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Abstract
Recent molecular dynamics simulations of trivalent rare-earth metal ions in dry chloroform have revealed a higher extraction efficiency than in their solution in water. In this work, we investigated the influence of counterion effects on the extraction of lanthanide cations (La, Eu, Gd, Dy, Ho, Er, Y, and Yb) for the substituted calixarene 4,4’,4”-tris(t-butylphosphinooxime)1,3,4-benzenetricarboxylate (L). We analyzed the coordination modes of the lanthanide cations and the steric hindrance of the calixarene in “bulk” conditions. The cation coordination strongly depends on the solvent environment and the rigidity of the interface. We observed a higher extraction efficiency and a more pronounced selectivity towards the trivalent lanthanide cations than for other lanthanide cations. The occupied coordination sites are of inclusive type in dry chloroform, while they are of exclusive type in water and chloroform mixtures. The presence of counterions at the interface reduces the extraction efficiency and the selectivity towards the lanthanide cations. In dry chloroform, the counterions are located at the edges of the calixarene. In water, the counterions are located at the center of the calixarene.

Introduction
The need for efficient receptor molecules for the extraction and separation of trivalent lanthanide cations is of increasing importance. A new class of neutral receptor molecules bearing a tridentate ligand and three phosphine oxides is under investigation in our laboratory. These molecules are based on the macrocyclic and macrobicyclic calixarenes.[1] Although the extraction properties of these species are well characterized, there is a lack of knowledge of the molecular recognition and coordination behavior of the trivalent lanthanide cations.[2] We present a theoretical investigation (MD calculations) of the lanthanide extraction behavior and coordination at water/chloroform interfaces. We studied the effect of the anionic environment on the lanthanide coordination behavior and morphology of the calixarene receptors. Our simulations confirm that the cation coordination strongly depends on the solvent environment and the rigidity of the interface. We observed a higher extraction efficiency and a more pronounced selectivity towards the trivalent lanthanide cations than for other lanthanide cations. In dry chloroform, the counterions are located at the edges of the calixarene. In water, the counterions are located at the center of the calixarene.

Methods
All initial structures were model built, starting from X-ray data for the unsubstituted calix[4]arene and introducing a cation into the cone. The simulation protocol was used in a modified version of AMBER 9. The force field parameters were taken from force field and force factor data. Charges were derived from electrostatic potentials that were calculated at the HF 6-31G** level. We chose a non-ambiguous representation of the interactions between the 3+ charged cation and the calix[4]arene, using a primitive additive 6-31G** potential.

Results
In all cases, the complex adopts an amphiphilic orientation at the interface. The cation orientation strongly depends on the solvent environment and the rigidity of the interface. In dry chloroform, the cation coordination is of exclusive type. In water, the cation coordination is of inclusive type. The contribution of the four ether oxygens, which are at 2.6 to 3.0 Å from the center of the calixarene, is important for the cation coordination at the interface. The distance between M3+ and O P=O/O OH2 decreases by 0.5 ns. The cation coordination strongly depends on the solvent environment and the rigidity of the interface. We observed a higher extraction efficiency and a more pronounced selectivity towards the trivalent lanthanide cations than for other lanthanide cations. The occupied coordination sites are of inclusive type in dry chloroform, while they are of exclusive type in water and chloroform mixtures. The presence of counterions at the interface reduces the extraction efficiency and the selectivity towards the lanthanide cations. In dry chloroform, the counterions are located at the edges of the calixarene. In water, the counterions are located at the center of the calixarene.

Conclusions
Our simulations confirm that the calixarenes are highly surface active. They should stimulate further experimental work on the nature of the species that are adsorbed at the interface and on the induced extraction mechanism (hydrophobic effects, ionic interactions, and mixing).

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Figures
Figure 1. Schematic representation of the calix[4]arene receptor. The liquid-liquid interface was built from 2-adjacent water and chloroform solvent boxes with about 1500 TIP3P water molecules and 500 OPLS chloroform molecules.

Figure 2. Simulation box for the water/chloroform interface. The liquid-liquid interface was built from 2-adjacent water and chloroform solvent boxes with about 1500 TIP3P water molecules and 500 OPLS chloroform molecules.

Figure 3. Simulation box for the water/chloroform interface. The liquid-liquid interface was built from 2-adjacent water and chloroform solvent boxes with about 1500 TIP3P water molecules and 500 OPLS chloroform molecules.

Figure 4. Simulation box for the water/chloroform interface. The liquid-liquid interface was built from 2-adjacent water and chloroform solvent boxes with about 1500 TIP3P water molecules and 500 OPLS chloroform molecules.