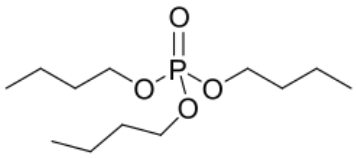
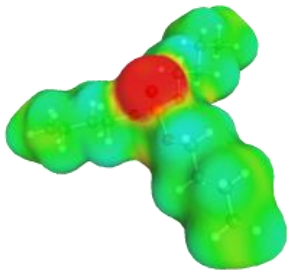
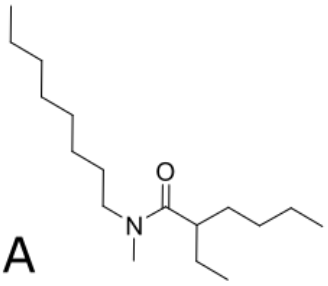
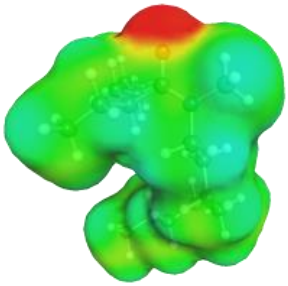
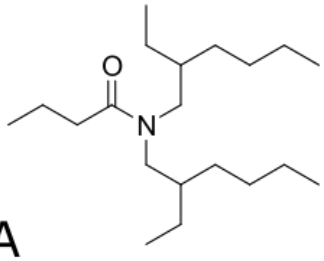
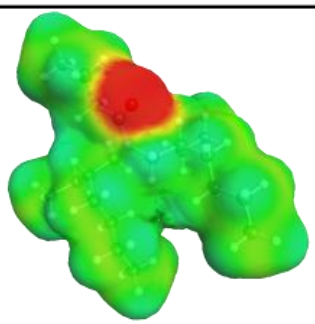
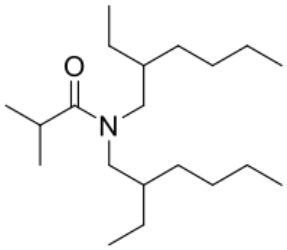
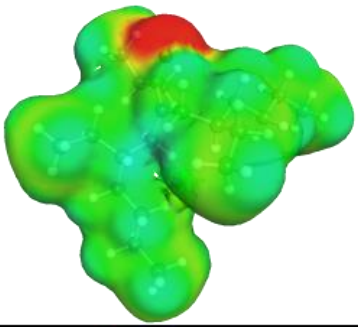
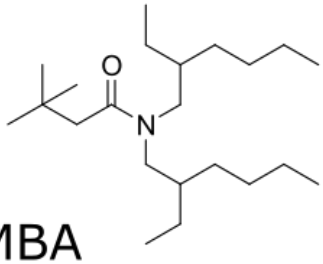
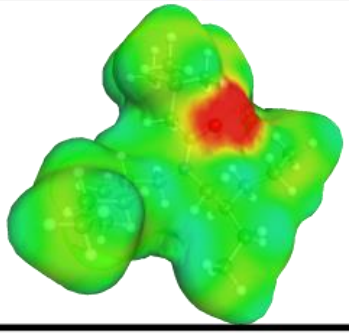
Supplementary Information

Extractant structures and COSMO cavities

 TBP	
 MOEHA	
 DEHBA	
 DEHiBA	
 DEHDMBA	

Estimation of the spontaneous packing parameter from geometry

In order to keep the model general and simple, the spontaneous packing parameter was estimated from geometry to explain the qualitative trends observed.

The chain length l_c as well as the volume $V_{\text{apolar, linear}}$ of the apolar part in case of linear chains can be calculated by Tanford's formulas: [1]

$$l_c \leq 0.15 + 0.127 n_c \text{ [nm]} \quad (1)$$

$$V_{\text{apolar, linear}} = 0.0274 + 0.0269 n_C \text{ [nm}^3\text{]} \quad (2)$$

where n_c represents the number of carbon atoms. For more than one chain, the volumes of all alkyl chains have to be summed up to obtain the total apolar volume. The equation for l_c calculates the length of the fully extended chain. In aqueous systems, the effective chain length of surfactant molecules in the micellar core is about 80% of the extended chain. For extractant molecules, where the chains point towards the organic solution, the chains are also expected to be smaller than the calculated chain length. But since to our knowledge, there is no general rule for the chain length in extractant systems, no factor is applied to implement the effective chain length and the maximal possible value is taken. Since this shortening is expected to be approximately by the same factor for the systems investigated, this assumption does not change the qualitative trends.

