Ionic Liquids $[M^{3+}][A^-]_3$ with Three-Valent Cations and Their Possible Use to Easily Separate Rare Earth Metals

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Author Contributions

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Experimental Procedures

H[C8E5c] (3,6,9,12,15,18-Hexaoxahexacosanoic acid/Akypo LF1, kindly provided by Kao Chemicals) was purified by hot water extraction (70 °C). The still hot aqueous layer was discarded, and the organic phase was dried via distillation. Lanthanum and yttrium hydroxides were prepared from their chlorides by precipitation from aqueous solution with sodium hydroxide. The precipitates were washed thoroughly with sodium hydroxide solution (1 mol l⁻¹) and water and dried. Europium carbonate (99.99%, Alfa Aesar) was used without further purification.

The rare earth metal (REM) ionic liquids were obtained by direct neutralisation of the REM salts (3.3 mmol) with three equivalents of H[C8E5c] (4 g, 9.8 mmol), dissolved in 5 mL of a 1 : 3 mixture of water and acetonitrile. This reaction mixture was refluxed until no solids remained. A slight excess (5 wt%) of the REM salt was added, and the reaction mixture was refluxed for an additional hour. After distillative removal of the solvent, the ILs were redissolved in acetone and filtered through a 0.2 µm PTFE syringe filter to remove any precipitate. The solvent was removed via distillation, and the resulting light yellow to yellow viscous liquids were pre-dried via lyophilisation and dried at 60 °C and 10⁻⁶ mbar. The water content was determined by volumetric Karl-Fischer titration using a Metrohm 870 KF Titriplus.

Melting points were determined by differential scanning calorimetry (DSC) using a PerkinElmer DSC 8000, which was gently flooded with N₂ to avoid condensation. The samples were sealed in aluminium crucibles and cooled to -80 °C for 60 min and then heated at 10 °C min⁻¹ until the upper boundary of 10 °C was reached. There, the temperature was held for 5 min before cooling to the minimum temperature at the same rate. An additional measurement was made in the range of −60 to 20 °C, with a heating/cooling rate of 2 °C min⁻¹. Each measurement was performed in triplicate.

Viscosities measurements were carried out on a Bohlin rheometer (type CVO 100) working with a CP20/4° cone at shear rates ranging from 0.1 to 250 s⁻¹. Measurements were performed at a temperature range from 15-60 °C.

Densities were measured in the same temperature range using an Anton Paar DMA60 oscillating tube densitometer. The device was calibrated with dry air and water prior to each measurement.

Conductivities were determined via impedance measurements in a frequency range of f = 10⁻¹ – 10⁷ Hz using a Novocontrol Alpha-Analyzer, equipped with a Quatro temperature controller in a temperature range of 15-60 °C. Two gold-plated disks (diameter: 10 mm) were used as electrodes, using three glass filaments (thickness: 50 µm) as spacers, which yielded a cell constant of 6·10⁻³ cm⁻¹. All samples were tempered in the closed cell at 80 °C for up to 6 h until the measurements were stable. The respective DC conductivities were deduced using the Random Free Energy Barrier Hopping model developed by Dyre[1], which describes the complex conductivity σ by the following equation:

\[ \sigma^*(\omega) = \sigma_0 \frac{i\omega \tau_e}{\ln(1 + i\omega \tau_e)} \]  

where \( \tau_e \) is the attempt frequency to overcome the largest barrier determining the DC-conductivity, and \( \sigma_0 \) is the respective DC conductivity. For the determination of \( \sigma_0 \), equation (1) was split into real and imaginary parts, and the real part was used to fit the data:

\[ \sigma' = \sigma_0 \tau_e \frac{\ln(1 + \omega^2 \tau_e^2)}{\frac{1}{2} \ln^2(1 + \omega^2 \tau_e^2) + 2(\arctan(\omega \tau_e))^2} \]  

The distribution coefficients P were determined by the shake-flask method. Solutions of all ionic liquids in water-saturated 1-octanol (c = 1 mM) were prepared and vigorously shaken with an equal volume of octanol-saturated water for ten minutes. The mixtures were left to separate for at least 24 h at a temperature of 25 °C. After separation, the REM ion concentration was determined via ICP-OES. Here, an ICP-OES Spectroblue TII by Spectro Analytical Instruments was used. Calibration was performed using a Supelco TraceCERT Rare earth element mix for ICP (50 mg/mL in nitric acid).

Fluorescence measurements of the neat ionic liquids were performed on a Horiba FL3-221HR Fluorolog in 10 mm quartz cuvettes from Starna and Hellma.
Results and Discussion

Figure S1. Glass transition temperature ($T_g$) scaled Arrhenius plot of the specific conductivities (left) and viscosities (right) of [REM][C8E5c]$_3$ ILs (◻, blue) [La][C8E5c]$_3$, (◇, green) [Eu][C8E5c]$_3$, (○, orange) [Y][C8E5c]). $T_g$ was estimated via Vogel-Fulcher-Tammann Fit of the viscosity and extrapolating to $\eta = 10^{12}$ Pas.

