SCIENCE CHINA
Chemistry

• ARTICLES •

• SPECIAL TOPIC • Nuclear Fuel Cycle Chemistry

September 2012 Vol.55 No.9: 1712–1718
doi: 10.1007/s11426-012-4686-7

Solvent extraction of thorium(IV) using W/O microemulsion

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Received April 28, 2012; accepted May 29, 2012; published online July 9, 2012

The extraction of thorium(IV) was investigated using two types of W/O microemulsion, one of which was formed by a surface-active saponified extractant sodium bis(2-ethylhexyl) phosphate (NaDEHP) and the other was formed by a mixture of an anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and an extractant bis(2-ethylhexyl)phosphoric acid (HDEHP) as the cosurfactant. The extraction capacities of the above two systems were higher than that of the HDEHP extraction system. High concentration of $NaNO_3$ showed no influence on the extraction in the NaDEHP based W/O microemulsion system, whilst reduced the extractability in the AOT-HDEHP W/O microemulsion system. The mechanism in acidic condition was demonstrated by the log-log plot method. The structure of the aggregations and the water content in the organic phase after extraction were measured by dynamic light scattering and Karl Fischer water titration, respectively. It was found that NaDEHP based W/O microemulsion broke up after extraction, while AOT-HDEHP W/O microemulsion was reserved.

W/O microemulsion, thorium ions, extraction

1 Introduction

Water-in-oil (W/O) microemulsions, the thermodynamically stable mixtures of water, oil, surfactant as well as cosurfactant in most cases, have nanometer-sized structures and extraordinarily large specific interfacial areas, bringing about various capabilities such as extraction of metal ions and preparation of functional materials [1–4]. In the metal ions extraction, W/O microemulsion is very effective for the improvement of extractability as well as for the acceleration of extraction, which is due to an enormous rise of the micro-interfacial surface area in the W/O microemulsion phase [3].

In liquid-liquid extraction, the extractant is usually a surface-active amphiphile, containing both a hydrophilic group and a long hydrophobic alkyl tail. It can usually form W/O microemulsion in organic phase under a certain condition, which helps explain the extraction mechanism. Wu *et al*. [5] first demonstrated that the utility of saponified organophosphorus extractant bis(2-ethylhexyl)phosphoric acid (HDEHP) in organic diluent to extract rare earth metal ions can get high extractability and speed, owing to the formation of W/O microemulsion in the organic phase. For the extraction system with neutral extractant, e.g., tributyl phosphate (TBP), the reversed micellar structures were also formed [6, 7]. The amine and amide extractants, especially those with long chains, can also aggregate to form reversed micelles in the organic phase during extraction [8, 9]. For example, the peculiar behavior of *N,N,N′,N′*-tetra(*n*-octyl) diglycolamide (TODGA) in the extraction of trivalent lanthanide and actinide ions arose from the affinity of these metal ions for the preformed TODGA reverse-micelle tetramers [9]. The basic thermodynamic properties of W/O microemulsion and its application in the extraction of metal ions were studied in our research group [1, 10–12]. A reversed micelle model was suggested in the extraction of uranium by trioctylamine and tributyl phosphate [11, 12]. By using tetradecyldimethylbenzylammonium chloride (TDMBAC) to extract gold, we also found the formation of

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*Corresponding author (email: xshen@pku.edu.cn) reversed micelle or W/O microemulsion in organic phase when the gold concentration reached a certain value [1].

Moreover, combining an anionic surfactant and an extractant in the extraction of metal ions in a W/O microemulsion causes a very strong synergistic effect. A W/O microemulsion formed by the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) could extract multivalent metals and the efficiency for high valence metal ions is higher than that for the low valence metal ions [13]. Naganawa *et al.* [14, 15] reported that reversed micelles containing both AOT and an extractant carbamoylmethylene phosphine oxide (CMPO) or TODGA exhibited much higher extractability of lanthanides(III) or strontium(II) and much better selectivity in their mutual separation than CMPO or TODGA alone did. Yang *et al.* [16] also designed a W/O microemulsion system to extract uranium(VI), showing a great efficiency. Furthermore, a microemulsion usually improves the solubility of extractant. For instance, calix[4]arene carboxyl derivative which had a poor solubility in normal organic solvents, could dissolve in AOT-isooctane reversed micellar solution [17].