For branched chains, the table of Fedors can be used to calculate the apolar volume [2].

$$V_{\text{apolar,branched}} = n_{\text{CH}_3} V_{\text{CH}_3} + n_{\text{CH}_2} V_{\text{CH}_2} + n_{\text{CH}} V_{\text{CH}} + n_{\text{C}} V_{\text{C}} \quad (3)$$

with n_x being the number of alkyl group x and V_x the corresponding molecular volume taken from the table of Fedors. Solvent penetration[87] is excluded in this calculation. For the monoamide extractants, only the two long chains are considered. The short chain is counted to the polar part, since the small chain defines the selectivity [3] and since the influence of the smaller chain on the headgroup size is seen in interfacial tension measurements (results not

shown). The volume of the polar head of the molecule can be calculated by the difference of the total volume of the molecule and the volume of the apolar part:

$$V_{\text{polar head}} = V_{\text{molecule}} - V_{\text{apolar}} = \frac{M_{\text{mol}}}{\rho \cdot N_A} - V_{\text{apolar}} \qquad (4)$$

where M_{mol} represents the molar mass of the amphiphile molecule, ρ its density and N_A the Avogadro number.

In the following, a spherical micelle formed by 4 extractant molecules (a typical value) is considered. It is further assumed that the geometry stays spherical, but the polar core can swell due to addition of water, acid and metal ions. The length of the extractant chains as well as its volume is not significantly influenced by this swelling. Only the area per headgroup at the polar/apolar interface increases with metal addition (*cf.* **Figure S1**).

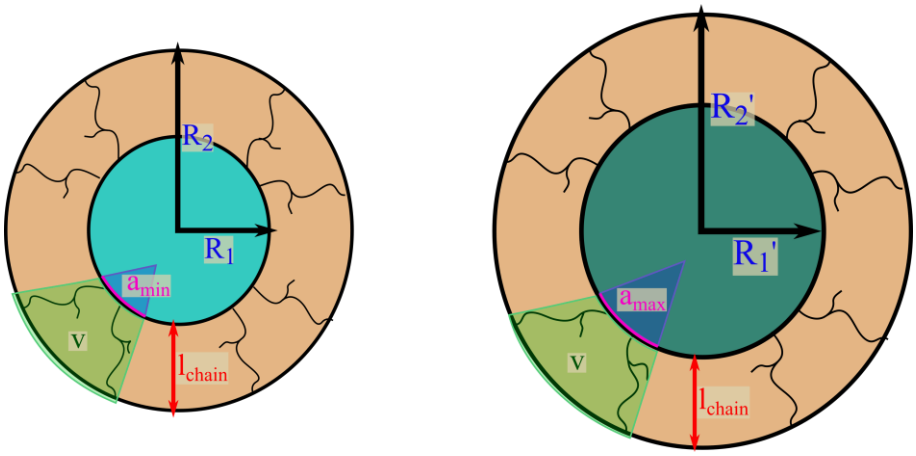


Figure S1. Schematic evolution of the area per headgroup per extractant due to volume increase of the polar core.

