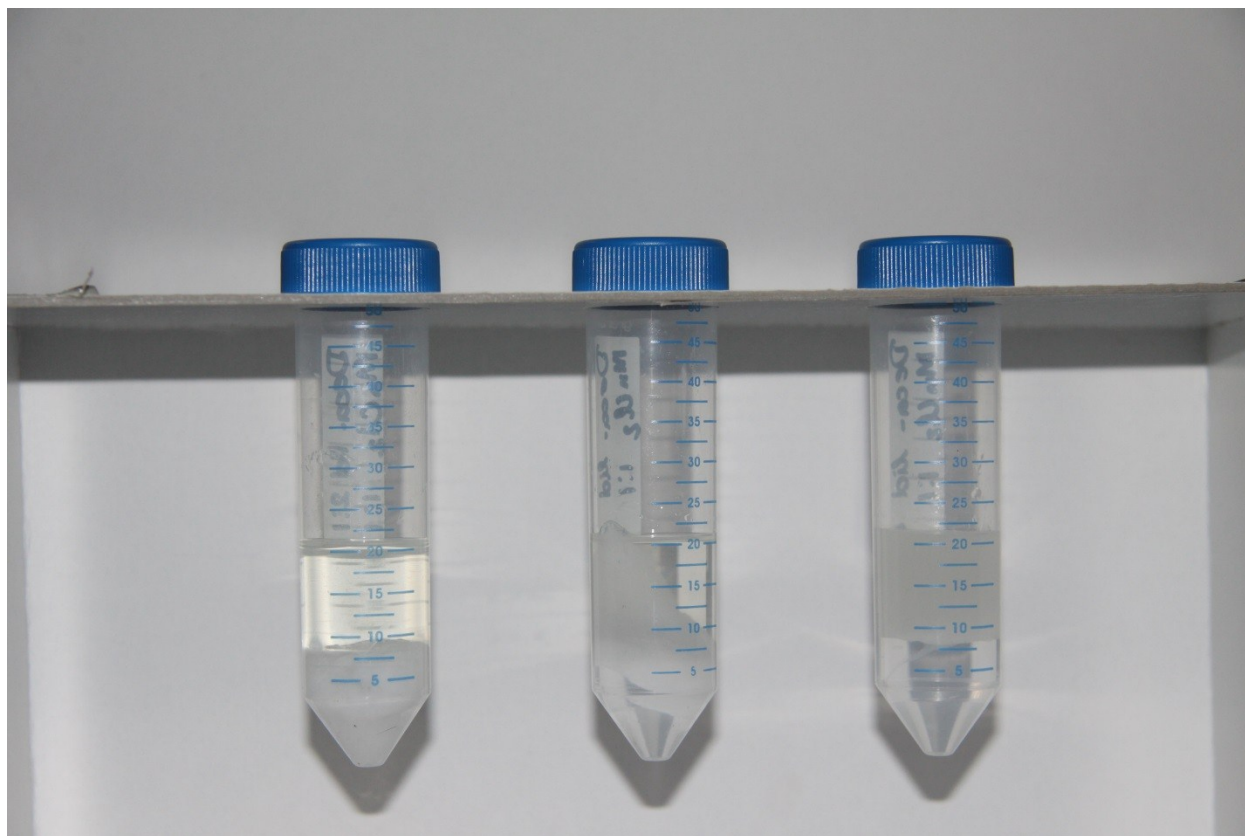


Figure S30 Photo after the extraction of 1.0 g/l Mn^{2+} from an aquatic environment, where approximately 10 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l K^+ from water with a 1:1 DES to water ratio

