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# Neutron Polarization Analysis for Biphasic Solvent Extraction Systems

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#### ABSTRACT

We performed neutron polarization analysis (NPA) of extracted organic phases containing complexes, comprised of Zr(NO<sub>3</sub>)<sub>4</sub> and tri-*n*-butyl phosphate, which enabled decomposition of the intensity distribution of small-angle neutron scattering (SANS) into the coherent and incoherent scattering components. The coherent scattering intensity, containing structural information, and the incoherent scattering compete over a wide range of magnitude of scattering vector, q, specifically when q is larger than  $q^* \approx 1/R_g$ , where  $R_g$  is the radius of gyration of scatterer. Therefore, it is important to determine the incoherent scattering intensity exactly to perform an accurate structural analysis from SANS data when  $R_{q}$  is small, such as the aforementioned extracted coordination species. Although NPA is the best method for evaluating the incoherent scattering component for accurately determining the coherent scattering in SANS, this method is not used frequently in SANS data analysis because it is technically challenging. In this study, we successfully demonstrated that experimental determination of the incoherent scattering using NPA is suitable for sample systems containing a small scatterer with a weak coherent scattering intensity, such as extracted complexes in biphasic solvent extraction systems.

#### **KEYWORDS**

Neutron polarization analysis; solvent extraction; tri-*n*-butyl phosphate

# Introduction

Small-angle neutron scattering (SANS) is a powerful technique for investigating microscopic structures formed in organic phases of biphasic solvent extraction systems.<sup>[1-6]</sup> The scattered neutrons from sample solutions in SANS experiments consist of coherent and incoherent scattering components,  $I_{coh}(q)$  and  $I_{inc}(q)$ ,<sup>[7,8]</sup> where  $q = (4\pi/\lambda)\sin(\theta)$ ,  $\lambda$  is the incident neutron wavelength and  $2\theta$  is the scattering angle] is the magnitude of the scattering vector. Thus, SANS measurements provide the sum of  $I_{coh}(q)$  and  $I_{inc}(q)$ ,  $I_{total}(q)$ . Only  $I_{coh}(q)$  contains complete structural information resulting from the intra- and inter-atomic interference of neutrons and exhibits q-dependence, whereas  $I_{inc}(q)$  contains the information about the single atoms (especially protons) in the samples and remains almost constant with q that is primarily governed by the elemental composition of the sample.<sup>[7,8]</sup> Therefore,  $I_{inc}(q)$  is normally an obstacle in SANS experiments. Incoherent scattering intensity from hydrogen atoms is much larger than that from other elements; thus,  $I_{inc}(q)$  increases as the volume fraction of hydrogen in a sample increases. Because hydrogen is a main element in the extracted organic phases, quantitative evaluation of  $I_{inc}(q)$  is essential in accurate SANS data analysis.

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In principle for solutions of particles,  $I_{coh}(q)$  in SANS increases in proportion to the square of the volume of the scatterer.<sup>[7,8]</sup>  $I_{coh}(q)$  is likely to be large compared with  $I_{inc}(q)$  at low q when the size of the scatterer in the sample is larger than tens of nanometers such as macromolecules. However,  $I_{coh}(q)$  and  $I_{inc}(q)$  tend to compete, especially in the high q region (typically  $q > 1.0 \text{ nm}^{-1}$ ) when the size of the scatterer is smaller than or around several nanometers, such as extracted coordination species, because of the weak intensity of  $I_{coh}(q)$ .<sup>[9]</sup> Thus, it is crucial to evaluate  $I_{inc}(q)$  accurately and subtract it from  $I_{total}(q)$  for accurate structural SANS analysis. An incorrect q dependence of  $I_{coh}(q)$  produces erroneous structural parameters. The calculated incoherent scattering intensity based on the sample composition tends to be smaller than the experimental value.<sup>[10]</sup> This is mainly because multiple neutron scattering takes place in experiments, which strongly depends on the transmittance of the neutrons through the sample.<sup>[11,12]</sup> Although some evaluation methods for  $I_{inc}(q)$  have been proposed, <sup>[13,14]</sup> the contribution of  $I_{inc}(q)$  to SANS data is not always analytically determined, because the methods are restricted by the sample thickness and the fraction of hydrogen atoms in the sample.