Figure S2. Angell plot of [REM][C8E5c]$_3$ ILs. All investigated ILs display similarly high fragility.
The Vogel-Fulcher-Tammann (VFT) equation was used to fit both the specific conductivities and the viscosities of the ionic liquids. It contains three adjustable parameters: a pre-exponential factor $\sigma_0$, or $\eta_0$, a pseudo activation energy $E$, and a Vogel temperature $T_0$. The individual VFT equations for the individual data sets differ in the sign of their exponent:

$$\sigma = \sigma_0 \cdot e^{-\frac{E}{R(T-T_0)}}$$
$$\eta = \eta_0 \cdot e^{\frac{E}{R(T-T_0)}}$$

The results of the respective fits are summarised in Tables S1 and S2.

**Table S1.** VFT parameters obtained from the fits of temperature-dependent viscosity data of [Y], [La] and [Eu][C8E5c]3.

| Cation | $\eta_0$ [Pa·s] | $E$ [J/mol] | $T_0$ [K] |
|--------|----------------|-------------|-----------|
| La     | $1.99 \cdot 10^{-3}$ | 9093        | 191.3     |
| Y      | $6.46 \cdot 10^{-4}$ | 9094        | 159.0     |
| Eu     | $5.69 \cdot 10^{-3}$ | 6781        | 206.7     |

**Table S2.** VFT parameters obtained from the fits of temperature-dependent specific conductivity data of [Y], [La] and [Eu][C8E5c]3.

| Cation | $\log(\sigma_0)$ [log(S/cm)] | $E$ [J/mol] | $T_0$ [K] |
|--------|-------------------------------|-------------|-----------|
| La     | -1.35                         | 12241       | 171       |
| Y      | -3.83                         | 3896        | 223       |
| Eu     | -2.18                         | 26600       | 75.1      |
### Table S3. Densities $\rho$ of the investigated ionic liquids at temperatures between 15 and 60 °C.

| $T$ [K] | $\rho$ [g/cm³] | [La][C8E5c]$_3$ | [Y][C8E5c]$_3$ | [Eu][C8E5c]$_3$ |
|---------|-----------------|------------------|-----------------|-----------------|
| 288.15  | 1.1639          | 1.1520           | 1.2270          |
| 293.15  | 1.1596          | 1.1478           | 1.2226          |
| 298.15  | 1.1554          | 1.1437           | 1.2182          |
| 308.15  | 1.1469          | 1.1354           | 1.2094          |
| 323.15  | 1.1343          | 1.1231           | 1.1962          |
| 333.15  | 1.1260          | 1.1149           | 1.1874          |

### Table S4. Logarithmic specific conductivities $\log(\sigma')$ of the investigated ionic liquids between 15 and 60 °C.

| $T$ [K] | $\log(\sigma')$ [log(S/cm)] | [La][C8E5c]$_3$ | [Y][C8E5c]$_3$ | [Eu][C8E5c]$_3$ |
|---------|-----------------------------|------------------|-----------------|-----------------|
| 288.15  | -6.75                       | -6.90            | -8.70           |
| 293.15  | -6.58                       | -6.74            | -8.55           |
| 298.15  | -6.39                       | -6.58            | -8.40           |
| 308.15  | -6.01                       | -6.26            | -8.14           |
| 323.15  | -5.55                       | -5.87            | -7.78           |
| 333.15  | -5.29                       | -5.69            | -7.56           |

### Table S5. Logarithmic molar conductivities $\log(\Lambda)$ of the investigated ionic liquids between 15 and 60 °C.

| $T$ [K] | $\log(\Lambda)$ [log(S·cm²/mol)] | [La][C8E5c]$_3$ | [Y][C8E5c]$_3$ | [Eu][C8E5c]$_3$ |
|---------|-----------------------------------|------------------|-----------------|-----------------|
| 288.15  | -3.69                             | -3.83            | -5.65           |
| 293.15  | -3.52                             | -3.66            | -5.50           |
| 298.15  | -3.33                             | -3.50            | -5.35           |
| 308.15  | -2.96                             | -3.18            | -5.08           |
| 323.15  | -2.49                             | -2.79            | -4.72           |
| 333.15  | -2.23                             | -2.61            | -4.50           |
Table S6. Dynamic viscosities $\eta$ of the investigated ionic liquids between 15 and 60 °C.

| $T$ [K] | $\eta$ [Pa·s] |
|---------|---------------|
|         | [La][C8E5c] | [Y][C8E5c] | [Eu][C8E5c] |
| 288.15  | 152.2       | 3.064     | 126.7       |
| 293.15  | 91.92       | 2.274     | 70.62       |
| 298.15  | 56.14       | 1.672     | 42.23       |
| 308.15  | 23.07       | 0.9888    | 18.00       |
| 323.15  | 7.991       | 0.5096    | 6.263       |
| 333.15  | 4.459       | 0.3452    | 3.607       |

