Dalton Transactions

Accepted Manuscript

www.rsc.org/dalton

Formation of W/O microemulsions in the extraction of Nd(III) by bis(2,4,4-trimethylpentyl)dithiophosphinic acid and its effect on Nd(III) coordination

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Abstract

The formation of water-in-oil (W/O) microemulsions during the extraction of Nd(III) by bis(2,4,4-trimethylpentyl)dithiophosphinic acid (also known as purified Cyanex 301, denoted as HC301) was studied. Results from the measurement of the concentration of Nd(III), Na^+ and NO_3^- in the organic phase, IR spectroscopy, and dynamic light scattering (DLS) all indicated that W/O microemulsions could form as the ratio of the neutralized ligand to Nd(III) in the aqueous phase is over 3:1. The coordination environment of Nd(III) in the extracted complexes was monitored by absorption spectroscopy and extended X-ray absorption fine structure (EXAFS) and was found to vary significantly with the formation of W/O microemulsions. When only 10% of HC301 was neutralized and with no formation of W/O microemulsions, the inner coordination shell of Nd(III) in the organic phase was occupied dominantly by sulfur atoms from HC301. As HC301 was further neutralized, the coordinated sulfur atoms around Nd(III) were replaced gradually by oxygen atoms from water. This work provide further insights into the extraction mechanism in the extraction system using purified Cyanex 301 as an extractant.

Introduction

The partitioning of minor actinides (MAs) from high level liquid waste (HLLW) and the subsequent transmutation of MAs to short lived or stable isotopes in accelerators or reactors (the so-called Partitioning and Transmutation strategy) are beneficial to the repository of radioactive nuclear waste. Several processes have been developed for the separation of MAs from HLLW in the past a few decades, such as trialkylphosphine oxide (TRPO), transuranium extraction (TRUEX), diisodecylphosphoric acid (DIDPA), and diamide extraction (DIAMEX), etc.[1,2] In these processes, a large amount of trivalent lanthanides are usually co-extracted along with MAs to form a mixed product. In this context, most of the lanthanides must be removed from the MAs prior to the transmutation since otherwise lanthanides would act as neutron poisons and prevent the transmutation of MAs.[3] However, the separation of trivalent lanthanides from MAs was proven to be a quite challenging task owing to the similar chemical properties of trivalent lanthanides (Ln(III)) and actinides (An(III)).[4] Some extractants containing soft donor N and S have been demonstrated to have a high selectivity toward trivalent MAs.[5,6] Among these extractants, the purified Cyanex 301, i.e., bis(2,4,4-trimethylpentyl)dithiophosphinic acid (denoted as HC301, Figure 1), is a S-donor ligand that can selectively extract Am(III) from lanthanides with an extremely high separation factor over 1000.[6-9]

In previous studies using HC301 as an extractant, researchers focused mainly on the extraction behaviors and identification of the extracted complexes. However, controversies over the structure and composition of An(III) and Ln(III) complexes in the organic phase still remain to be clarified. The complexes $An(C301)_3$ and $Ln(C301)_3$ with no discernible nitrate or water molecules in the inner coordination shell of the metal were reported by Jensen and coworkers, where C301 is the bis(2,4,4-trimethylpentyl)dithiophosphinic anion.[10] Differently, Tian et al. found that the molecular formula of the An(III) complexes might be $An(C301)_3{\cdot}HC301$.[11-13] As to the Ln(III) complexes with HC301, they reported very recently that light Ln(III) were mainly coordinated by the sulfur atoms of HC301, while heavy Ln(III) were completely hydrated in the organic phase.[14] Other studies by theoretical calculation also suggested different extracted complexes of An(III) and Ln(III).[15-17]

Another aspect need to be clarified in the study of the HC301 extraction system is the aggregation behavior of the extracted complexes in the organic phase. Jensen et al. studied the dimerization of HC301 in organic solutions, and found that at high Nd(III) capacity the extracted complex is dinuclear with an average formula of $Nd_2(C301)_6$.[18,19] With respect to this phenomenon, we speculate that an even more interesting supramolecular organization, i.e., water-in-oil (W/O) microemulsions, could form in the HC301 extraction system under certain conditions due to the amphiphilic property of the HC301 molecules. It is well known that amphiphilic extractants and the extracted complexes can form various aggregates including W/O microemulsions in the organic phase.[20] In 1980s, Wu et al. first demonstrated the formation of W/O microemulsions in the extraction system using neutralized bis(2-ethylhexyl)phosphoric acid (HDEHP) to separate rare earth metals.[21]

To the best of our knowledge, the formation of W/O microemulsions in the extraction of An(III)/Ln(III) by HC301 has not been reported in the literature. In this work, we studied the formation of W/O microemulsions in the extraction of Nd(III) by HC301 and its effect on the coordination environment of Nd(III) extracted into the organic phase. Results from this work will help researchers to further understand the extraction behavior of HC301.