Neutron polarization analysis (NPA) is the best method for evaluating  $I_{inc}(q)$  to accurately determine the  $I_{\rm coh}(q)$  in SANS.<sup>[15]</sup> NPA has not been used frequently in SANS data analysis owing to technical complexities, such as installing a spin polarizer, the spin flippers, an analyzer, the coils for a guide magnetic field, and so on. However, NPA should be used more in SANS analysis, particularly for small scatterers, such as coordination species in solvent extraction systems, because of the competitive strength of  $I_{\rm coh}(q)$  and  $I_{\rm inc}(q)$ . In this article, we report NPA for extracted organic phases that contain complexes comprised of Zr(NO<sub>3</sub>)<sub>4</sub> and tri-*n*-butyl phosphate (TBP), Zr(NO<sub>3</sub>)<sub>4</sub>·2TBP, and demonstrate the suitability of this method. Additionally, we use NPA for heavy and light organic phases generated by the phase separation of organic phase during solvent extraction.<sup>[16]</sup> The phase separation is induced by the aggregation of the complexes in the organic phase, when the complex concentration is sufficient. TBP is an important extractant for separating hexavalent uranium and tetravalent plutonium from spent nuclear fuel by solvent extraction in the PUREX process.<sup>[16-18]</sup> Therefore, investigating the microscopic structure of Zr(NO<sub>3</sub>)<sub>4</sub>·2TBP will provide useful insights into the structural analysis of organic phases containing uranium and plutonium complexes. More quantitative analysis of  $I_{\rm coh}(q)$  in SANS determined here will contribute to developing new extractant and separation systems for nuclear reprocessing. This is the first report of the use of NPA for organic phases in biphasic solvent extraction systems.

#### Experimental

#### Materials

TBP (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan; purity, >99%) and deuterated octane, *n*-octane- $d_{18}$  (Sigma-Aldrich Japan, Tokyo, Japan; purity >98%), were dried overnight over molecular sieves (Wako Pure Chemical Industry Co., Ltd., Osaka, Japan) before use. The water used in this study was deionized by a Millipore Milli-Q purification system (Merck Millipore, Billerica, MA, USA). Aqueous 10.5 M nitric acid solutions containing (0, 0.049, or 0.376) M Zr(NO<sub>3</sub>)<sub>4</sub> were prepared according to the literature<sup>[4]</sup> and were used as the aqueous phases for solvent extraction. Note that M denotes a unit of mol/L.

#### Sample Preparation for NPA Measurements

Samples 1–4 (Table 1) were prepared by the biphasic solvent extraction method. For samples 1 and 2, equal volumes (3.0 mL) of 10.5 M aqueous nitric acid solution containing (0 or 0.049) M Zr(NO<sub>3</sub>)  $_4$  and the organic phase (*n*-octane- $d_{18}$ ) containing 0.5 M TBP were shaken for 1 h at room temperature in a glass tube. After centrifugation and separation of distinct phases, an aliquot of each organic phase was loaded into a titanium cell with quartz windows, which has a sample space of 2 mm thick and 40 mm in diameter sample volume for the NPA experiments. Note that the extracted coordination species in the organic phase only consist of  $Zr(NO_3)_4$ -2TBP when the

Sample no.	[Zr(NO <sub>3</sub> ) <sub>4</sub> ·2TBP] <sub>org</sub> (M)	[HNO3] <sub>org</sub> (M)	[TBP] <sub>org</sub> (M)	$[H_2O]_{org}$ (M)	l <sub>inc,calc.</sub> (q) (cm <sup>-1</sup> )	$I_{\rm inc}(q)^{\rm b}~({\rm cm}^{-1})$
1	0	0.28	0.50	0.045	0.057	0.122 ± 0.005
2	0.032	0.30	0.50	0.074	0.059	0.116 ± 0.005
3 <sup>a</sup>	0.237	-	3.0	0.501	-	0.469 ± 0.008
4 <sup>a</sup>	0.022	-	0.13	0.025	-	0.051 ± 0.003
5 <sup>c</sup>	-	-	-	-	0.379	0.738 ± 0.014
6 <sup>c</sup>	-	-	-	-	0.007	0.026 ± 0.001

Table 1. Compositions of extracted organic phases and their incoherent scattering intensities.

