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TECHNICAL NOTE

Aggregation of Organic Phase of Saponified Naphthenic Acid Extraction System and Its Application in Preparation of Ultrafine Particles

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ABSTRACT

The aggregation states of the extracted organic phase in a saponified naphthenic acid extraction system were studied with FT-IR. TEM, and SAXS methods. Ultrafine particles of lanthanum hydroxide were prepared in the water core of a water-in-oil microemulsion formed by a saponified extractant and the extracted complex thereof.

Key Words. Naphthenic acid; Extraction; Aggregation; Ultrafine particles

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INTRODUCTION

Naphthenic acid (NA) is a commonly used extractant in the separation and purification of lanthanide ions. In the early 1980s, Wu and coworkers presented the saponification of naphthenic acid as a process of the formation of a water-in-oil (w/o) microemulsion (ME) in the organic phase (1). Since then, the aggregation behavior of this sort of extractant in bulk phases has been investigated for about 20 years (2, 3). It is universally recognized that for saponified acidic extractants reversed micelles (RM) or w/o microemulsions are present in apolar media (4, 5). These RM and ME have properties similar to those formed by typical surfactants (6, 7). More and more attention is presently being paid to the preparation of ultrafine particles by chemical reactions in w/o microemulsions (8). However, microemulsions formed by saponified acidic extractants have not yet been used in the preparation of ultrafine particles. Therefore, in the present work, based on an investigation of the microstructure of a saponified naphthenic acid extraction system, we investigated the preparation of ultrafine particles of lanthanide hydroxide in situ in the extracted organic phase. The preliminary result suggests a possible application of extraction systems, i.e., preparation of ultrafine particles from a lanthanide-loading organic phase, in which the particle sizes are controlled by the "water core" of w/o microemulsions.

EXPERIMENTAL

Reagents

Naphthenic acid (Fluka) was purified by distillation at 100–170°C under a vacuum pressure of 1.0 mmHg. The mean molecular weight was determined to be 276. 2-Octanol was a B.D.H. reagent. $LaCl_3$ solution was prepared from La_2O_3 (purity $> 99.9\%$) through a reaction with hydrochloric acid; the pH adjusted to 4.0 with 1.0 M NaOH solution. Na_2S solution was prepared with doubly distilled water just before use; it was filtered through a No. 4 glass funnel to remove any suspended particles. All the other chemicals used were of AR grade.

Instruments

A JEOL JEM-100CX II transmission electron microscope (Hitachi) was used. Solution samples for TEM measurements were centrifuged at a rotational speed of 20,000 rpm and then filtered through a microporous filter membrane of 0.2 μm to remove any dust. The sample drop was spread on a copper net with a carbon film, and the TEM observation was directly performed when the copper net dried.

SAXS measurements were carried out on the small-angle x-ray scattering instrument of Beijing Synchrotron Radiation Lab (BSRL) at the 1.54 Å wavelength. The sample solution was placed in a self-made cell with a Kapton membrane which does not absorb x-rays.

A Nicolet Magna 750 FT-IR spectrometer was used to characterize the extracted organic phase with a demountable BaF_2 cell to prepare IR samples. IR spectra averaged over 32 scans in the 800–4000 cm^{-1} range with a resolution of 4 cm^{-1}.

Procedure

A 1 M naphthenic acid–2 M 2-octanol–*n*-heptane solution was saponified with 10 M $NH_3 \cdot H_2O$ to obtain a microemulsion system (I) of (0.25 M naphthenic acid + 0.75 M ammonium naphthenate)–2 M 2-octanol–*n*-heptane. The microemulsion (I) was used to extract lanthanum chloride, and the lanthanum-loading organic phase ($[La]_{(o)} = 0.125$ M)-formed microemulsion (II).

Adding 3 M Na_2S (freshly prepared) solution into microemulsion (I), which had been deoxygenated by bubbling N_2 through it for 15 minutes prior to Na_2S addition, we obtained microemulsion (III). In the water core of microemulsion (III), OH^- anions were supplied by the slow hydration of Na_2S. Microemulsion (III) was aged over 24 hours prior to mixing with (II).