Experimental section

Materials

Cyanex 301 was purchased from Cytec Inc. and purified as described in the reference.[7] Unless specially noted, all other materials used in this work were of analytical grade. The toluene solution of HC301 was prepared by dissolving purified HC301 in toluene, while the aqueous solution of Nd(III) was prepared by dissolving $Nd(NO_3)_3 \cdot 6H_2O$ in water.

Methods

In a typical extraction, 3 mL of 1 mol/L HC301 in toluene and 3 mL of aqueous solution were mixed in a plastic tube. The initial concentration of Nd(III) in the aqueous phase was 0.1 mol/L. The neutralization degree of HC301 (nd, defined by Eq. 1) in the extraction system was adjusted by adding certain amounts of 1 mol/L NaOH in the mixed system.

$$\mathrm{nd} = \frac{n(\mathrm{NaOH})}{n(\mathrm{HC301})} \times 100\% \qquad (1)$$

where *n*(NaOH) and *n*(HC301) are the initial mole numbers of NaOH and HC301, respectively. After thorough mixing, centrifugation and phase separation, both the aqueous phase and the organic phase samples were taken for characterization.

The concentration of Nd(III) in the aqueous phase after extraction was determined by EDTA titration. Nd(III), Na^+ and NO_3^- extracted into the organic phase were stripped by 1 mol/L HCl, and their concentrations in the solution were then determined by EDTA titration, atomic absorption spectrophotometry and ionic chromatography, respectively. IR spectrum of the organic phase was recorded on a Nicolet Nexus 470 spectrometer (Thermo Fisher Scientific, USA) between 1000 and 4000 cm^{-1}. Dynamic light scattering (DLS) measurements of the organic solutions were performed on a Malvern Nano ZS3000 instrument (Malvern Instruments, UK) at 293.2 K and at a scattering angle of 90°. The absorption spectra were collected on a Lambda 800 spectrophotometer.

Samples for extended X-ray absorption fine structure (EXAFS) measurements were loaded in 2 mm thick holders with a rectangular opening sealed with two Kapton film windows. The L_3-edge EXAFS spectra of Nd(III) were collected in transmission mode on the beam line 1W1B at Beijing Synchrotron Radiation Facility (BSRF), China. Data reduction and analysis were conducted according to standard procedures with pre-edge background removal, edge normalization to a unit step height, conversion to momentum space, and extraction of the EXAFS with a spline function. The data analysis was carried out using the Athena and Artemis interfaces to the IFEFFIT program package.[22]

Results and discussion

Formation of W/O microemulsions

As shown in Figure 2, the change of concentrations of Nd(III) in the aqueous and organic phases after extraction at different neutralization degrees indicated that more Nd(III) was extracted into the organic phase as the neutralization degree increased. At a neutralization degree over 30%, almost no Nd(III) was detected in the aqueous phase. Note that the concentration of Nd(III) in the organic phase slightly decreased as the neutralization degree was over 50%. This decrease of concentration was likely caused by the increase of volume of the organic phase. The initial volume ratio in the extraction experiments was 1:1. However, at a neutralization degree over 50%, the volume of the organic phase increased slightly (inset picture in Figure 2), indicating the entering of water into the organic phase from the aqueous phase, and thus resulting in the decrease of the concentration of Nd(III) in the organic phase.

The change of concentrations of Na^+ and NO_3^- in the organic phase is shown in Figure 3. It can be seen that no Na^+ and NO_3^- was detected in the organic phase at neutralization degrees lower than 30%. When the neutralization degree further increased, the concentrations of Na^+ and NO_3^- in the organic phase increased gradually. It is worth noting that only a small fraction of NO_3^- was extracted into the organic phase even at very high neutralization degrees, and we speculate that these nitrate anions were carried into the organic phase by the extracted water.