As a consequence, the spontaneous packing parameter decreases with the addition of metal ions. The volume V_{chain} and the length l_c of extractant chains can be calculated as described above.

$$P_0' = \frac{V_{chain}}{a_0 \cdot l_c} \qquad (5)$$

For the estimation of the area per headgroup, one can assume the polar core as formed by different geometries. We have decided to assume an octahedron embedded in the polar core. For an assumption of four extractant molecules, two faces of the octahedron represent the estimated interfacial area that is needed for the calculation of the spontaneous packing parameter P_0' (*cf.* **Figure S2**)

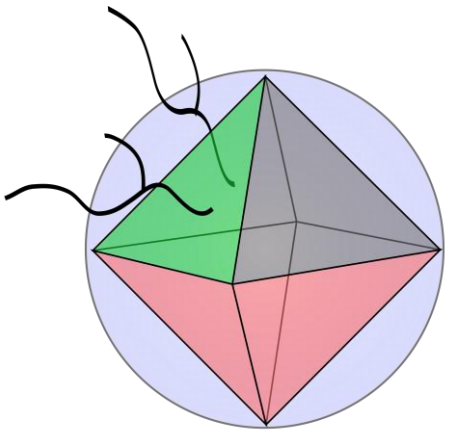


Figure S2. Estimation of the interfacial area per extractant to calculate the spontaneous packing parameter from geometry using an approximation of the polar core as an octahedron. Two triangular faces represent the polar area per extractant.

The radius of the polar core at '*zero loading*' and at '*maximum loading*' with uranyl can be calculated as follows. At zero loading, the size of the polar core is determined by the sum of the volume of four polar head groups and the water and acid uptake. In the case of maximum loading, the volume of the complexed uranyl must be also considered. In total, the volume of a polar core V_{core} can be approximated by the mean stoichiometry of a spherical aggregate.

$$V_{core} = 4 \cdot \left(V_{\text{polar head}} + \frac{n_{\text{H}_2\text{0}}}{n_{\text{Ex}}} \cdot V_{\text{H2O}} + \frac{n_{\text{NO}_3-}}{n_{\text{Ex}}} \cdot V_{\text{NO}_3-} + \frac{n_{\text{UO}_2}}{n_{\text{Ex}}} \cdot V_{\text{UO}_2} \right) \qquad (6)$$

with $V_{\text{polar head}}$ being the polar head volume derived from equation (26), $\frac{n_x}{n_{\text{Ex}}}$ being the stoichiometric mol ratio between compound *x* and the extractant and V_x being the molecular volume of compound *x*.

The core radius yields then to

$$R_{\text{core}} = \left(\frac{3V_{\text{core}}}{4\pi}\right)^{\frac{1}{3}} \quad (7)$$

In case of assuming octahedral geometry, the polar surface area of an extractant is twice that of one triangular face of the octahedron.

$$b_{\text{octahedron}} = \frac{2 \cdot R_{\text{core}}}{\sqrt{2}} \quad (8)$$

$$a_0(\text{octahedron}) = 0.5 \cdot a_0(\text{extractant}) = \frac{{b_{\text{octahedron}}}^2 \cdot \sqrt{3}}{4} \quad (9)$$

The equations for the calculations of the volume, the surface area and the radius of the circumcircle of tetrahedrons and octahedrons were taken and rearranged from [4].

Table S1. Characteristic properties of the main extractants investigated

	TBP	MOEHA	DEHBA	DEH*i*BA	DEHDMBA
Formula	$C_{12}H_{24}O_4P$	$C_{17}H_{35}NO$	$C_{20}H_{41}NO$	$C_{20}H_{41}NO$	$C_{22}H_{45}NO$
Molar mass [g/mol]	266.32	269.47	311.55	311.55	339.61
Molar volume [Å³/molecule]	451.2	521.5	595.4	604.4	652.8
l_{chain} [Å]	6.5	10.3	9.1	9.1	9.1
V_{apolar} [Å³]	407.4	459.2	486.5	486.5	486.5
V_{polar} [Å³]	43.8	62.2	108.9	117.9	166.3
$V_{\text{pol.core}}$ [Å³] at x = 0	335	355	564	576	770
$V_{\text{pol.core}}$ [Å³] at x = 0.43	422	488	673	709	903

Table S2. Calculation of the spontaneous packing parameter at x = 0 and x = 0.43 assuming an octahedral arrangement of the extractant headgroups around the core calculated for the main extractants investigated