<sup>a</sup>Concentration of HNO<sub>3</sub> in heavy and light organic phases could not be evaluated by the titration method of the aqueous phase after solvent extraction because of the phase separation.  $l_{inc,calc.}(q)$  of heavy and light organic phases were not calculated because it was difficult to estimate [HNO<sub>3</sub>]<sub>ora</sub>.

 ${}^{b}I_{inc}(q)$  was determined as a constant value from Figure 3b.

<sup>c</sup>Sample nos. 5 and 6 correspond to pure TBP and *n*-octane- $d_{18}$ , respectively.

concentration of nitric acid in aqueous solution is 10.5 M.<sup>[4]</sup> Samples 3 and 4 correspond to the heavy and light organic phases, which were obtained by solvent extraction with a high concentration of 0.376  $M Zr(NO_3)_4$  in the aqueous phase. This is because the organic phase caused phase separation as a result of the inclusion of an excess of extracted  $Zr(NO_3)_4$ ·2TBP. The heavy and light organic phases were loaded into the quartz cells. All extracted organic phases also contained some HNO3 and H2O (see Table 1). Samples 5 and 6 in Table 1 correspond to pure TBP and *n*-octane- $d_{18}$ , respectively. The concentrations of Zr(NO<sub>3</sub>)<sub>4</sub>·2TBP, HNO<sub>3</sub>, and H<sub>2</sub>O in the organic phase ([Zr(NO<sub>3</sub>)<sub>4</sub>·2TBP]<sub>org</sub>) [HNO<sub>3</sub>]<sub>org</sub>, and [H<sub>2</sub>O]<sub>org</sub>) were determined in accordance with literature procedures.<sup>[4]</sup> The concentration of TBP in heavy and light organic phases was determined by 400 MHz <sup>1</sup>H NMR (400-MR, Agilent Technologies, Inc., USA). The intensity ratio of the methine proton peak of TBP (4.1 ppm) to methyl proton peak of *n*-octane- $h_{18}$  (0.9 ppm) obtained for light and heavy organic phases were compared with that obtained for the initial organic phase to evaluate the concentration of TBP. Note that a small amount of *n*-octane- $h_{18}$  was originally contained in *n*-octane- $d_{18}$ . The concentration of HNO<sub>3</sub> in light and heavy organic phases was not evaluated; however, the majority of HNO<sub>3</sub> may be assumed to be contained in the heavy organic phases.<sup>[4]</sup> All titanium cells were set in the neutron incident beam path, and the NPA measurements were performed at room temperature.

#### NPA with a Spin-Echo Spectrometer

NPA was performed using the neutron spin-echo (NSE) spectrometer<sup>[19,20]</sup> installed at NG5, National Institute of Standard Technology Center for Neutron Research, USA. Figure 1 shows a schematic of the NSE spectrometer used for NPA. Cold neutrons were monochromatized by a velocity selector with  $\lambda = 0.6$  nm, and the wavelength distribution was  $\Delta\lambda/\lambda = 0.20$ . Spin-polarized neutrons were produced by passing the incident beam through a polarizer, composed of magnetic Si/Fe multilayer.<sup>[21]</sup> The up spin state of the incident neutrons was selected and the beam was shaped into a 20-mm-diameter circle by a pinhole slit at the sample position. The first and second precession coils were set at 20 A to maintain the neutron polarization state in front of and behind the sample. A  $\pi$ -flipper was set at the exit of the first precession coil. The  $\pi$ -flipper changed the spin state of the incident neutrons from up to down. Accordingly, the spin states of incident neutrons, up or down, depended on whether the  $\pi$ -flipper was on [spin flip (SF)] or off [nonspin flip (NSF)]. The flipping ratio of the incident neutrons, *R*, was measured as approximately 9. *R* is defined as

$$R = N_+/N_-,\tag{1}$$

where  $N_+$  and N- correspond to the intensity of the direct beam at q = 0 without the sample when the  $\pi$ -flipper is off (NSF) and on (SF), respectively. The spin analyzer for scattered neutrons, composed of a Co/Ti multilayer, was placed in front of the <sup>3</sup>He-detector. Only the scattered neutrons with an up spin were reflected along the scattered beam path to pass through the analyzer, whereas