In IR spectroscopy of the organic phase (Figure 4), the absorption band belonged to the absorption of water appeared at around 3396 and 1635 cm^{-1} as the neutralization degree was over 30%. No characteristic absorption band of water could be observed in the IR spectra when the neutralization degree was lower than 30%. The peak at about 1605 cm^{-1} is assigned to the C=C stretching vibration of toluene. By plotting the change of the relative absorption intensity at 3396 cm^{-1} in the IR spectra with the neutralization degree, similar trend was observed to that of the change of Na$^+$ and NO_3^- concentration shown in Figure 3. The results of IR spectra confirmed the entering of water into the organic phase at high neutralization degrees (> 30%), which was consistent with the observation of the phase volume variation.

In a previous work by Tian and coworkers, the solvent (toluene) of the organic phase for IR determination were vaporized before measurement.[11] For comparison, we also recorded the IR spectra of the organic phase after the vaporization of toluene, as shown in Figure 5. The characteristic peak of toluene at 1605 cm^{-1} no longer appeared. The relative intensity of the stretching vibration absorption of S–H at 2408 cm^{-1} gradually decreased with the increase of neutralization degree. A new peak at around 1600 cm^{-1} was arisen when 10% HC301 was neutralized, which was from the scissors vibration of water according to the literature.[11] The relative peak intensity gradually increased as the neutralization degree increased. In addition, the peak started to broaden over 30% neutralization degree, reflecting the association of water molecules. The absorption band from 3050 cm^{-1} to 3700 cm^{-1} belong to the stretching vibration of H_2O also emerged at 10% neutralization degree, although it was not as significant as that around 1600 cm^{-1}.

DLS measurement provided more reliable evidences for the formation of W/O microemulsions in the organic phase, and the results are shown in Figure 6. DLS can be used to analyze the size of microemulsions droplets via determination of the hydrodynamic radius which can be extracted from measurements of the diffusion constants of droplets undergoing Brownian motion.[23] At neutralization degrees less than 30%, no scattering signal was detected. At a neutralization degree of 35%, the DLS signal indicated the formation of aggregates with a diameter around 2 nm, and the aggregates quickly swelled to about 40 nm in diameter as the neutralization degree increased to 40%. Further increase of the neutralization degree led to no obvious variation of the aggregates dimension. The DLS results obviously demonstrated the formation of W/O microemulsions in the extraction of Nd(III) by HC301 in toluene at high neutralization degrees.

Based on the changes of the concentrations of Nd(III), Na^+ and NO_3^- in the organic phase, and results from IR spectroscopy and DLS measurements, it can be concluded that W/O microemulsions could be formed in the extraction of Nd(III) by HC301 in toluene at high neutralization degrees. As there was a large amount of Na^+ in the organic phase after the formation of W/O microemulsions, a preliminary inference is that the hydration of sodium ions might be one of the driving force for the formation of W/O microemulsions.[24-27] W/O microemulsions seemed to be formed only in the presence of hydrated Na^+ in the organic phase after all Nd(III) was exchanged into the organic phase. As shown in Figure 2, the extraction of Nd(III) appears to linearly correlate with the neutralization degree until almost all the Nd(III) was extracted at a neutralization degree of 30%. At a starting HC301 concentration of 1 mol/L, and a neutralization degree of 30%, the concentration of C301 was 0.3 mol/L, exactly the value needed to complex with all of Nd(III) (starting concentration of 0.1 mol/L). After all of the hard Nd(III) is extracted, extra C301 anions generated by further neutralization of HC301 begin interacting with the softer Na^+, and it gets extracted. The extraction of the hydrated Na^+ into the organic phase induced the formation of W/O microemulsions. Accordingly, not only the neutralization degree but also the initial concentrations of HC301 in the organic phase and Nd(III) in the aqueous phase are the key factors affecting the formation of W/O microemulsions. In a previous work by Tian and coworkers,[12] the initial concentrations of HC301 and Ln(III) were 0.5 and 0.087 mol/L, respectively, with a volume ratio Vo/Va = 1:1.15. Although the neutralization degree was as high as 30%, no W/O microemulsions could form due to the relatively high concentration of Ln(III) in the system. A higher neutralization degree (calculated to be about 60%) should be required to result in the exchanging of all Ln(III) into the organic phase, and W/O microemulsions would form as HC301 was further neutralized.