	TBP	MOEHA	DEHBA	DEHiBA	DEHDMBA
$b_{\text{octahedron}}$ at x = 0 [Å]	6.10	6.21	7.25	7.30	8.04
$b_{\text{octahedron}}$ at x = 0.43 [Å]	6.58	6.91	7.69	7.83	8.48
$a_{0,\text{oct}}$ at x = 0 [Å²]	16.09	16.71	22.74	23.07	27.99
$a_{0,\text{oct}}$ at x = 0.43 [Å²]	18.74	20.67	25.61	26.51	31.14
P_0' at x = 0	3.87	2.66	2.36	2.33	1.92
P_0' at x = 0.43	3.32	2.15	2.10	2.03	1.72

Hexagon definition for the Monte-Carlo-like Simulation

For this model, the aggregation number per microphase is needed since it has an influence on the free energy of bending per microphase and consequently on the microphase distribution. Since the size definition is also relevant for the hexagonal grid in the case of the Monte-Carlo-like simulation, a hexagonal grid was also relevant for the estimation of the aggregation numbers per microphase. The microphase units were defined in a way that each unit fits approximately into one hexagon.

The aggregation number can be then calculated as

$$N_{\mathrm{agg}}(\mathrm{microphase}) = \frac{V_{\mathrm{apol}}(\mathrm{microphase})}{V_{\mathrm{apol}}(\mathrm{extractant})} \qquad (10)$$

with V_{apol}(extractant) being the apolar volume of the extractant, in the case of two di-ethyl hexyl chains, V_{apol}(extractant) can be calculated from the table of Fedors[206] as 486.5 Å³.

Endcaps:

Endcaps were defined as half a spherical aggregate with a core radius R_c and a total aggregate radius of R_{tot}. The resulting volume of the apolar part can be calculated as follows:

$$V_{\mathrm{apol}}(\mathrm{endcap}) = \frac{1}{2} \cdot \frac{4}{3}\pi \cdot (R_{\mathrm{tot}}^3 - R_{\mathrm{C}}^3) \qquad (11)$$

Cylinder:

For cylinder units, a cylindrical aggregate with the same R_{tot} and the same R_c as in the case of endcaps was assumed. The length L of one cylinder unit was defined as the uranyl-uranyl distance of around 1 nm seen in SAXS measurements. The volume of the apolar part of a cylinder unit can be estimated as:

$$V_{\mathrm{apol}}(\mathrm{cylinder}) = \pi \cdot (R_{tot}^2 - R_{\mathrm{C}}^2) \cdot L \qquad (12)$$

Junction:

The definition of junctions is more complex, since the shape of junctions can vary from system to system. Therefore, one junction units was put together of three cylinders of half the length of cylinder microphase units and a prism. The prism represents the bilayer part of a junction. As base area of a prism, a equilateral triangle was chosen. The side length of one triangle corresponds to the diameter of a cylinder unit, just as well as the height of this prism, allowing to connect this prism to all three small cylinder units to result in a junction. As polar part, three smaller cylinders and a smaller prism were chosen that are connected via three further cylinders. The length of these cylinders can be approximated as 1/3*(h_1-h_2), since the center mass of an equilateral triangle lies on 1/3 of the height. The characteristic lengths are shown in **Figure S3.**

$$V_{\mathrm{apol}}(\mathrm{junction}) = \frac{3}{2} V_{\mathrm{apol}}(\mathrm{cylinder}) + V_{\mathrm{apol}}(\mathrm{prism}) \qquad (13)$$

$$V_{\mathrm{apol}}(\mathrm{prism}) = \frac{(2R_{tot})^2\sqrt{3}}{4} - \frac{(2R_c)^2\sqrt{3}}{4} - \frac{1}{3}\left(\frac{\sqrt{3}}{2}(2R_{\mathrm{tot}} - 2R_{\mathrm{c}})\right) \qquad (14)$$

