

# In Situ Determination of the Size and Polydispersity of Concentrated Emulsions

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Droplet size distributions of concentrated, polydisperse oil-in-water emulsions have been measured using ultra small angle neutron scattering (USANS). The mean radii calculated by fitting a model for polydisperse hard spheres with excluded volume interactions to the USANS data were consistent with those derived from electroacoustics on diluted emulsions after correction for conductance behind the shear plane. The Porod radii measured by USANS were similarly consistent with the mean surface-area-weighted radii derived from electroacoustics, irrespective of the drop concentration or polydispersity.

## Introduction

Many physical properties of emulsions are affected by the drop size distribution, including stability to coalescence and gravity-induced separation, flow and deformation behavior, visual appearance, texture, and flavor (the release of volatile components from drops).<sup>1–4</sup> A wide variety of techniques is used to size emulsion drops.<sup>1,3,4</sup> Optical microscopy is often regarded as the most precise method, since individual drops are observed and measured. Other methods measure the drop size, or separate drop distributions by size, on the basis of the response of the drops to applied forces (such as electric fields, gravity, or magnetic forces). A third type of measurement uses the time- or angle-dependent scattering of light, neutrons, or X-rays by emulsions to estimate the drop size. Despite the large number of techniques available, the accurate measurement of emulsion drop sizes is often not straightforward. Determination of the drop size distribution often requires that the emulsions be diluted (to 1% v/v or less), which may itself alter the size distribution, especially in highly concentrated, polydisperse, or marginally stable systems.

The drop size of polydisperse emulsions is characterized by measuring both the mean drop size and the spread of the distribution.<sup>5</sup> Either large numbers of drops are measured to determine the variation in the drop frequency with size over the entire size range or the drop size distribution is estimated from some average (size dependent) property of the emulsion. The latter process is common to many sizing techniques, and small errors in the measurement of the average property can result in significant uncertainty in the calculated size distribution.<sup>6</sup> Depending on whether the technique is sensitive to the number, surface area, or volume of drops, the distributions obtained are weighted toward smaller or larger drop sizes. A number of

distribution functions has been proposed for describing drop size data; however, few are widely used.<sup>6–8</sup> They may need to be transformed to enable comparison with distributions measured by different techniques<sup>6,9</sup> which can also generate errors.<sup>6,10,11</sup>

Interactions between drops in concentrated emulsions adversely affect many sizing techniques. Light scattering measurements, for example, are limited to dilute emulsions since the drop radius is obtained by extrapolation to infinite dilution to eliminate interaction effects. The large difference between the refractive indices of the drops and the continuous phase also leads to multiple scattering effects in concentrated samples. The analysis of drop sizes in concentrated emulsions which are unstable to flocculation is further complicated by the presence of nonspherical aggregates of drops.<sup>12</sup>

In this work we combine ultra small angle neutron scattering (USANS) and electroacoustics to determine the drop size distributions of polydisperse concentrated emulsions in situ. Neutrons are weakly scattered by the nuclei in materials at angles that are inversely related to the length scales of the material, so neutron scattering is less subject to the effects of multiple scattering and readily applicable to opaque systems. Small angle neutron scattering has been used previously to investigate structure in concentrated emulsions,<sup>13–15</sup> particularly the structure of surfactant and polymer adsorbed layers at the oil/water interface.<sup>15–17</sup> Ultra small angle scattering<sup>14,18–20</sup> has the advantage that larger length scales (up to about 1  $\mu\text{m}$ ) can be

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**Table 1. Emulsion Composition, Number of Passes, and Temperature during Homogenization**

oil volume fraction, $\phi$	[SDS] (mM)	number of passes	$T$ ( $^{\circ}\text{C}$ )
Sunflower Oil-in- $\text{D}_2\text{O}$ Emulsions			
0.1	20	20	25
0.3	50	20	25
0.5	60	20	25
0.5	60	20	50
Bromohexadecane-in- $\text{D}_2\text{O}$ Emulsions			
0.1	20	10	25
0.5	60	10	25

characterized, so USANS can be applied to measuring emulsion drop size distributions.