Effect of W/O microemulsions formation on Nd(III) coordination

The effect of W/O microemulsions formation on the coordination environment of Nd(III) in the organic phase was characterized by absorption spectroscopy and EXAFS. In the visible region, Nd(III) has characteristic absorptions that are very sensitive to the coordination environment. As shown in Figure 7, the absorption spectra of Nd(III) in the organic phase varied gradually as the neutralization degree increased. At a low neutralization degree of 10% (bottom curve in Figure 7), strong characteristic peaks of Nd(III) complexes were found at 531, 592, 753 and 808 nm, all are largely red-shifted compared to that in an acidic aqueous solution (top curve in Figure 7), indicating that the coordination environment of Nd(III) in the organic phase is quite different from that in Nd(III) aqua ions. When the neutralization degree further increased, the absorptions were blue-shifted to short wavelengths and the intensities weakened. At high neutralization degrees (e.g., 55%), the absorptions of Nd(III) in the organic phase were very similar to those of Nd(III) in aqueous solutions, suggesting that the Nd(III) ion was surrounded almost by water molecules in the organic phase. Recently, the interactions of HC301 with Nd(III) in a homogeneous medium (1% v/v water/ethanol) were studied by spectrophotometry and microcalorimetry, and the molar absorptivities of $Nd(C301)_3$, $Nd(C301)_2^+$, $Nd(C301)^{2+}$ and Nd^{3+} were fitted out.[28] By comparing the absorptions in the present work with those reported in the literature, it can be inferred that the C301 anions coordinated with Nd(III) in the organic phase were replaced by water molecules gradually as the neutralization degree increased.

Results from EXAFS experiment (Figure 8 and Table 1) further confirmed the change of the coordination environment of Nd(III) in the extracted complexes along with the neutralization degree. At 10% neutralization degree, Figure 8 showed that sulfur donors were dominant in the first coordination shell of Nd(III). The fitting results (Table 1) implied that some oxygen donors (assigned to the coordination of H_2O) might exist in the first coordination shell of Nd(III), which is consistent with the appearance of the absorption band of water in the IR spectrum (Figure 5). The structural parameters from the fitting results, e.g, distance between the Nd(III) center and the sulfur atoms, and the relative number of phosphorous atoms in the second coordination shell (P shell), all indicate that each C301 ligand directly bonded to

Nd(III) through two sulfur atoms in bidentate mode. As the neutralization degree increased, the coordination number of oxygen atoms increased apparently while that of S decreased with the increase of the neutralization degree, indicating the replacement of HC301 by water molecules in the coordination with Nd(III), which is in good accordance with the results from absorption spectroscopy. At a sufficiently high neutralization degree (e.g., 50%), the inner coordination shell of Nd(III) was almost occupied by O atoms, suggesting that the Nd(III) ion was in an "aqueous environment" provided by the W/O microemulsions formed in the organic phase. The results in Figure 3 has demonstrated the partitioning of NO_3^- into the organic phase after the formation of W/O microemulsions, thus whether NO_3^- coordinates with Nd(III) or not in the W/O microemulsions is an important issue to be clarified. As aforementioned, NO_3^- in the organic phase is speculated to be carried by the extracted water. Therefore, NO_3^- was located in the water pool of the W/O microemulsions with a concentration of about 0.3 mol/L (initial concentration in the aqueous phase). Rao et al. studied the complexation of Nd(III) with NO_3^- in the aqueous phase at different temperatures.[29] Nd(III) and NO_3^- can form a $NdNO_3^{2+}$ complex with a binding constant ($K_M = [NdNO_3^{2+}]/([Nd^{3+}][NO_3^-])$) of only 0.64 at 25 °C.[29] A rough calculation based on these results suggested that less than 20% of Nd(III) would interact with NO_3^- in an aqueous solution when the concentration of NO_3^- is 0.3 mol/L and without competition from any other strong ligands. Considering that Nd(III) still electrostatically interacted with the C301 anion in the W/O microemulsions, the interaction between Nd(III) and NO_3^- should be very weak.

Both the absorption spectroscopic and EXAFS results in this work suggest that the coordination environment of Nd(III) depends greatly on the neutralization degree and thus provide useful information to understand the extraction behavior of HC301 in the extraction of Ln(III). As mentioned in the introduction section, there are still some controversies in previous studies over the structure and composition of light Ln(III) complexes formed during the extraction by HC301. One main argument is whether there is water molecule or not existing in the first coordination shell of Ln(III).[14] In the work by Jensen et al., Ln(III) was extracted into the organic phase by adjusting the aqueous pH, which means a very low neutralization degree of HC301, and there was no water molecule coordinated with Ln(III).[10] While in the work by Tian and coworkers,[9] 0.5 mol/L of HC301 was 25% neutralized, and water molecules were found in the first coordination shell of Ln(III).[11] Based on the results in this work, we found that the coordination number of water molecules strongly depends on the neutralization degrees. In general, high neutralization degree would result in more water molecules replacing HC301 to coordinate with Ln(III). Furthermore, we noticed that different diluents were used in previous studies, e.g., toluene was used by Tian et al., while n-dodecane was used by Jensen et al. The property of diluents might have significant influence on the formation of aggregates and W/O microemulsions in addition to the coordination environment during the extractions, and work on this issue are currently underway in our lab.