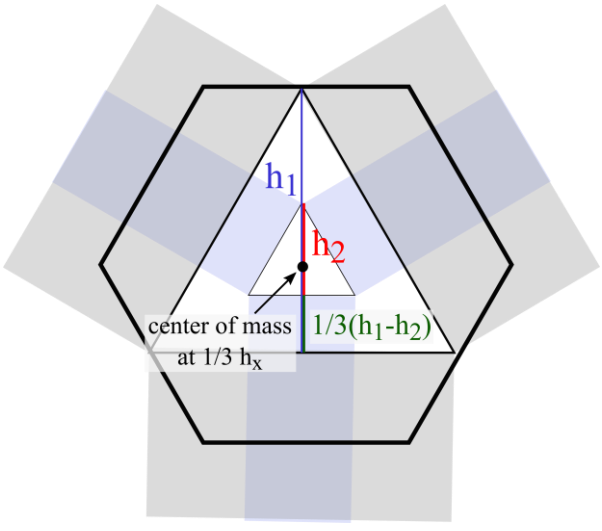


Figure S3. Scheme to calculate the volume of the apolar part of the junction

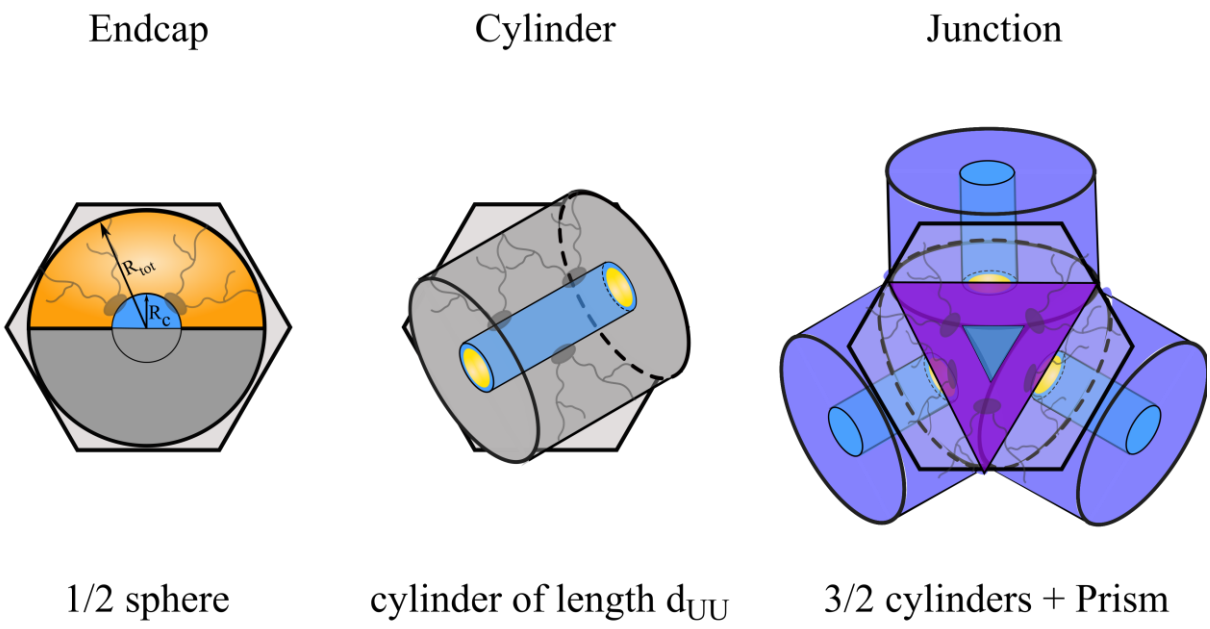


Figure S4. Scheme of microphase definition with help of a hexagonal grid

References

[1] C. Tanford, Micelle shape and size, J. Phys. Chem. 76 (1972) 3020–3024.

[2] R.F. Fedors, A method for estimating both the solubility parameters and molar volumes of liquids, Polym. Eng. Sci. 14 (1974) 147–154.

[3] P.N. Pathak, L.B. Kumbhare, V.K. Manchanda, Structural effects in N ,N -Dialkyl amides on their extraction behavior towards uranium and thorium, Solvent Extraction and Ion Exchange 19 (2001) 105–126.

[4] H. Gärtner, H. Gascha, Formelsammlung: Mathematik, Physik, anorganische Chemie, 4. Aufl. ed., Compact SilverLine Taschenbuch, Compact, München, 2013.