So far, solvent extraction has been regarded as a main method of separating Th^{4+} from aqueous solution [18–21]. While many investigations have been carried out on the extraction of Th^{4+} by solvent extraction, there has been no literature focusing on its extraction by W/O microemulsion. In this paper, we mainly focused on the designation of two microemulsion systems to extract Th^{4+} from aqueous solution, one of which was formed by sodium bis(2-ethylhexyl) phosphate (NaDEHP) and the other was formed by AOT and the extractant HDEHP. The structures of NaDEHP and AOT are shown in Figure 1.

2 Experimental

2.1 Reagents

HDEHP (CP, Sinopharm) was purified by copper salt crystallization, according to the literature [22]. NaDEHP was synthesized and purified according to the reported method [23]. AOT (99%, sigma) was used as received. Arsenazo III (Sinopharm), $NaNO_3$, NaOH, HNO_3, *n*-octanol and *n*-heptane (Beijing Chemical Plant) were of analytical grade.

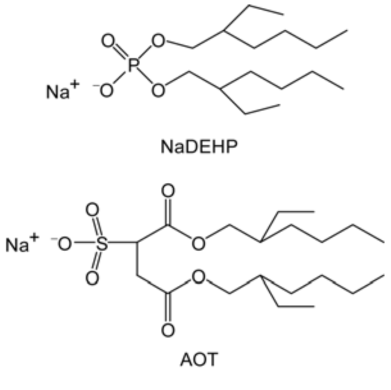

Figure 1 Structures of NaDEHP and AOT.

2.2 Instruments

The absorption spectrum of Th^{4+} in the aqueous phase after color reaction was recorded by U-3010 UV-vis spectrometry (Hitachi, Japan). FTIR spectrum was measured on a Nicolet iN10 MX FT-IR spectrometer (Thermo-Fischer, USA) between 600 and 4000 cm^{-1}. The average dynamic radii of the aggregates in the organic phase were determined with the dynamic light scattering (DLS) method, which was carried out at 25 °C via a Nano ZS90 instrument (Malvern, UK) with the scattering angle of 90° (wavelength: 633 nm). The water content of the organic phase (ω_f) was determined with a Karl Fischer water titrator (Mettler Toledo, Switzerland).

2.3 Methods

2.3.1 *Preparation of W/O microemulsions*

W/O microemulsions were prepared according to the reported method [23]. When preparing stock solutions of 0.1 mol/dm^3 of NaDEHP based W/O microemulsion, NaDEHP and *n*-octanol (molar ratio 1:1) were first added into *n*-heptane, then a certain amount of water was added. The solution became transparent after gentle handshaking. The water content (ω_0) in the system was expressed by the molar ratio of added water to surfactant and fixed at 10 in the extraction. The AOT based W/O microemulsion and AOT-HDEHP W/O microemulsion were prepared by the same method in the absence of cosurfactant (*n*-octanol) and ω_0 is fixed at 20. Besides, HDEHP solution was prepared by dissolving HDEHP in *n*-heptane.

2.3.2 *Extraction experiments*

0.5 mL of the W/O microemulsions was mixed with 0.5 mL aqueous solution of Th^{4+} in the vibrator for 1 h (preceding experiments have demonstrated that the equilibrium can be achieved in 5 min), followed by centrifuging (2000 rpm) to ensure fully phase separation. The concentration of Th^{4+} in the aqueous phase was determined by UV-vis spectrometry with Arsenazo III as a coloring reagent. The concentration of Th^{4+} extracted into the *n*-heptane phase can be calculated by subtracting the concentration of Th^{4+} in the aqueous from the total concentration because the volume is equal (the volume change is less than 0.5%) (Eq. 1). Finally, the extractability *E* and distribution ratio *D* were calculated by the following equations, respectively:

$$C_{\mathrm{Th,\,org}} = C_{\mathrm{Th,\,total}} - C_{\mathrm{Th,\,aq}} \tag{1}$$

$$E = \frac{C_{\mathrm{Th,\,org}} V_{\mathrm{org}}}{C_{\mathrm{Th,\,org}} V_{\mathrm{org}} + C_{\mathrm{Th,\,aq}} V_{\mathrm{aq}}} \times 100\% \tag{2}$$