Conclusion

In the extraction of Nd(III) by HC301 in toluene, W/O microemulsions was found to form at high neutralization degrees. As W/O microemulsions formed, the concentrations of Na^+, NO_3^- and water in the organic phase increased obviously with the increase of neutralization degree. The formation of microemulsions significantly affected the coordination environment of Nd(III) in the organic phase. As the neutralization degree increased, the C301 anions coordinated with Nd(III) in the inner coordination shell were replaced gradually by water molecules and finally resulted in an almost fully hydrated Nd(III) ion in the organic phase at sufficiently high neutralization degrees.

Acknowledgment

The study was supported by Program for Changjiang Scholars and Innovative Research Team in University (IRT13026), and National Natural Science Foundation of China under Project 21401115 and 91426302.

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Table 1 EXAFS fitting parameters for Nd(III) coordination in the organic phase under different neutralization degrees.

sd (%)	O shell				S shell				P shell			
	CN	R_O (Å)	ΔE_0 (eV)	σ^2 (Å^2)	CN	R_S (Å)	ΔE_0 (eV)	σ^2 (Å^2)	CN	R_P (Å)	ΔE_0 (eV)	σ^2 (Å^2)
10	1(1)	2.56(6)	0(2)	0.001(fixed)	7(1)	2.89(2)	0(2)	0.009(fixed)	4(1)	3.48(2)	0(2)	0.006(fixed)
20	3(1)	2.52(3)	1(1)	0.009(5)	4(1)	2.91(1)	1(1)	0.008(fixed)	2(1)	3.51(2)	1(1)	0.006(fixed)
30	6(2)	2.51(5)	0(2)	0.010(5)	2(2)	2.90(4)	0(2)	0.01(1)				
40	8(2)	2.51(3)	0(1)	0.009(4)	1(1)	2.91(4)	0(1)	0.01(1)				
50	8(2)	2.50(3)	0(1)	0.010(3)	0(1)	2.90(6)	0(1)	0.01(2)				
Nd(III) aq	8(1)	2.50(1)	1(1)	0.009(2)								

Figure captions

Figure 1 The chemical structure of HC301.

Figure 2 The concentrations of Nd(III) in the aqueous phase and organic phase after extraction at different neutralization degrees. The inset picture shows the comparison of the phase volume at 55% neutralization degree with that of no neutralization.

Figure 3 The concentrations of (A) Na^+ and (B) NO_3^- in the organic phase at different neutralization degrees.

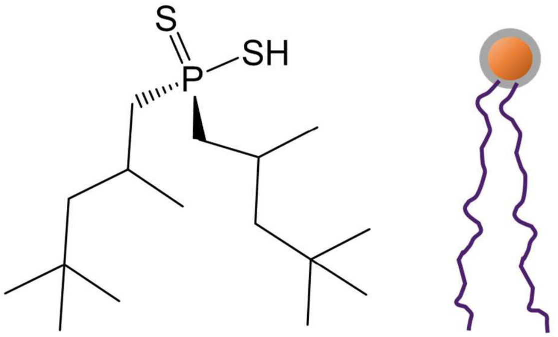
Figure 4 (A) IR spectra of the organic phase and (B) relative absorbance at 3396 cm^{-1} with the variation of the neutralization degree.

Figure 5 IR spectra of the organic phase after toluene was vaporized.

Figure 6 DLS of the organic phase at different neutralization degrees.

Figure 7 Absorption spectra of Nd(III) in the organic phase at different neutralization degrees.

Figure 8 The L_3-edge EXAFS of Nd(III) in the organic phase and the magnitude of the Fourier Transformations at different neutralization degrees.



bis(2,4,4-trimethylpentyl)dithiophosphinic acid, HC301

Figure 1 The chemical structure of HC301.