Table 7. Vertical deviations $\Delta W$ from the ideal KCl line in the Walden plot.

| $T$ [K] | $\Delta W$ [log(Scm²/mol)] |
|---------|-----------------------------|
|         | [La][C8E5c] | [Y][C8E5c] | [Eu][C8E5c] |
| 288.15  | -0.51         | -2.34      | -2.65       |
| 293.15  | -0.56         | -2.31      | -2.73       |
| 298.15  | -0.59         | -2.28      | -2.83       |
| 308.15  | -0.59         | -2.18      | -2.92       |
| 323.15  | -0.58         | -2.08      | -2.94       |
| 333.15  | -0.58         | -2.07      | -2.65       |

Figure S4. Uncorrected excitation (blue) and emission (red) spectra of [H][C8E5c]. Excitation wavelengths were 286 nm (primary maximum) and 337 nm (secondary maximum), emission wavelengths 310 nm (primary maximum) and 400 nm (secondary maximum).
NMR Analysis

$^1$H (CDCl$_3$) and $^{13}$C (CDCl$_3$) NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz with tetramethylsilane (TMS) as standard.

3,6,9,12,15,18-Hexaoxahexacosan-1-oic acid [H][C8E5c]:

$^1$H NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 6.29 (s, COO$^-$H), 4.14 (q, 2H, CH$_2$COOH), 3.64 (m, 22H, OCH$_2$CH$_2$O), 1.55 (m, 2H, OCH$_2$C$_7$H$_{15}$), 1.37 – 1.15 (m, 12H, CH$_2$), 0.84 (t, 3H, CH$_3$).

$^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 172.14 (C OO$^-$H), 71.57 (O C$^-$H$_2$C$_7$H$_{15}$), 70.94, 70.51, 70.40, 70.28 (O C$^-$H$_2$O), 69.99 (C H$_2$COOH), 31.83, 29.45, 29.27, 26.06, 22.66 (CH$_2$), 14.12(CH$_3$).

Yttrium (III) tris-(3,6,9,12,15,18-Hexaoxahexacosan-1-oate) [Y][C8E5c]:

$^1$H NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 3.63 (m, 22H, OCH$_2$CH$_2$O), 3.43 (t, 2H, CH$_2$COOH), 1.56 (m, 2H, OCH$_2$C$_7$H$_{15}$), 1.27 (m, 12H, CH$_2$), 0.87 (t, 3H, CH$_3$).

$^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 71.56 (O C$^-$H$_2$C$_7$H$_{15}$), 70.57 (O C$^-$H$_2$C$_7$H$_{15}$), 70.05 (C H$_2$COOH), 31.84, 29.64, 29.47, 29.29, 26.11, 22.68 (CH$_2$), 14.14 (CH$_3$).

Lanthanum (III) tris-(3,6,9,12,15,18-Hexaoxahexacosan-1-oate) [La][C8E5c]:

$^1$H NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 3.55 (m, 22H, OCH$_2$CH$_2$O), 3.41 (t, 2H, CH$_2$COOH), 1.41 (m, 2H, OCH$_2$C$_7$H$_{15}$), 1.15 (m, 12H, CH$_2$), 0.73 (t, 3H, CH$_3$).

$^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 71.56 (O C$^-$H$_2$C$_7$H$_{15}$), 70.57 (O C$^-$H$_2$C$_7$H$_{15}$), 70.04 (C H$_2$COOH), 31.87, 29.63, 29.46, 29.28, 26.10, 22.67 (CH$_2$), 14.13 (CH$_3$).

Europium (III) tris-(3,6,9,12,15,18-Hexaoxahexacosan-1-oate) [Eu][C8E5c]:

$^1$H NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 3.6 (m, 22H, OCH$_2$CH$_2$O), 3.44 (t, 2H, CH$_2$COOH), 1.55 (m, 2H, OCH$_2$C$_7$H$_{15}$), 1.27 (m, 12H, CH$_2$), 0.88 (t, 3H, CH$_3$).

$^{13}$C NMR (300 MHz, CDCl$_3$, 25 °C, TMS) δ = 71.57 (O C$^-$H$_2$C$_7$H$_{15}$), 70.60 (O C$^-$H$_2$C$_7$H$_{15}$), 70.06 (C H$_2$COOH), 31.85, 29.65, 29.48, 29.30, 26.11, 22.69 (CH$_2$), 14.15 (CH$_3$).

References

[1] F. Kremer, A. Schönhals, Eds., Broadband Dielectric Spectroscopy, Springer-Verlag Berlin Heidelberg GmbH, 2002.

Author Contributions

M. Rothe designed and performed the majority of the experiments and data interpretation and wrote the manuscript. M. Tress performed the conductivity measurements, aided in the respective data analysis and assisted in writing the manuscript. C. Allacher performed the fluorescence measurements and helped with the interpretation of the data and with writing the manuscript. P. Nuernberger helped with the interpretation of the fluorescence data and assisted in writing the manuscript. W.K. supervised the project and assisted in writing the manuscript.