The molecular ratio (w) of water to total extractant ($[HA] + [A^-] + 3[LaA_3]$) was adjusted to be 10 in both microemulsions (II) and (III) by the addition of doubly distilled water. The preparation of ultrafine lanthanum hydroxide particles was achieved by mixing microemulsions (II) and (III) under a N_2 atmosphere, and the reaction occurred in the water core of the microemulsions.

$$S^{2-} + 2H_2O = H_2S + 2OH^-$$

$$3OH^- + LaA_{3(i)} = La(OH)_3 + 3A^-_{(i)} \qquad \text{(i: interface)}$$

RESULTS AND DISCUSSION

Aggregates Formation in Saponified Naphthenic Acid Extraction System

In a previous paper (1) we studied the microstructure of the extracted organic phase in organophosphorus acid and naphthenic acid extraction systems which were saponified with KOH, NaOH. LiOH, or $NH_3 \cdot H_2O$. w/o microemulsions were proven to be present in the organic phase by the methods of conductance measurement and FT-IR spectroscopy. In the present work the w/o microemulsion drops were directly observed with TEM (Fig. 1). The TEM images show that a microemulsion drop has an open hole. The mean diameter of the hole is 10 nm as determined with a reading microscope. We think this open hole is the water core of the w/o microemulsion from which the solubilized water was removed due to the high vacuum in the TEM apparatus. As the solvent (*n*-heptane) and the solubilized water evaporated, NA, NH_4A, and 2-octanol were left on the interface of the w/o microemulsions to form the open hole particles.

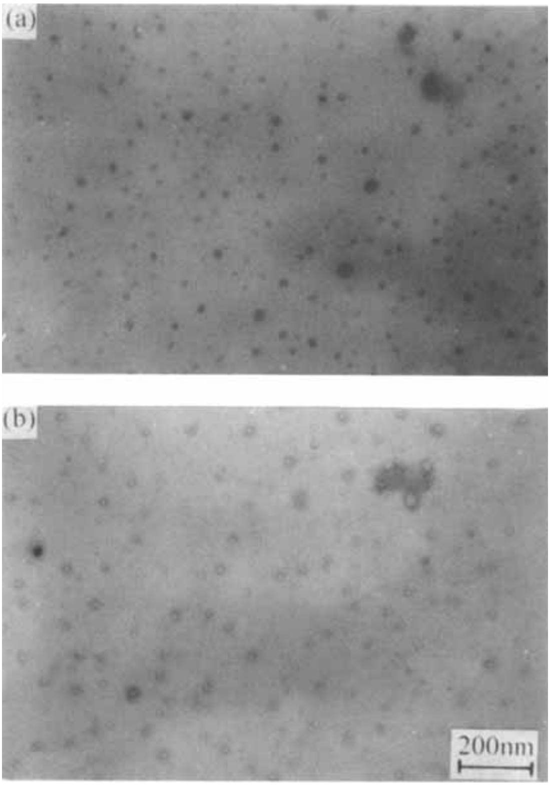

FIG. 1 TEM micrograph of w/o microemulsion formed by (0.25 M NA + 0.75 M NH_4A)–2 M 2-octanol-*n*-heptane, w = 10. (a) 33,000×, (b) 49,000×.

Microstructure of Extracted Organic Phase Containing Lanthanum Naphthenate

As is known, naphthenic acid cannot extract lanthanum ions from the aqueous phase before being saponified with alkali metals or alkali hydroxides. So the loading percentage (*L*, %) of lanthanum in the organic phase is expressed as the ratio $[A^-]/[A^-]_t$, where [A] is the concentration of extractant anion coordinating with the lanthanum ion, and $[A^-]_t$ is the total concentration of extractant anion in the initial organic phase. By taking the bending vibrational band of CH_3 (1378 cm^{-1}) as an internal standard (9), Fig. 2 shows that with an increase of lanthanum concentration in the organic phase, the intensity of the $\nu C{=}O$ band (1709 cm^{-1})

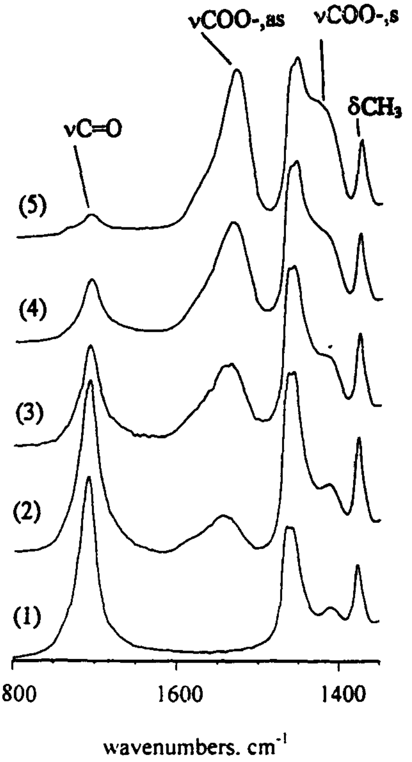

FIG. 2 FT-IR spectra of extracted organic phase containing lanthanum in naphthenic acid extraction system at various saponification percentage (*S*, %): (*1*) 0, (*2*) 25, (*3*) 50, (*4*) 75, (*5*) 100. *L* = 100% in all cases.