After centrifuging and making the picture immediately

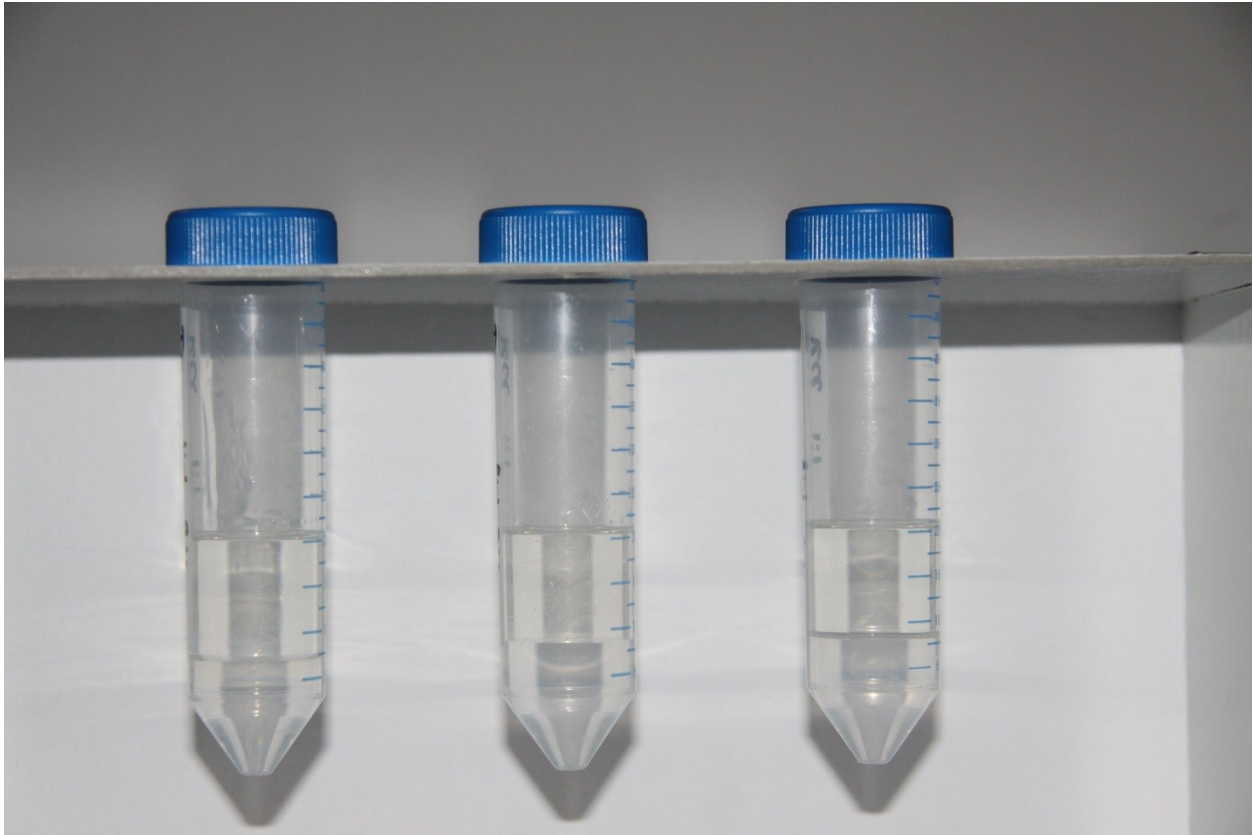


Figure S31 Photo immediately after the extraction of 1.0 g/l K^+ from an aquatic environment, where approximately 10 gram DES and 10 ml of water solution was used. The top phase is the DES phase, while the bottom phase is the water phase. From left to right the ratio of the DESS are varied from 2:1 to 4:1.

After centrifuging and standing for several days

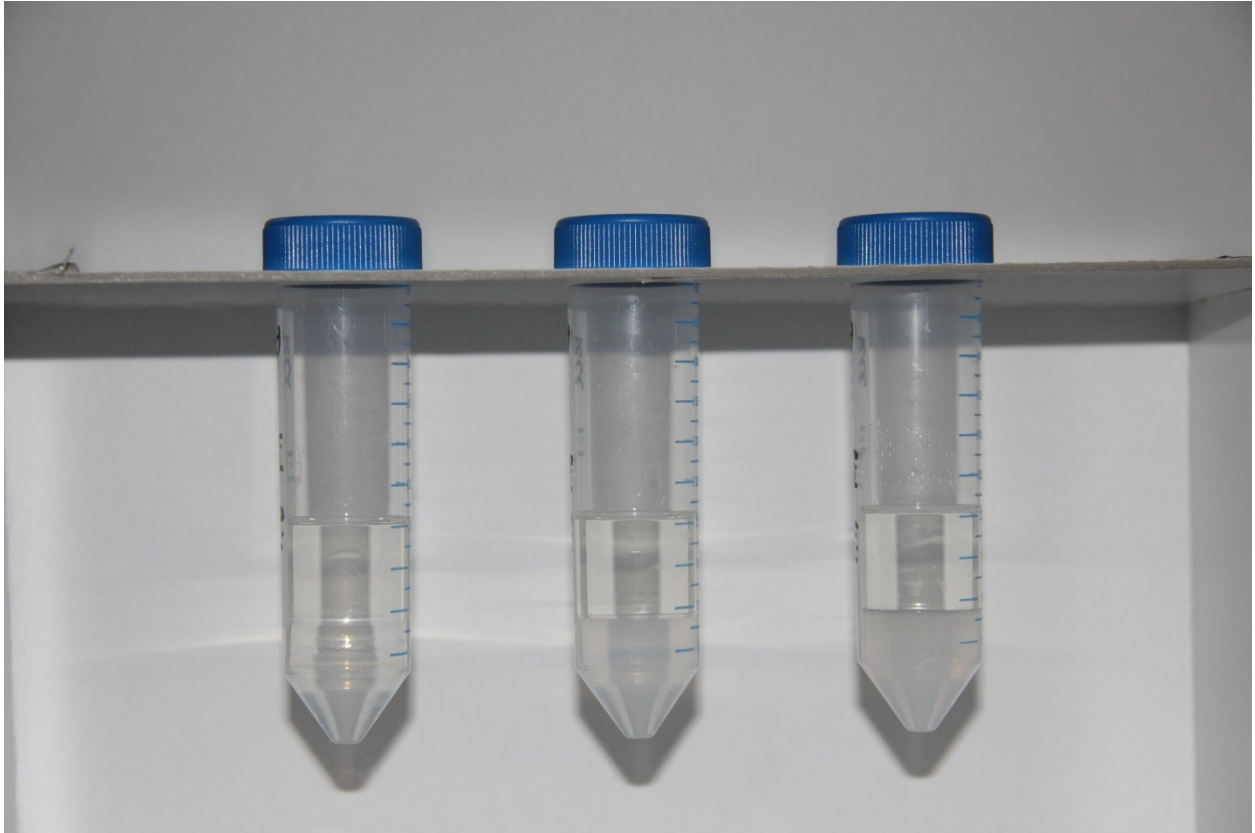


Figure S32 Photo after the extraction, and standing for several days, of 1.0 g/l K^+ from an aquatic environment, where approximately 10 gram DES and 10 ml of water solution was used. The top phase is the DES phase, while the bottom phase is the water phase. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Na^+ , K^+ , Li^+ from water with a 1:1 DES to water ratio