$$D = \frac{C_{\mathrm{Th,\,org}}}{C_{\mathrm{Th,\,aq}}} \tag{3}$$

3 Results and discussion

3.1 Extraction capability of W/O microemulsion

The extraction of Th^{4+} by NaDEHP W/O microemulsion is shown in Figure 2, compared with that of HDEHP. In the absence of added HNO_3, the pH value of Th^{4+} aqueous solution is 2.88. Additionally, 1 mol/dm^3 $NaNO_3$ is added to prevent the formation of the third phase and the loss of extractant [24]. Under this circumstance, the extractability increases as the concentration of NaDEHP increases. Furthermore, it can be found that the extractability of Th^{4+} by NaDEHP W/O microemulsion is higher than that of HDEHP, which is possibly attributed to an enormous rise of the micro-interfacial surface area in the W/O microemulsion [5]. However, when 1 mol/dm^3 HNO_3 is added, the extraction efficiencies of the two extractants are nearly the same. In the purification of HDEHP, the bis(2-ethylhexyl) phosphate is converted back to the acid form by mixing the organic solution of $Cu(DEHP)_2$ with a dilute aqueous acid [22]. Here, when 1 mol/dm^3 HNO_3 exists, similar reaction takes place, leading to the conversion of NaDEHP to HDEHP and the destruction of the W/O microemulsion.

The extractability of Th^{4+} by AOT-HDEHP W/O microemulsion is also measured (Figure 3). 1 mol/dm^3 $NaNO_3$ is also added as in NaDEHP W/O microemulsion system. The extractability of Th^{4+} by HDEHP without the addition of AOT is about 75%, and increases as AOT is added, suggesting that the formation of AOT-HDEHP W/O microemulsion improves the extractability. Actually, the AOT W/O microemulsion in the absence of HDEHP also shows an extraction of Th^{4+}. This result consists with the report in the literature, in which AOT W/O microemulsion could extract multivalent metals by electrostatic interaction [13].

3.2 Effect of inorganic salt on the extraction

When the concentration of $NaNO_3$ is below 0.1 mol/dm^3, a third phase forms in all W/O microemulsion system. Therefore, the concentration of $NaNO_3$ is above 0.1 mol/dm^3 in the extraction system. The effect of $NaNO_3$ on the extraction of Th^{4+} by W/O microemulsion is shown in Figure 4. The addition of $NaNO_3$ has little influence on both NaDEHP W/O microemulsion and HDEHP extraction system. On the contrary, the extractability of Th^{4+} by the AOT W/O microemulsion system decreases dramatically when the salt concentration increases. According to literature, the interactions between metal ions and AOT are electrostatic interactions [13]. Thus, the competition between Na^+ and Th^{4+} with $-SO_3^-$ group of AOT increases with the increase of Na^+ concentration, leading to the decrease of AOT W/O microemulsion extractability. The decrease of extractability is also found in AOT-HDEHP microemulsion system in both low and high concentration of extractants. Because $NaNO_3$ has little influence on HDEHP extraction, the extractability decrease in AOT-HDEHP microemulsion is attributed to the salt effect on AOT extraction.

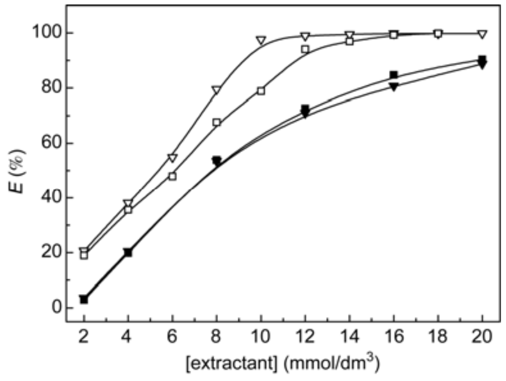

Figure 2 The extractability of Th^{4+} by NaDEHP W/O microemulsion (▽, ▼) and by HDEHP (□, ■) in 1 mol/dm^3 $NaNO_3$ (open) and in 1 mol/dm^3 HNO_3 (solid) condition. $[Th^{4+}]$ = 4 mmol/dm^3.