Electroacoustics measures the dynamic mobility ( $\mu_{\text{D}}$ ), which is the frequency response of a dispersion of emulsion drops to an alternating electric field, and depends on the size and zeta potential of the drops.<sup>21</sup> The dynamic mobility can be measured at almost any dispersed phase volume fraction and, as a nonoptical technique, is also well suited to concentrated emulsions. Analytical solutions relating the dynamic mobility to the size and zeta potential of drops (or particles) in concentrated dispersions have been derived.<sup>22</sup> O'Brien et al.<sup>21</sup> showed that good agreement was achieved between the size distributions calculated for polydisperse particle dispersions and those measured by sedimentation. Here we examine the consistency between the drop size distributions measured by USANS and electroacoustics for emulsions at different drop volume fractions and polydispersities.

### Experimental Section

Commercial sunflower oil (92 g/100 mL total fat, Meadow Lea Foods, Australia) and 1-bromohexadecane (97%, Sigma Aldrich) were used as received.  $\text{D}_2\text{O}$  (99.9%) was purchased from Sigma Aldrich. Sodium dodecylsulfate (SDS, 99.9%, Sigma Aldrich) and sodium chloride (NaCl, 99%, Ajax Chemicals) were used as received.

Emulsions were prepared at various oil volume fractions from mixtures of oil and solutions of SDS and 0.1 M NaCl in  $\text{D}_2\text{O}$ . The deuterated water phases were prepared by first dissolving NaCl in the required volume of  $\text{D}_2\text{O}$  and then adding a known amount of SDS. The solutions were gently sonicated (at 20 kHz in an ultrasonic bath) to speed dissolution of the surfactant. The oil phase was then added, and the mixtures passed through a high-pressure homogenizer (Milko-tester Mark III F3140, A/S N. Foss Electric, Denmark) a number of times at a given temperature (see Table 1 for details) to prepare the emulsions. The temperature was controlled during homogenization by equilibrating the emulsions in a water bath (Julabo F20) maintained at the desired temperature.

The dynamic mobility of the emulsions was measured in the flow-through cell of a prototype Colloidal Dynamics Acoustosizer-II, which has been described elsewhere.<sup>21</sup> The emulsions were first diluted to an oil volume fraction of 0.02 in solutions of SDS and NaCl in  $\text{D}_2\text{O}$ . The diluted emulsions were gently sonicated to remove trapped air bubbles and then left to rest for 1 h prior to measurements. The measurement cell was flushed with  $\text{D}_2\text{O}$  three times to remove any traces of (hydrogenated) water prior to measurements.

Neutron scattering spectra of the emulsions were measured using the BT-5 ultra high resolution small angle neutron scattering (USANS) spectrometer at the National Center for Neutron Research at the National Institute of Standards and Technology, Gaithersburg, MD.<sup>23</sup> Using a double crystal diffractometer, the neutron scattering was measured at ultra small angles ( $q = 3 \times 10^{-5}$  to  $0.01 \text{ \AA}^{-1}$ ), to extend the size range studied from about 100 to  $10^5 \text{ \AA}$ . The diffractometer has excellent horizontal resolution but poor vertical

resolution, which is analogous to the smearing that occurs when slits are used for angular collimation in one direction. The measured smeared intensity ( $I_s(q)$ ) is related to the true intensity ( $I(q)$ ) by<sup>24</sup>

$$I_s(q) = \frac{1}{\Delta q_v} \int_0^{\Delta q_v} I(\sqrt{q^2 + u^2}) du \quad (1)$$

The width of the slit was  $\sim 2 \times 10^{-5} \text{ \AA}^{-1}$ , and the length was  $\sim 0.04 \text{ \AA}^{-1}$ . The vertical divergence of the beam ( $\Delta q_v$ ) was  $\pm 0.037 \text{ \AA}^{-1}$ . Although it was possible to desmear the data, the results were very sensitive to noise. Thus, the variation in the slit smeared absolute cross-section with scattering angle was analyzed directly, and fitted to model scattering functions.<sup>23,25</sup>

USANS spectra were recorded over 6–12 h, by stepping the monochromator and analyzer crystals. The absence of multiple scattering effects was verified by comparing results recorded at different path lengths between 0.4 and 1 mm by inserting spacers into the cell. Sample transmissions were greater than 0.92. During each experiment a small amount of creaming was observed in some samples.