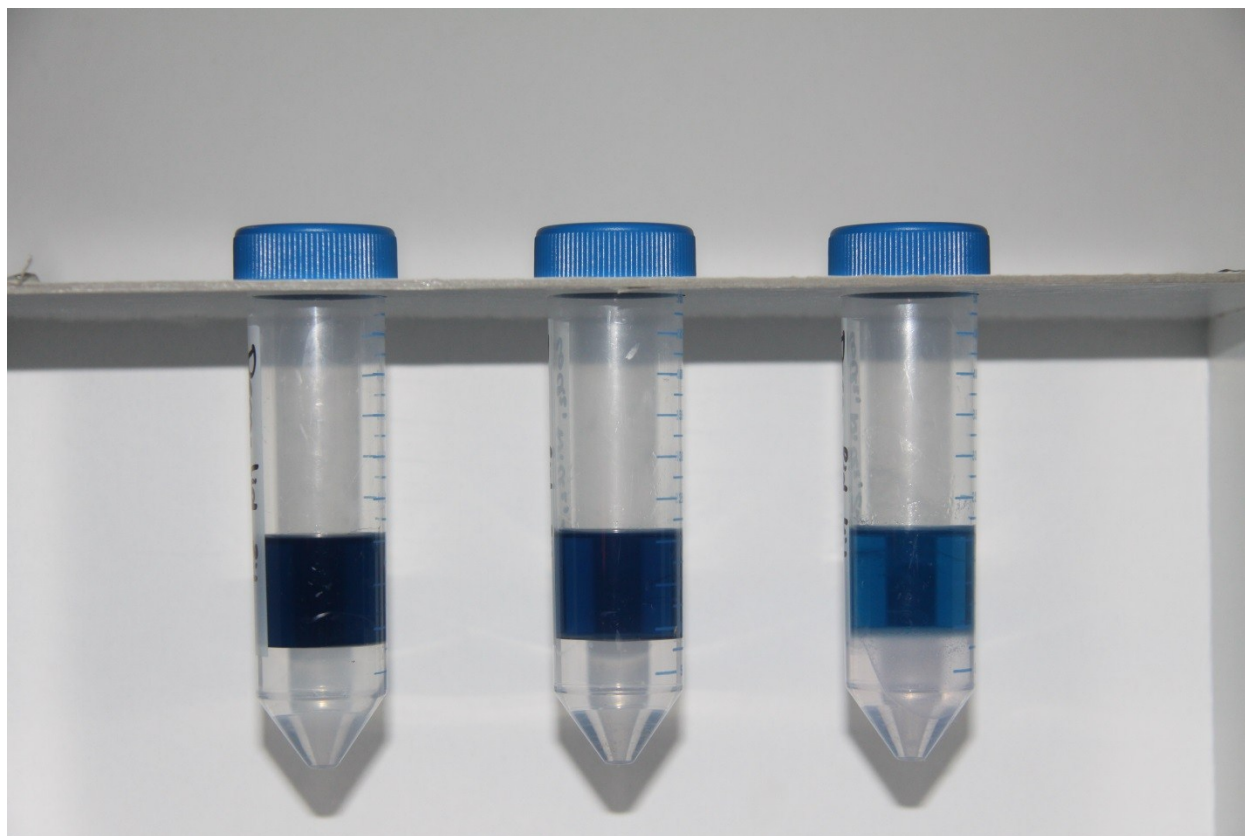


Figure S33 Photo after the extraction of 1.0 g/l Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Na^+ , K^+ , Li^+ from an aquatic environment, where approximately 10 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 0.5 g/l Co^{2+} from water with a 1:1 DES to water ratio