Figure 1. Schematic diagram of the NSE spectrometer used for the NPA experiments. The two  $\pi/2$  flippers were not used in our NPA experiment.

those with a down spin were absorbed by the absorber including <sup>10</sup>B.<sup>[8]</sup> The scattered neutrons with an up spin were counted with a two-dimensional <sup>3</sup>He detector. The NSE measurements covered a q range of  $1 \text{ nm}^{-1} \le q \le 10 \text{ nm}^{-1}$ , corresponding to  $5.5^{\circ} \le 2\theta \le 57^{\circ}$  with a  $\theta - 2\theta$  scan mode with a step interval of 0.05 nm<sup>-1</sup>. A measurement time of up to 1 h was typically required for one scan to observe this q region. The scattering data were corrected for monitor counts, instrumental and air scattering background, the angle dependent of neutron transmission, and the irradiated sample area.

To decompose  $I_{\text{total}}(q)$  into  $I_{\text{coh}}(q)$  and  $I_{\text{inc}}(q)$ , a q scan under SF conditions with the  $\pi$ -flipper on and a q scan under NSF conditions with the  $\pi$ -flipper off were conducted for each sample. The measured scattering intensity distributions obtained from SF and NSF conditions are written as  $I_{\text{SF}}(q)$  and  $I_{\text{NSF}}(q)$ , respectively. By considering the effect of R on  $I_{\text{SF}}(q)$  and  $I_{\text{NSF}}(q)$ , corrected intensity distributions of those,  $I_{\text{SF}}'(q)$  and  $I_{\text{NSF}}'(q)$ ,  $I_{\text{NSF}}^{[22]}$  are given by

$$I_{\rm SF}'(q) = I_{\rm SF}(q) + \frac{1}{R-1} [I_{\rm SF}(q) - I_{\rm NSF}(q)],$$
(2)

$$I_{\rm NSF}'(q) = I_{\rm NSF}(q) + \frac{1}{R-1} [I_{\rm NSF}(q) - I_{\rm SF}(q)]. \tag{3}$$

Thus,  $I_{coh}(q)$  and  $I_{inc}(q)$  can be determined as follows:

$$I_{\rm coh}(q) = I_{\rm NSF}'(q) - \frac{1}{2}I_{\rm SF}'(q), \tag{4}$$

$$I_{\rm inc}(q) = \frac{3}{2} I_{\rm SF}'(q).$$
 (5)

The decomposition into  $I_{coh}(q)$  and  $I_{inc}(q)$  described above was performed by using DAVE software, which was developed at NIST.<sup>[23]</sup> Equations (4) and (5) are based on the rule that coherent neutron scattering events do not involve a spin-flip of the scattered neutrons, whereas 1/3 of the incoherent scattering events do not involve a spin-flip, whereas the other 2/3 do.<sup>[15]</sup> We converted the scattering intensities  $I_{coh}(q)$  and  $I_{inc}(q)$  to absolute units of reciprocal centimeters (cm<sup>-1</sup>) by using scattering from H<sub>2</sub>O sample.