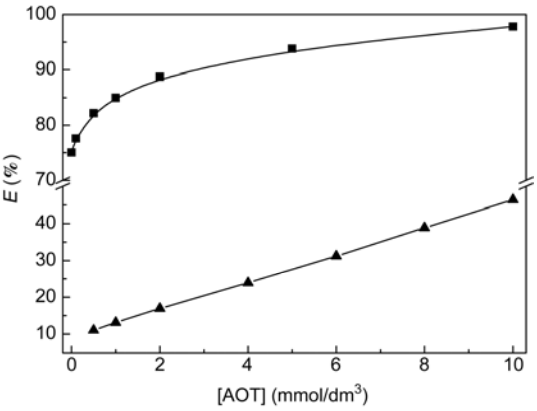

Figure 3 The extractability of Th^{4+} by AOT-HDEHP W/O microemulsion (■, [HDEHP] = 10 mmol/dm^3) and by AOT W/O microemulsion (▲) when the AOT concentration varies. $[Th^{4+}]$ = 4 mmol/dm^3, $[NaNO_3]$ = 1 mol/dm^3.

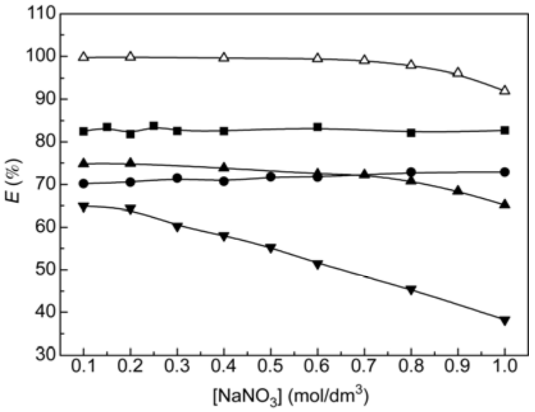

Figure 4 Dependence of the extractability of Th^{4+} on the concentration of $NaNO_3$ in aqueous phase by different W/O microemulsions, NaDEHP (8 mmol/dm^3) (■), AOT (8 mmol/dm^3) (▼), AOT (4 mmol/dm^3) + HDEHP (4 mmol/dm^3) (▲), AOT (8 mmol/dm^3) + HDEHP (8 mmol/dm^3) (△), compared with HDEHP system (8 mmol/dm^3) (●). $[Th^{4+}]$ = 4 mmol/dm^3.

3.3 Determination of the stoichiometry of the thorium complex in the organic phase

The classical log-log plot method is performed to determine stoichiometry of the thorium complex in the organic phase, in the case that the concentration of NaDEHP is greatly larger than that of Th^{4+}. The same treatment is also used when the acidity varies. The relationship between log*D* and log[NaDEHP] as well as between log*D* and log[HNO_3] is shown in Figure 5. One can see that log*D* is a linear function of log[NaDEHP] with a slope $k = 2.0 \pm 0.1$ and also a linear function of log[HNO_3] with a slope $k = -1.7 \pm 0.1$. According to the principle of log-log plot method,

$$\mathrm{Th^{4+}}_{\mathrm{(aq)}} + n\mathrm{HDEHP}_{\mathrm{(org)}} \rightarrow [\mathrm{Th(DEHP)}_n^{4-n}]_{\mathrm{(org)}} + n\mathrm{H^+}_{\mathrm{(aq)}} \quad (4)$$

$$\log D = \log K + \log[\mathrm{HDEHP}]^n_{\mathrm{(org)}} + \log[\mathrm{H^+}]^n_{\mathrm{(aq)}} \quad (5)$$

where *K* is the equilibrium constant, *n* equals the slopes of the above two plots. From Figure 5 the slopes of the two plots are close to each other, approaching to 2, thus *n* is proposed to be 2, which means that there are two NaDEHP molecules participating in the formation of the extracted species.

Referring to log-log plot method and charge balance, we propose that the extraction mechanism of Th^{4+} by NaDEHP in acidic condition is:

$$\mathrm{Th^{4+}}_{\mathrm{(aq)}} + 2\mathrm{NO}^-_{3\mathrm{(aq)}} + 2\mathrm{HDEHP}_{\mathrm{(org)}} \rightarrow [\mathrm{Th(NO_3)_2(DEHP)_2}]_{\mathrm{(org)}} + 2\mathrm{H^+}_{\mathrm{(aq)}} \quad (6)$$

According to this mechanism, the increase of NO_3^- concentration could improve the extraction of Th^{4+}. Meanwhile, when the concentration of $NaNO_3$ increases, the concentration of Na^+ also increases. In the literature, it was reported that there was an electrostatic interaction between Na^+ and $DEHP^-$ [23, 25]. Thus the increase of Na^+ concentration enhances the competition between Na^+ and Th^{4+} with $DEHP^-$. As a result, little effect of $NaNO_3$ on NaDEHP and HDEHP extraction occurs (Figure 4).