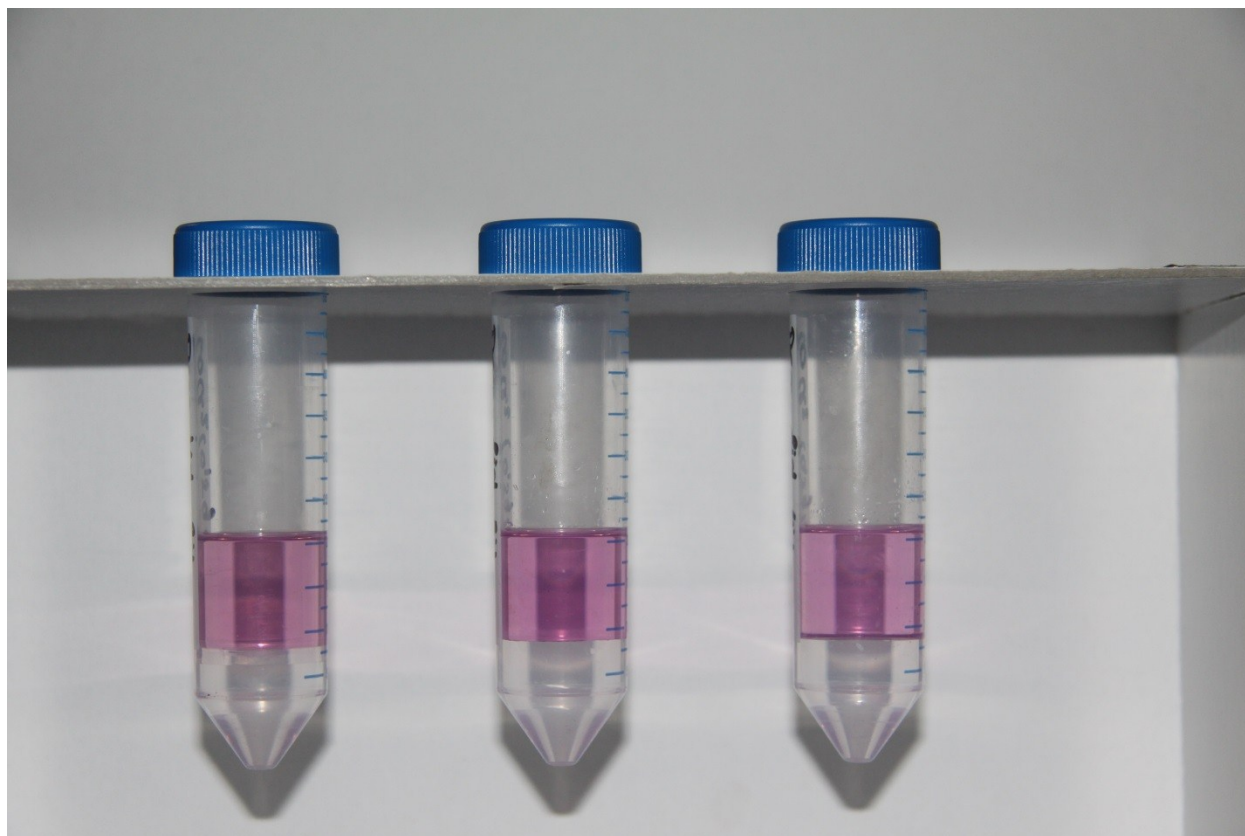


Figure S34 Photo after the extraction of 0.5 g/l Co^{2+} from an aquatic environment, where approximately 10 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 2.0 g/l Co^{2+} from water with a 1:1 DES to water ratio

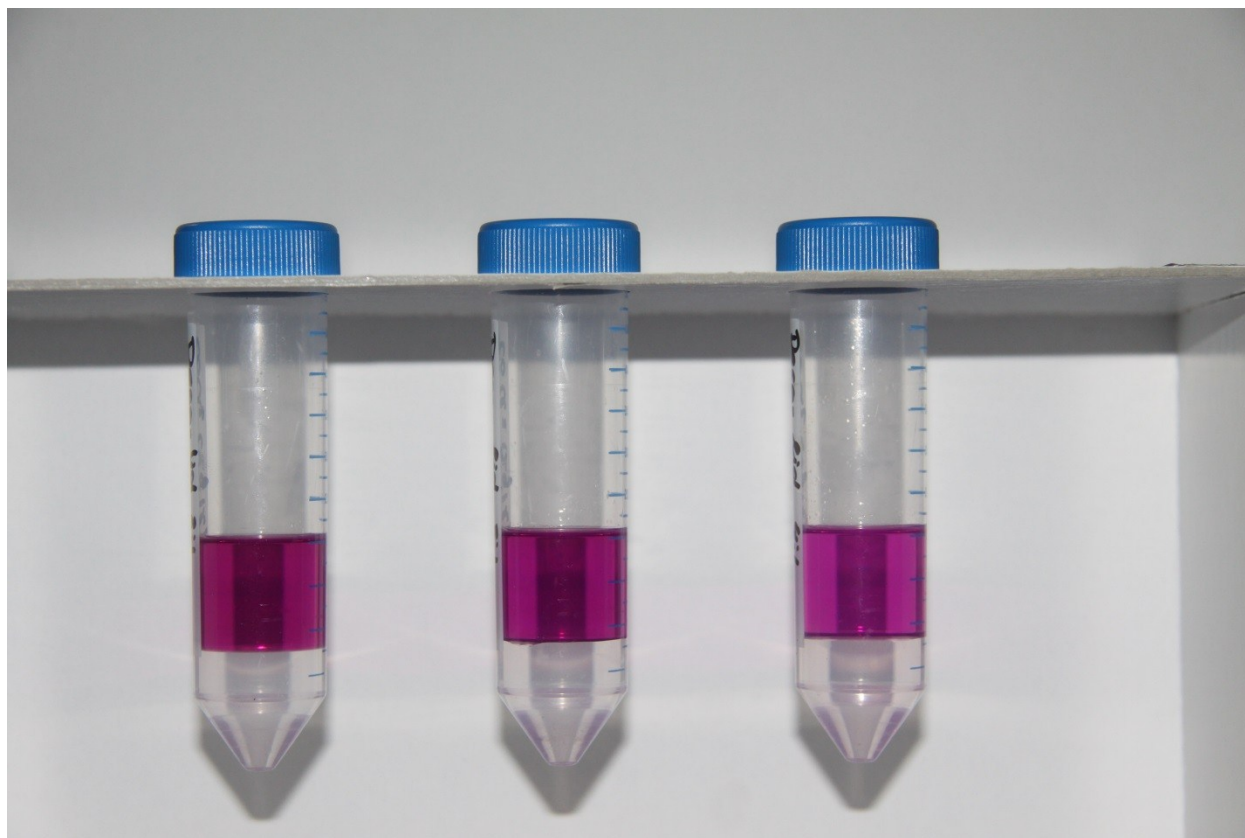


Figure S35 Photo after the extraction of 2.0 g/l Co^{2+} from an aquatic environment, where approximately 10 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 4.0 g/l Co^{2+} from water with a 1:1 DES to water ratio