#### SANS Diffractometer

SANS measurements were performed with the time-of-flight extended *q*-range SANS (EQ-SANS) diffractometer of the Spallation Neutron Source (SNS), Oak Ridge National Laboratory, USA.<sup>[24]</sup> As

in the NPA experiment, a 2-mm-thick quartz cell was used for the SANS measurements. A sampleto-detector distance of 1.3 m was employed with a single band of neutrons with wavelengths from 0.10 to 0.56 nm. This configuration of the EQ-SANS provides a *q* range of 0.15 nm<sup>-1</sup> < *q* < 10 nm<sup>-1</sup>. The divergence of the incident beam was defined by using a 25-mm-diameter source aperture and a 10-mm-diameter sample aperture. The scattered neutrons were detected with a two-dimensional position-sensitive <sup>3</sup>He detector of 1.0 m × 1.0 m composed of tube detectors, which provides 256 × 192 pixels. Data reduction followed standard procedures, as implemented in the Mantid software package.<sup>[25]</sup> The scattering data were corrected for wavelength-dependent sample transmission, for detector counting efficiency, and for instrumental background on a pixel-to-pixel basis. The reduced scattered intensity was then azimuthally averaged. Data output by the reduction was in absolute units of reciprocal centimeters (cm<sup>-1</sup>) through a scale factor determined by measuring a porous SiO<sub>2</sub> standard.<sup>[12]</sup> After subtracting the scattering contribution of the empty quartz cell from that of the sample, the corrected scattered intensity distributions are designated as *I*(*q*).

#### **Results and Discussion**

Figure 2 shows the decomposition of  $I_{\text{total}}(q)$  (open triangles) into  $I_{\text{coh}}(q)$  (open squares) and  $I_{\text{inc}}(q)$  (filled circles) obtained for sample 2 by NPA.  $I_{\text{inc}}(q)$  shows an almost constant value with q as expected. This experimental value (0.122 cm<sup>-1</sup>) was about 2.0 times larger than that calculated from the composition of sample 2 because of contribution of the multiple neutron scattering. All calculated values of the incoherent scattering intensity,  $I_{\text{inc,calc.}}(q)$ , from the compositions in samples 1–6 are listed in Table 1.

In Figure 2,  $I_{\rm coh}(q)$  increased with decreasing q at  $q < 7.0 \text{ nm}^{-1}$ , whereas  $I_{\rm coh}(q)$  slightly increased with increasing q at  $q > 7.0 \text{ nm}^{-1}$ . The increase of  $I_{\rm coh}(q)$  at  $q < 7.0 \text{ nm}^{-1}$  arises from the structures with a size of several nanometers formed in *n*-octane- $d_{18}$  by aggregates of  $Zr(NO_3)_4$ ·2TBP complexes. Chiarizia and coworkers,<sup>[4]</sup> studying a higher-order structure formed in extracted organic phase by SANS, also reported the aggregation of  $Zr(NO_3)_4$ ·2TBP complexes in *n*-octane. On the other hand, the increase of  $I_{\rm coh}(q)$  at  $q > 7.0 \text{ nm}^{-1}$  originates from intramolecular interactions



**Figure 2.** Comparison of the SANS data (open circles) measured by the EQ-SANS diffractometer for sample 2 and its  $I_{total}(q)$ , which is decomposed into  $I_{coh}(q)$  (open squares) and  $I_{inc}(q)$  (filled circles) by NPA. Error bars represent  $\pm$  one standard deviation throughout the paper.

between TBP and octane. Here,  $I_{\text{total}}(q)$  strongly depended on  $I_{\text{inc}}(q)$  over a wide q region because the scattering intensity of  $I_{\text{coh}}(q)$  was comparable with that of  $I_{\text{inc}}(q)$ . Because  $I_{\text{coh}}(q)$  was obtained by subtracting  $I_{\text{inc}}(q)$  from  $I_{\text{total}}(q)$  in the conventional SANS data reduction,<sup>[26]</sup> ambiguous calculation and estimation of  $I_{\text{inc}}(q)$  could give an erroneous  $I_{\text{coh}}(q)$  value, leading to incorrect structural analysis in relation to the aggregation of  $Zr(NO_3)_4$ ·2TBP, including its size and shape. In particular, for small scatterers, such as those presented here, the determination of  $I_{\text{inc}}(q)$  by NPA is essential and ensures structural analysis in SANS data.