3.4 Assignment of IR spectra of the thorium-loaded organic phase

FTIR spectroscopy was applied to detect the interaction in the Th(IV)-loaded organic phase. The FTIR spectra of the organic phase contain two distinct regions. The first region from 850 to 1350 cm^{-1} contains the variations of P=O, P–O, S=O and other bands (Figure 6). In HDEHP extraction system, the band of P=O stretching vibration shifts from 1230 to 1159 cm^{-1}, and the band of P–O stretching vibration splits and shifts opposite directions, from 1034 to 1090 cm^{-1} and 1059 cm^{-1}. The red shift of P=O stretching vibrations and blue shift of P–O stretching vibrations indicate that both P=O and P–O have interactions with Th^{4+} [26]. As to the absorption peak at 1280 cm^{-1}, it is attributed to the stretching vibration of NO_3^-, indicating NO_3^- ions enter into the organic phase, which conforms with our proposed mechanism. In NaDEHP W/O microemulsion extraction system, both the bands of P=O and P–O stretching vibration of NaDEHP shift to high wavenumber compared with HDEHP, and P–O stretching vibration splits. After extraction, the IR spectra of NaDEHP W/O microemulsion are similar to that of HDEHP (Figures 6(a,b)), implying the formation of a same complex in the two systems. In the AOT-HDEHP W/O microemulsion, the broad profile of frequency range from 1000 to 1330 cm^{-1} consists of the absorbance of the S=O stretching mode, the C–O and C–C stretching band of ester linkage, as well as P=O and P–O stretching mode, overlapping each other (Figure 6(d)). The frequency range from 1100 to 1300 cm^{-1} changes after extraction, showing that Th^{4+} interacts with P=O and P–O. In AOT W/O microemulsion (Figure 6(c)), the symmetric S=O stretching (1052 cm^{-1}) and asymmetric $-SO_3^-$ stretching (1260 and 1215 cm^{-1}) do not move evidently after extraction. According to literature, the process of AOT based W/O microemulsion to extract trivalent metals could be explained by a simple electrostatic model [13]. According to the extraction result that

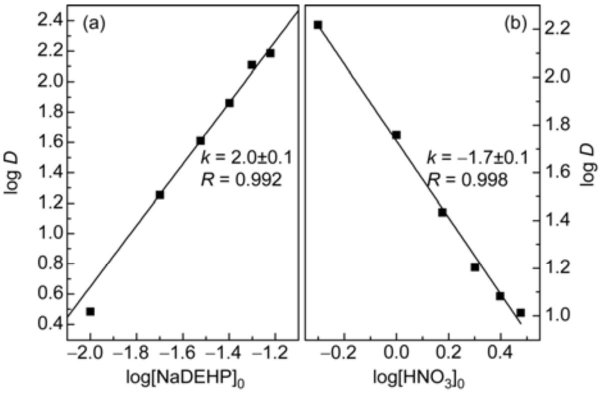

Figure 5 Log-log plot of log*D* vs. log[NaDEHP] ([Th^{4+}] = 1 mmol/dm^3, [HNO_3] = 4 mol/dm^3) (a) and log[HNO_3] ([Th^{4+}] = 1 mmol/dm^3, [NaDEHP] = 15 mmol/dm^3) (b).