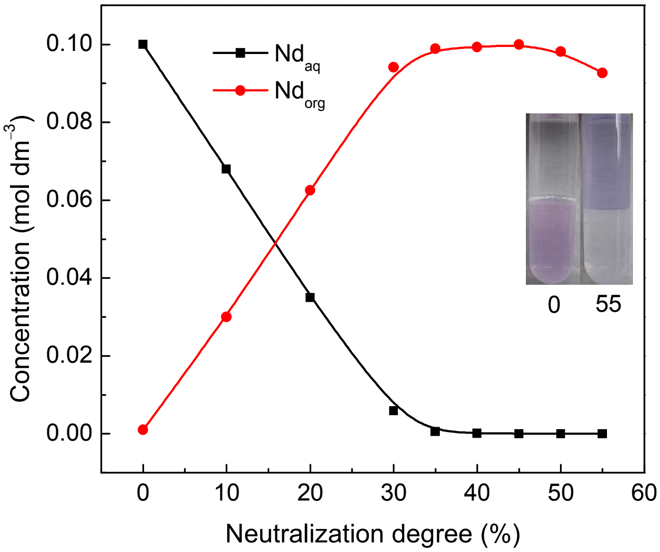


Figure 2 The concentrations of Nd(III) in the aqueous phase and organic phase after extraction at different neutralization degrees. The inset picture shows the comparison of the phase volume at 55% neutralization degree with that of no neutralization.

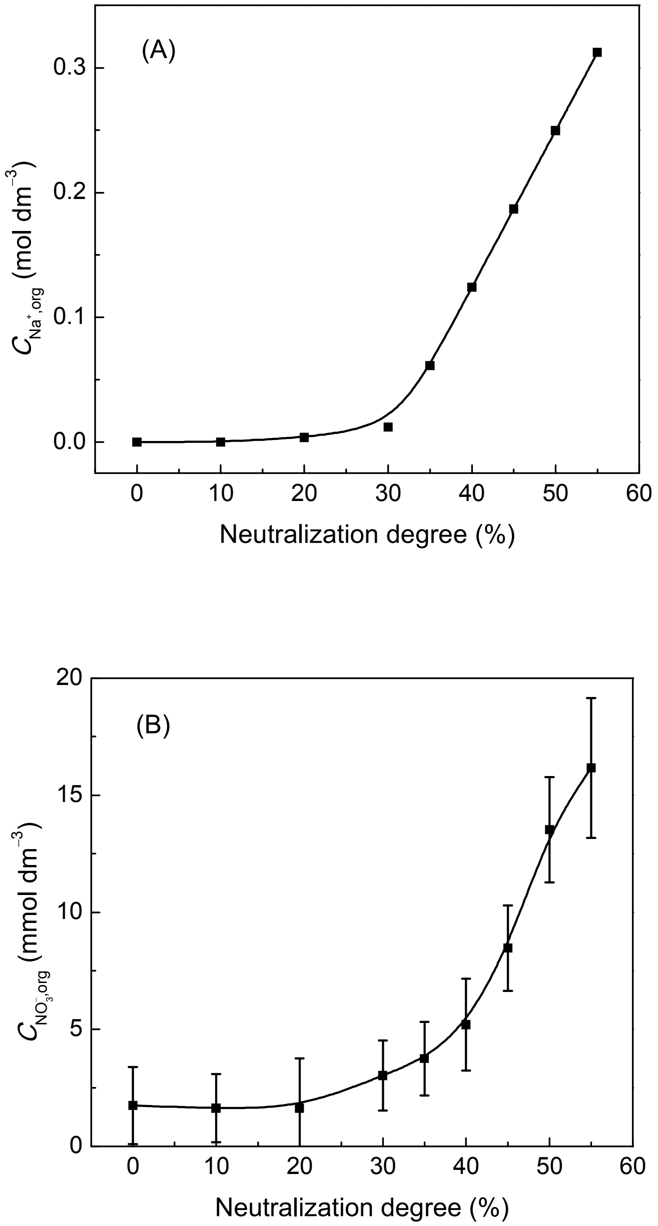


Figure 3 The concentrations of (A) Na^+ and (B) NO_3^- in the organic phase at different neutralization degrees.