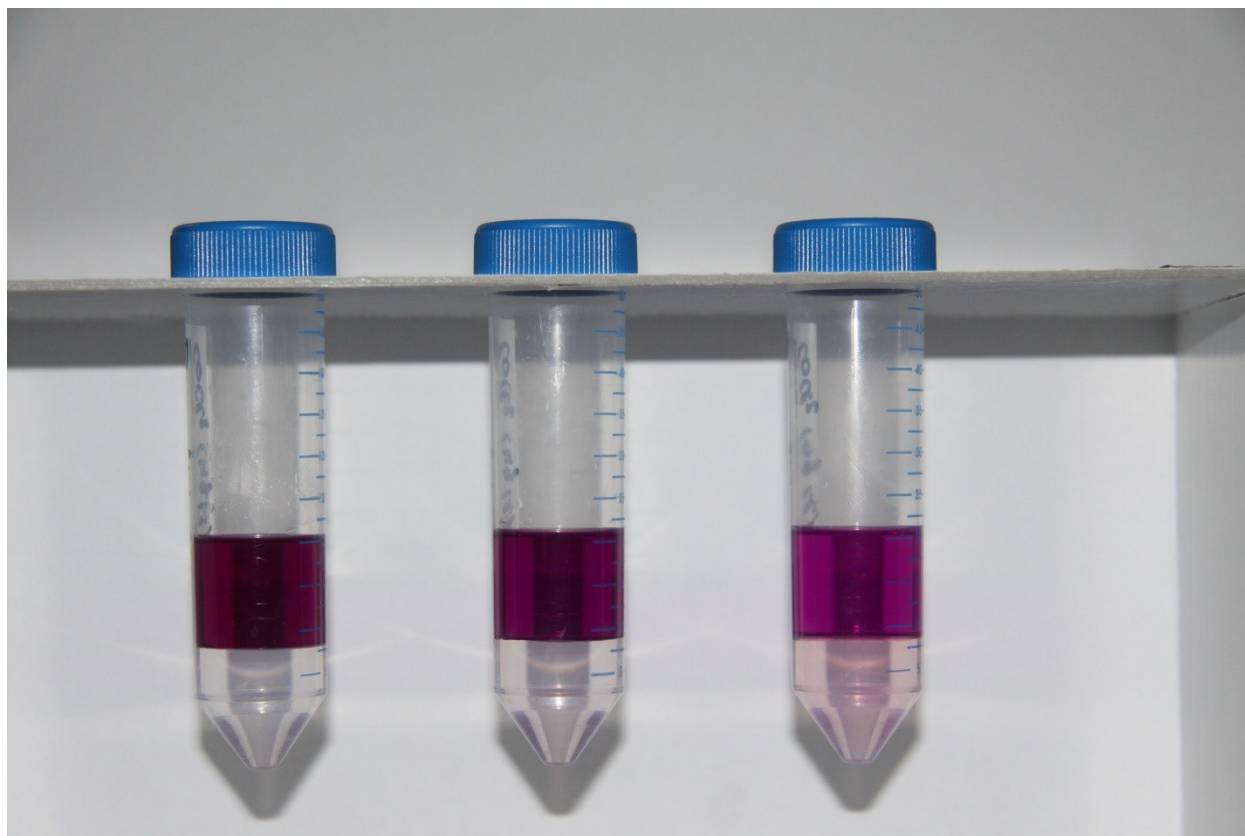


Figure S36 Photo after the extraction of 4.0 g/l Co^{2+} from an aquatic environment, where approximately 10 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l Co^{2+} from water with a 2:1 DES to water ratio