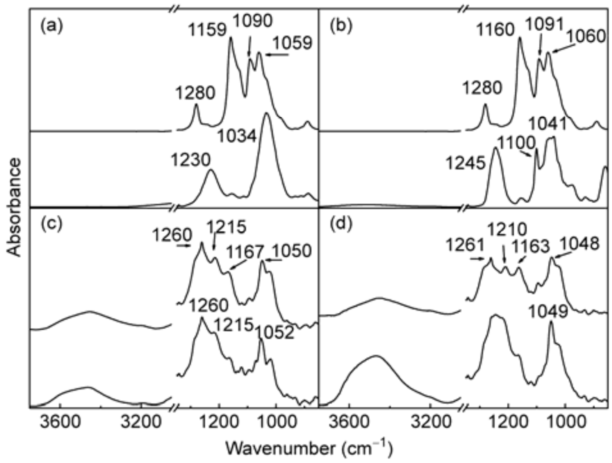

Figure 6 IR spectra of different extraction systems in the organic phase in the frequency range of 850–1350 cm^{-1} and 3050–3750 cm^{-1} before extraction (bottom) and after extraction (up): (a) HDEHP system ([HDEHP] = 20 mmol/dm^3); (B) NaDEHP W/O microemulsion ([NaDEHP] = 20 mmol/dm^3); (c) AOT W/O microemulsion ([AOT] = 20 mmol/dm^3); (d) AOT-HDEHP W/O microemulsion ([AOT] = 20 mmol/dm^3, [NaDEHP] = 6 mmol/dm^3). [Th^{4+}] = 4 mmol/dm^3.

AOT W/O microemulsion could extract Th^{4+}, we suggest that there is an electrostatic interaction between the $–SO_3^-$ group of AOT and Th^{4+}.

IR bands in the region of 3050–3750 cm^{-1} are assigned to the O–H stretching vibration of water in the organic phase (Figure 6). In W/O microemulsion, there are four types of water, i.e. trapped, anion-bound, cation-bound and bulk-like water [23]. In our experiment, the vibration of water in NaDEHP, AOT, AOT-HDEHP W/O microemulsion can be detected. And no water vibration could be found in HDEHP system. However, after extraction, there is no band of vibration of water in HDEHP and NaDEHP system. On the contrary. In the AOT based system, the band of water can be detected, indicating water exists in the organic phase after extraction. To investigate the water components and their roles in the organic phase after extraction, the bands of the O-H stretching vibration in the range 3150–3700 cm^{-1} in AOT and AOT-HDEHP W/O microemulsion were analyzed by the Fourier self-deconvolution technique (Figure 7). According to refs. [23, 27, 28], for AOT W/O microemulsion, the subpeak around 3612 cm^{-1} is assigned to water trapped by alkyl chains of *n*-heptane or surfactants. The peak around 3538 cm^{-1} is attributed to the O-H stretching vibration of water binding to S=O. The peak around 3460 cm^{-1} is due to the bulk-like water, while IR bands of the water bound by interaction with cations, e.g., Na^+ and Th^{4+}, are located around 3358, 3397, 3272 and 3183 cm^{-1}. For AOT-HDEHP W/O microemulsion, the trapped water is located around 3614 cm^{-1}, consistent with that in AOT W/O microemulsion. The peaks around 3554 and 3473 cm^{-1} are assigned the O–H stretching oibration of water which interacted with S=O and P=O, respectively. The location of bulk-like water is around 3436 cm^{-1}, shifting to low wavenumber compared to AOT W/O microemulsion. The peaks around 3378, 3340, 3274 and 3190 cm^{-1} are attributed to the water bound by interaction with Na^+ and Th^{4+}. The curve-fitting results of the O–H stretching mode of water in the organic phase mean that after extraction W/O microemulsions also exist in AOT and AOT-HDEHP system.

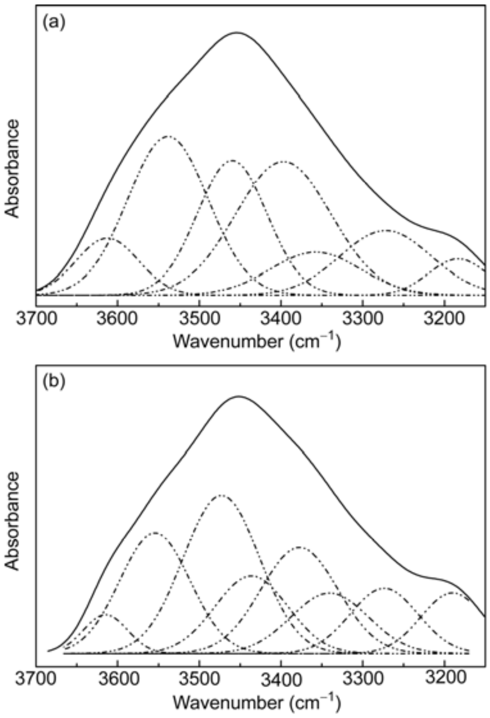

Figure 7 The curve-fitting results of the O–H stretching mode of water in the organic phase after extraction in AOT (a) and AOT-HDEHP (b) W/O microemulsion.