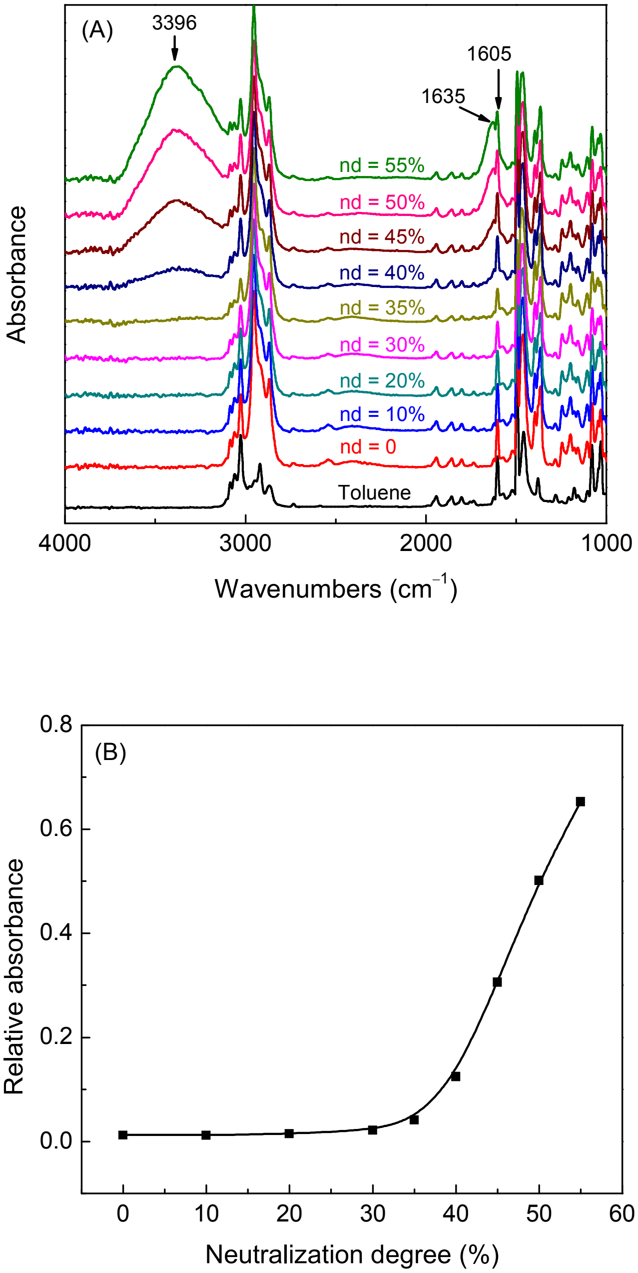


Figure 4 (A) IR spectra of the organic phase and (B) relative absorbance at 3396 cm^{-1} with the variation of the neutralization degree.

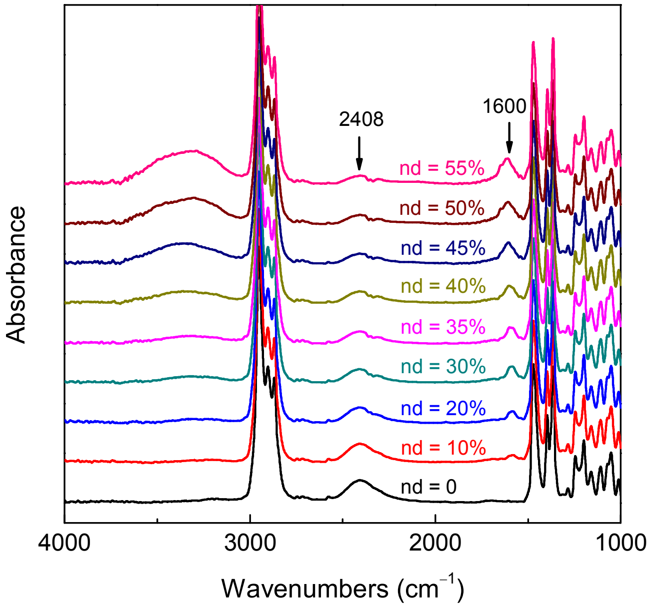


Figure 5 IR spectra of the organic phase after toluene was vaporized.

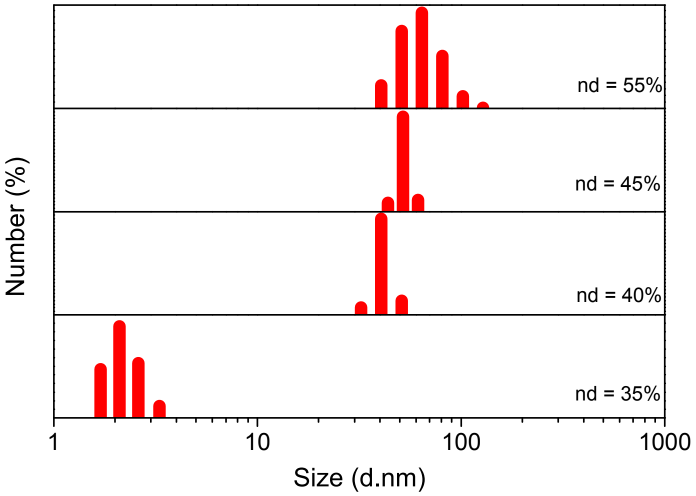


Figure 6 DLS of the organic phase at different neutralization degrees.