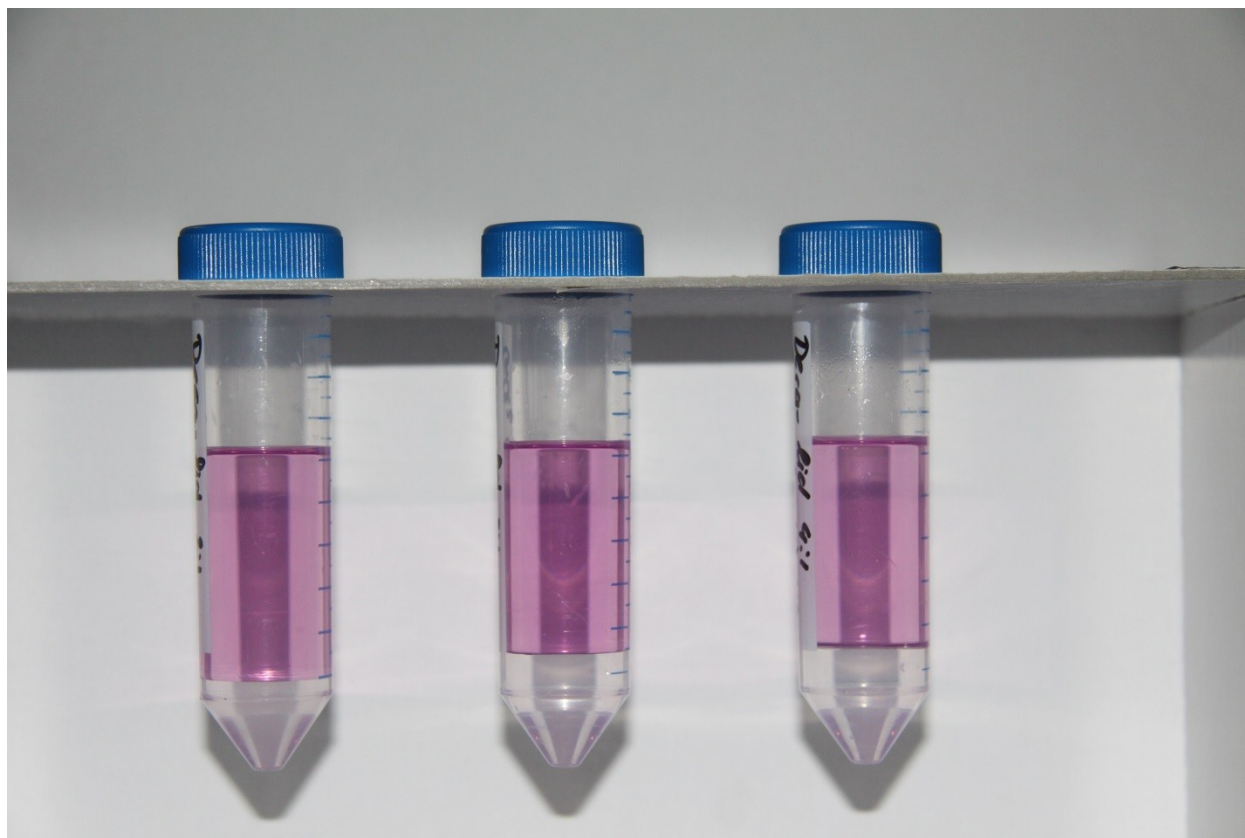


Figure S37 Photo after the extraction of 1.0 g/l Co^{2+} from an aquatic environment, where approximately 20 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l Co^{2+} from water with a 1:2 DES to water ratio

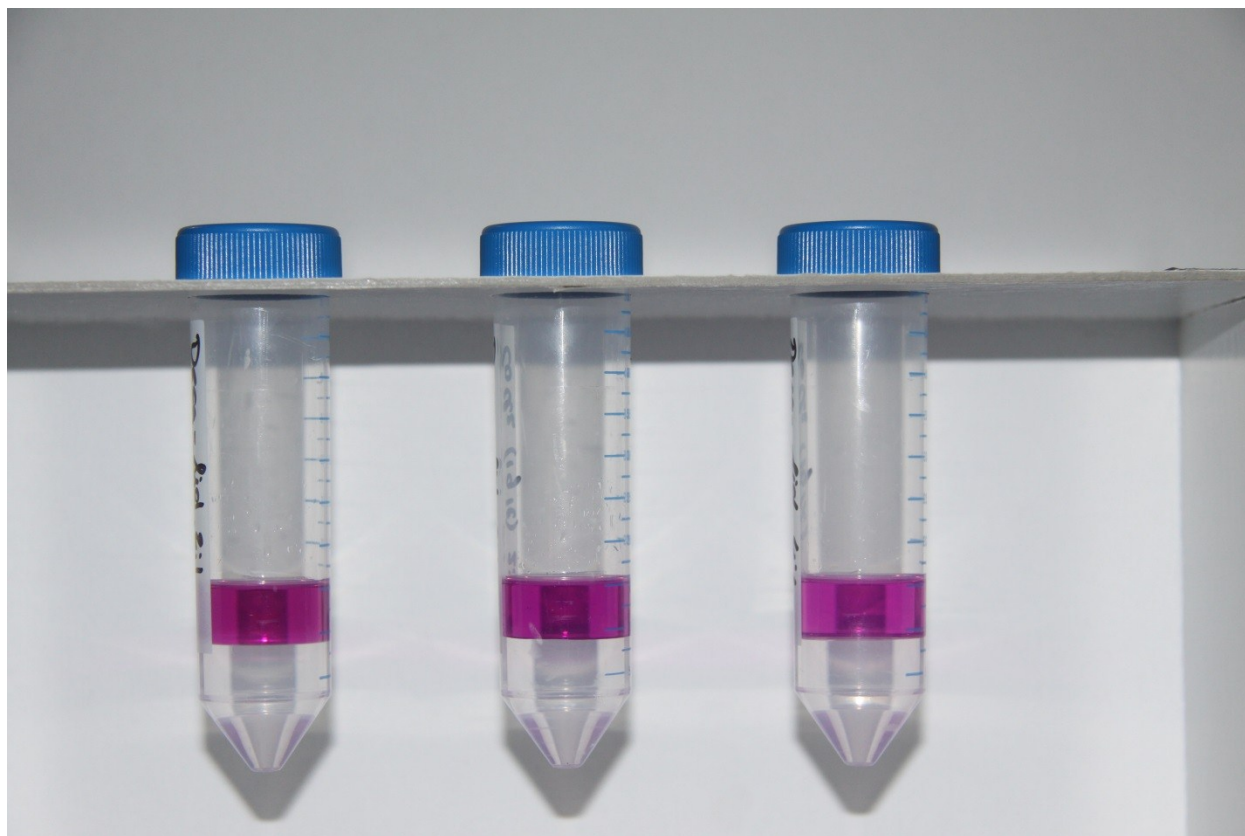


Figure S38 Photo after the extraction of 1.0 g/l Co^{2+} from an aquatic environment, where approximately 5 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l Co^{2+} from water with a 1:5 DES to water ratio