decreases, while the absorption bands of νCOO-s (1536 cm^{-1}) and νCOO-s (1411 cm^{-1}) appear and their intensities gradually increase. The coordination interaction between extractant and lanthanum ions leads to this variation. The bending vibrational band of water (ca. 1650 cm^{-1}) does not appear in the IR spectra. This indicates that the 100% lanthanum-loading organic phase contains very little water.

SAXS measurements were made with the extracted organic phase, and the variation of size of the aggregates is shown in Fig. 3. In the organic phase, A^- is a sort of anion surfactant, and the surface activity of NA is weaker than that of A^-. As for LaA_3, the coordination interaction between lanthanum ions and extractant anions reduces its surface activity greatly. The formation of extracted complexes causes a decrease of extractant concentration, and the surface activity of the extraction system becomes weaker. Thereafter the aggregate size becomes smaller with the entrance of more lanthanum ions into the organic phase. The SAXS data process is based on the hypothesis that the aggregates are spherical, which is in agreement with experimental results (10).

Preparation of Ultrafine Particles in Extracted Organic Phase

From the above discussion we know that not only can saponified naphthenic acid form w/o microemulsions, lanthanum naphthenate can also

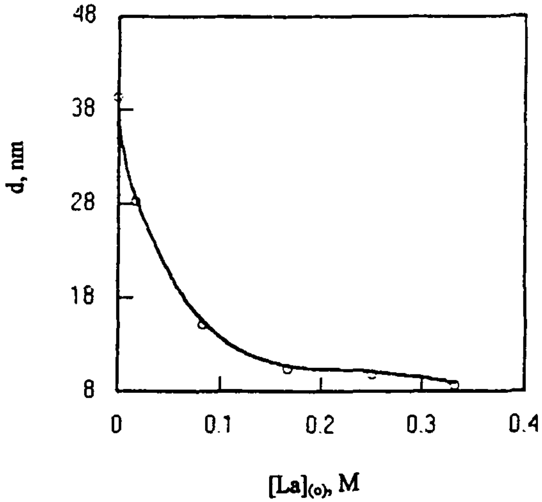

FIG. 3 Variation of the aggregate size with lanthanum concentration in the extracted organic phase 1 M NA–2 M 2-octanol–*n*-heptane.

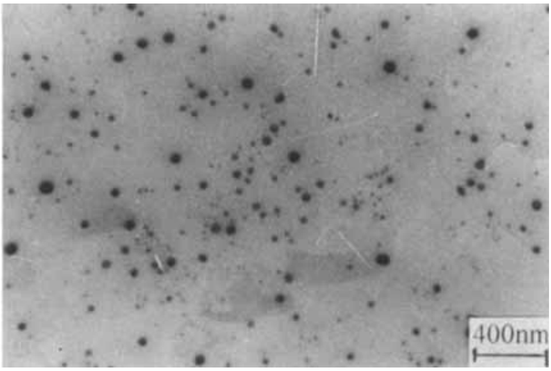

FIG. 4 TEM micrograph of $La(OH)_3$ particles prepared in microemulsions of the saponified naphthenic acid extraction system.

aggregate to form spherical particles in the organic phase. The water core of such aggregates provides a microenvironment in which chemical reaction occurs under controlled and stable conditions (11). $La(OH)_3$ particles were produced through the reaction between LaA_3 contained in microemulsion (III) and OH^- provided by the hydration of Na_2S solubilized in microemulsion (III) (Fig. 4). The mean size of $La(OH)_3$ particles is 84.7 nm, much bigger than those of the water cores of initial microemulsions (I), (II), and (III). This phenomenon is attributed to the rapid exchange of contents between different water cores, which could promote the coalescence of angstrom- or nanometer-size precipitated nuclei to form the much larger particles actually observed in the collected product (12).

FT-IR spectra show that the particles precipitated from the mixed microemulsion are not pure $La(OH)_3$ but also contain extractant and extracted complexes, i.e., molecules of extractant and extracted complexes are absorbed on the surface of the particles.

CONCLUSION

In this paper we have shown a general method to produce ultrafine particles with controlled size by means of chemical reactions in microemulsions formed in the extracted organic phase. This technique allows ultrafine particles to be produced directly in the solvent extraction process.

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