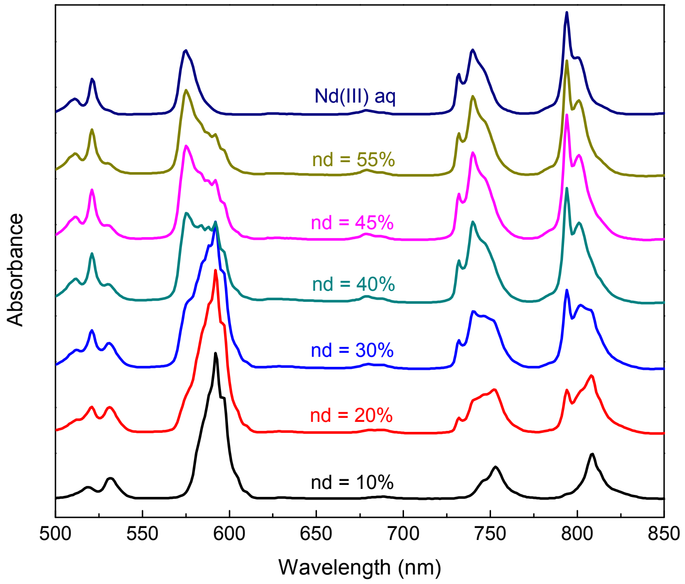


Figure 7 Absorption spectra of Nd(III) in the organic phase at different neutralization degrees.

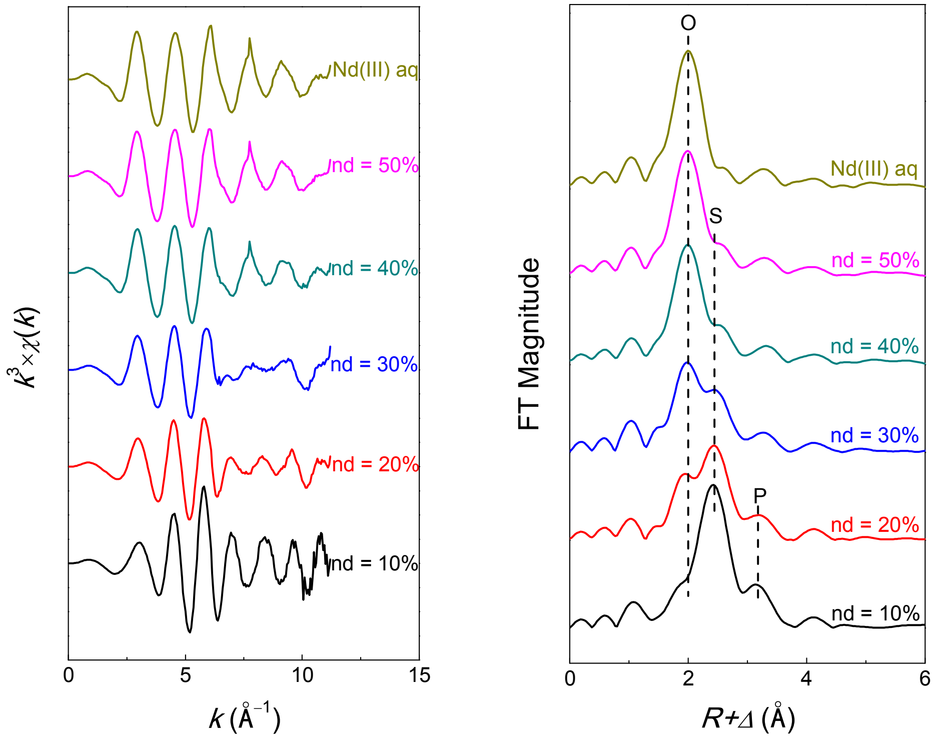


Figure 8 The L_3-edge EXAFS of Nd(III) in the organic phase and the magnitude of the Fourier Transformations at different neutralization degrees.

Our work describes the formation of W/O microemulsions and its effect on the coordination environment of Nd(III) in the extraction using purified Cyanex 301 as extractant.