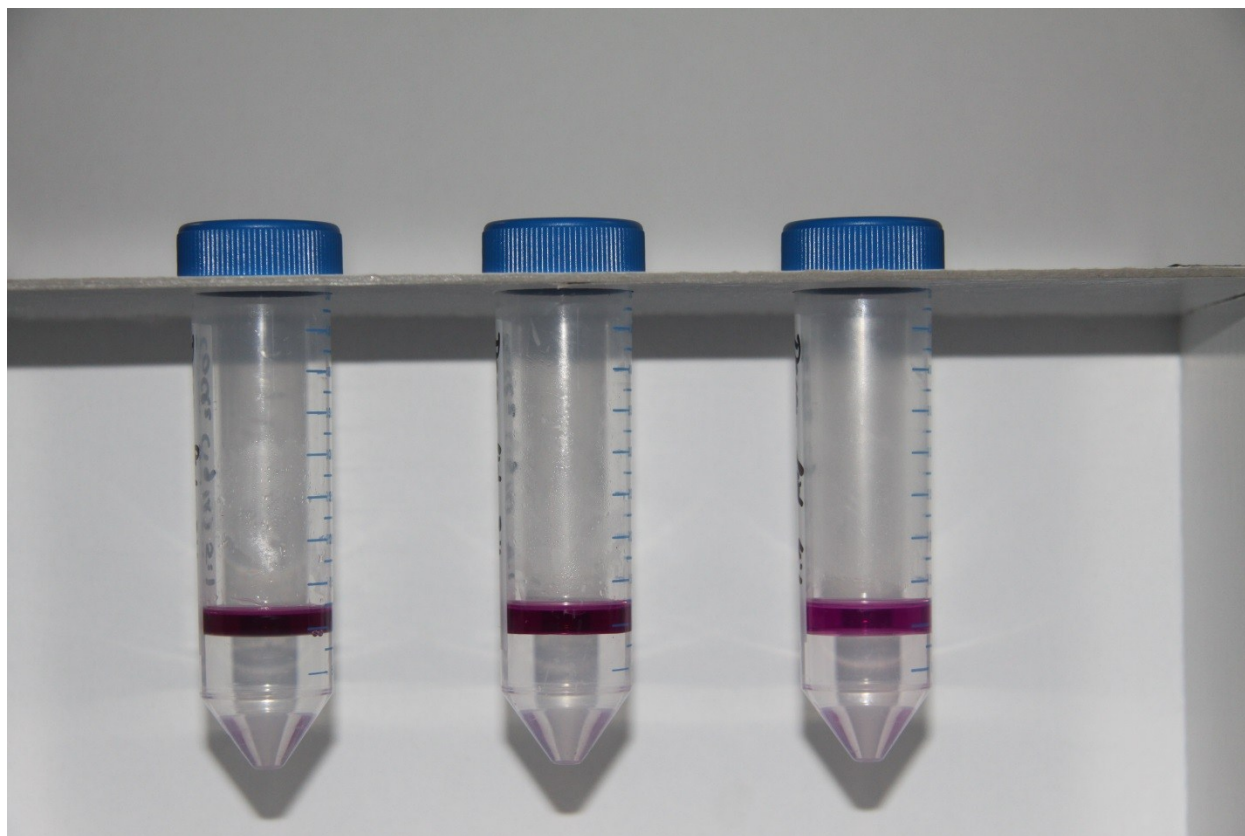


Figure S39 Photo after the extraction of 1.0 g/l Co^{2+} from an aquatic environment, where approximately 2 gram DES (top phase) and 10 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