3.5 Aggregations in the organic phase after extraction

The structure of aggregations in the organic phase, which plays an important role in the extraction, has been widely researched [29–36]. To investigate the aggregation in the organic phase, the hydrodynamic radius of the aggregation and the water content in the organic phase are determined (Table 1). In NaDEHP W/O microemulsion system, when the concentration of extractant is 20 $mmol/dm^3$ and the concentration of Th^{4+} is 4 $mmol/dm^3$, no light scattering phenomenon in the organic phase was observed after extraction. Meanwhile, the water content in the organic phase is below 200 ppm ($\omega_f < 0.4$), meaning the breakup of W/O microemulsion in the organic phase, which is similar with that in rare earth extraction by W/O microemulsion [5]. This result is consistent with FTIR spectra, in which no band of vibration of water existed. The coordination between NaDEHP and Th^{4+} may lead to the breakup of W/O microemulsion.

Table 1 The hydrodynamic radius of the aggregation and the water content in the organic phase after extraction

	HDEHP	NaDEHP W/O microemulsion	AOT W/O microemulsion	AOT-HDEHP W/O microemulsion
R_h (nm)	–	–	2.3 ± 0.3	2.5 ± 0.3
ω_f	<0.3	<0.4	8	7

In AOT W/O microemulsion, aggregations with hydrodynamic radius 2.3 ± 0.3 nm are detected, and the ω_f value is determined to be 8. Compared with the organic phase before extraction (the hydrodynamic radius is 4.6 ± 0.3 nm, ω_0 = 20), the aggregation becomes smaller with the decrease of water content. The aggregations are also found in AOT-HDEHP W/O microemulsion. The hydrodynamic radius is 2.5 ± 0.3 nm, nearly the same as that in AOT W/O microemulsion. From FTIR spectra, the band of water can be detected in both AOT and AOT-HDEHP W/O microemulsions. Both the DLS and FTIR results show that the reversed micelles exist in the organic phase. The interaction between AOT and Th^{4+} is electrostatic interaction, not leading to the breakup of W/O microemulsions. This is obviously different from interaction between NaDEHP and Th^{4+}.

4 Conclusions

The extraction capacity of Th^{4+} was improved by two types of W/O microemulsion compared with the HDEHP extraction system. High concentration of inorganic salt (i.e., $NaNO_3$) showed no influence on the extraction of NaDEHP W/O microemulsion system, while reduced the efficiency in the AOT and AOT-HDEHP W/O microemulsion systems. The mechanism in acidic condition was demonstrated by the log-log plot method. According to the results of DLS and FTIR, NaDEHP based W/O microemulsion broke up after extraction, while AOT and AOT-HDEHP W/O microemulsions were reserved. The scheme of organic phase before and after extraction was shown in Figure 8.

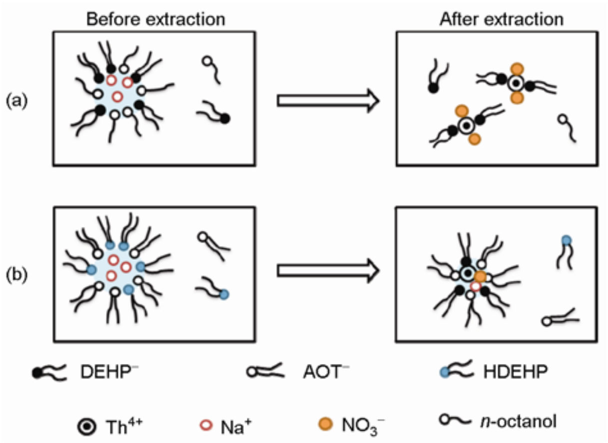

Figure 8 The organic phase of NaDEHP W/O microemulsion (a) and AOT-HDEHP W/O microemulsion (b).

This work was supported by National Natural Science Foundation of China (20871009) and the Fundamental Research Funds for the Central Universities. We thank Mr. Shifu Weng for his help with FTIR measurements.

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