SANS profiles for sample 2 (open circles) are also plotted in Figure 2 to confirm the validity of the result of our NPA. The SANS profile well agreed with  $I_{total}(q)$  obtained by NPA on the absolute intensity scale with some minor discrepancies, which were attributed to the difference in instrumental resolution for SANS and NPA. Therefore, we conclude that our NPA experiment successfully enabled for the decomposition of  $I_{total}(q)$  into  $I_{coh}(q)$  and  $I_{inc}(q)$ .

Figures 3a and b show the decomposed  $I_{\rm coh}(q)$  and  $I_{\rm inc}(q)$  for samples 1–6.  $I_{\rm coh}(q)$  increased at  $q < 7.0 \text{ nm}^{-1}$  in samples 1–4 owing to the aggregation of  $Zr(NO_3)_4$ ·2TBP complexes, whereas  $I_{\rm coh}(q)$  in samples 5 and 6 remained constant. In Figure 3b,  $I_{\rm inc}(q)$  in all samples were nearly constant with q (Table 1). The magnitude of  $I_{\rm inc}(q)$  was consistent with the composition of each sample. Namely,  $I_{\rm inc}(q)$  increased proportionally with the hydrogen content of the sample.  $I_{\rm inc}(q)$  of TBP shows a maximum in these samples. The heavy organic phase (sample 3), with a secondary large  $I_{\rm inc}(q)$ , contained a high concentration of  $Zr(NO_3)_4$ ·2TBP, HNO<sub>3</sub>, and H<sub>2</sub>O (Table 1) because the phase separation of organic phase concentrates these components. In contrast,  $I_{\rm inc}(q)$  of the light organic phase (sample 4) was smaller than that of samples 1 and 2 because of the low concentrations of HNO<sub>3</sub> and H<sub>2</sub>O.  $I_{\rm inc}(q)$  of *n*-octane- $d_{18}$ , which did not contain hydrogen, is the smallest but not zero. Deuterium has a nonzero incoherent scattering length.<sup>[7,8]</sup> The ratios of the experimental-to-calculated  $I_{\rm inc}(q)$  value were from 1.9 to 3.7 (Table 1), indicating the nonlinear dependence of  $I_{\rm inc}(q)$  against the volume fraction of hydrogen atom in the sample.

A scattering maximum arising from the interference among  $Zr(NO_3)_4$ ·2TBP complexes was observed at  $q = 6.0 \text{ nm}^{-1}$  in  $I_{coh}(q)$  of sample 3 (Figure 3a). This peak may be attributed to the interference of the scattered neutrons among the complexes because of the large concentration of the complexes. Such important information pertaining to the nanostructure of the fluid would not be apparent without NPA. The intensity of the peak was much smaller than  $I_{inc}(q)$  of sample 3. Therefore, this peak would be hidden by  $I_{inc}(q)$  in a SANS measurement and would probably not



Figure 3. Decomposition of  $I_{total}(q)$  into (a)  $I_{coh}(q)$  and (b)  $I_{inc}(q)$  by NPA in samples 1–6.

be detected in  $I_{\text{total}}(q)$  without NPA. This result also indicates that NPA is significant for analyzing SANS data. The NPA results for samples 1–4 will be used for structural analysis of SANS data in the future work.

### Conclusion

We performed NPA of extracted organic phases containing  $Zr(NO_3)_4$ ·2TBP complexes in *n*-octaned<sub>18</sub> to decompose  $I_{total}(q)$  into  $I_{coh}(q)$  and  $I_{inc}(q)$  using an NSE spectrometer. The validity of the NPA result was confirmed by comparing the SANS data with  $I_{total}(q)$  on an absolute scattering intensity scale. Although NPA has never been used for structural analysis of SANS data obtained for samples of extracted coordination species in organic phases, we have demonstrated that NPA is suitable for this purpose. Our method is particularly effective for characterizing microscopic structures quantitatively by using SANS data for sample systems containing a small scatterer with a weak scattering intensity, such as extracted complexes, because their  $I_{coh}(q)$  and  $I_{inc}(q)$  compete over a wide q region.

#### Disclaimer

Mention of any commercial products in this article does not imply approval or endorsement by NIST, nor does it imply that such products are necessarily the best available for the purpose.

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