Extraction of 1.0 g/l Co^{2+} from water with a 1:10 DES to water ratio

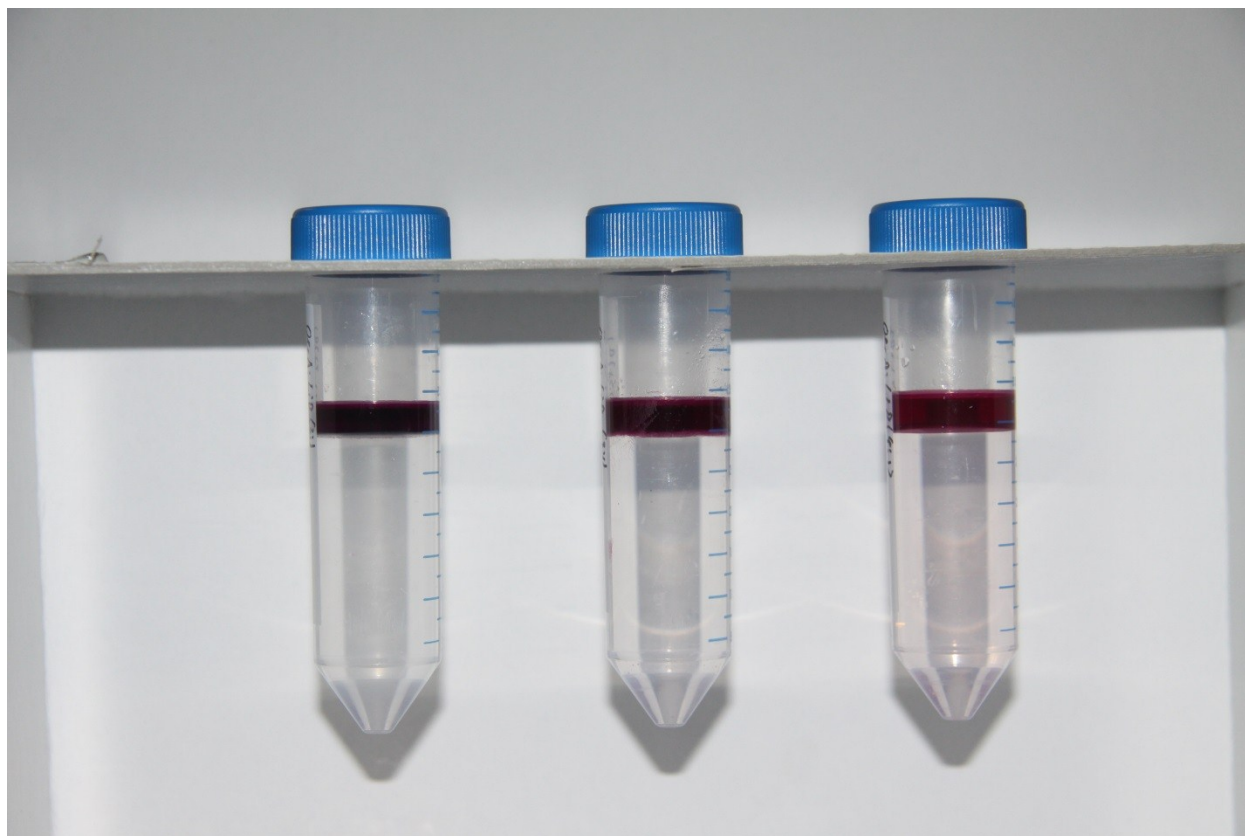


Figure S40 Photo after the extraction of 1.0 g/l Co^{2+} from the aquatic environment, where approximately 3 gram DES (top phase) and 30 ml of water solution (bottom phase) was used. From left to right the ratio of the DESs are varied from 2:1 to 4:1.

DES, 1.0 g/l Co^{2+} in water and extraction of Co^{2+} from water with a 1:1 DES to water ratio

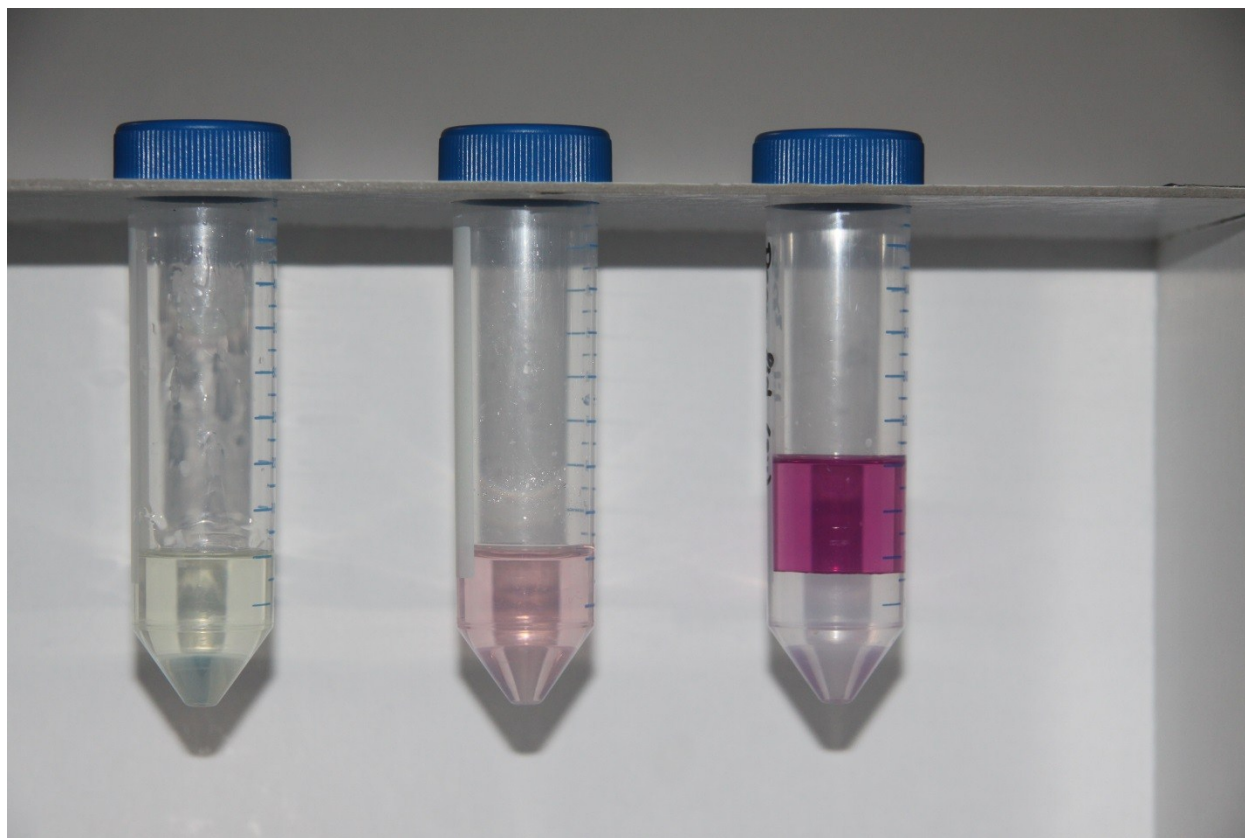


Figure S41 The photo depicts from left to right the pure DES DecA:Lid in a 2:1 ratio, 1.0 g/l CoCl_2 dissolved in water and the DES and water phase after extraction (this flask was shaken and afterwards centrifuged).