### Results and Discussion

Emulsions with varying degrees of polydispersity were prepared by high-pressure homogenization of sunflower oil or 1-bromohexadecane in  $\text{D}_2\text{O}$  (containing SDS and salt). In a high-pressure homogenizer, a coarse emulsion is forced through a number of narrow slits which breaks the dispersed phase into fine drops.<sup>26</sup> The final drop size is a function of the resulting laminar elongational flow and the ratio of the oil and water viscosities.<sup>26</sup> In general, drops fragment more easily where the viscosity ratio is low. Sunflower oil is a mixture of long chain fatty acids, mainly oleic acid and linoleic acid, with a viscosity about 2 orders of magnitude larger than that of water at  $20 \text{ }^{\circ}\text{C}$ .<sup>27</sup> The drop size distributions in the sunflower oil-in- $\text{D}_2\text{O}$  emulsions prepared at  $25 \text{ }^{\circ}\text{C}$  were thus expected to be more polydisperse and centered at larger radii compared to the drop size distributions in the bromohexadecane-in- $\text{D}_2\text{O}$  emulsions where the oil–water viscosity ratio is closer to unity. Some sunflower oil-in- $\text{D}_2\text{O}$  emulsions were homogenized at  $50 \text{ }^{\circ}\text{C}$ , where the viscosity of both liquids is lower, to reduce the polydispersity of the emulsions. The drop size distributions were first measured by electroacoustics.

**Dynamic Mobility.** The dynamic mobility, ( $\mu_{\text{D}}$ ), is the AC analogue of the electrophoretic mobility measured using a direct electric field.<sup>21,28</sup> When an alternating field (assumed to be sinusoidal) is applied to an emulsion, the (charged) drops oscillate at the same frequency ( $\omega$ ) as the applied field, and the resulting compression and decompression of the emulsion generates an ultrasonic wave known as the electrokinetic sonic amplitude (ESA) signal. The amplitude of the sound wave depends on both the drop size and charge, and the phase lag ( $\omega\Delta t$ ) between the applied field and the drop oscillations depends on the drop size. The dynamic mobility spectrum is calculated from the ESA signal using

$$\text{ESA} = A\phi \frac{\Delta\rho}{\rho} \langle \mu_{\text{D}} \rangle EZ \quad (2)$$

where  $A$  is an instrument constant,  $\phi$  is the drop volume fraction,  $\Delta\rho$  is the difference between the density of the particles and the density of the continuous phase ( $\rho$ ),  $E$  is the amplitude of the applied field, and  $Z$  depends on the acoustic impedance of the

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emulsion and the measuring equipment. The radius ( $r$ ) and zeta potential ( $\zeta$ ) of the drops are determined from the variation in the dynamic mobility with the frequency of the applied field. O'Brien showed that the dynamic mobility of spherical particles with a thin double layer is given by<sup>28</sup>

$$\mu_D = \frac{2\epsilon\zeta(1+f)}{3\eta} G(\omega r^2/\nu) \quad (3)$$

where  $\epsilon$  is the permittivity,  $\eta$  is the viscosity,  $\nu$  is the kinematic viscosity of the continuous phase,  $1+f$  represents the component of the electric field which generates the electrophoretic motion, and  $G$  describes the effect of inertia forces.

These concentrated emulsions exhibit high surface conduction due to the mobility of adsorbed ions behind the plane of shear, in the so-called stagnant layer.<sup>29–34</sup> Previous work has shown that neglecting the effects of surface conduction can lead to misinterpretation of the electrokinetic behavior of dispersions.<sup>33–35</sup> As it is not yet possible to determine the particle size distribution at high concentrations when both surface conduction and particle interactions affect the ESA signal,<sup>36</sup> all emulsions were diluted (in aqueous solutions of surfactant and salt) to an oil volume fraction of 0.02 so that the effects of surface conduction could be isolated.

Figure 1a shows dynamic mobility spectra for the sunflower oil-in-D<sub>2</sub>O emulsions prepared at volume fractions  $\phi = 0.1$  and 0.5 at 25 °C. For the diluted  $\phi = 0.1$  system, the magnitude of the dynamic mobility decreases with increasing frequency as expected; however, the argument remains about constant over a wide range of frequencies. This is contrary to expectations that the argument should become increasingly negative as the motion of the drops lags further behind applied field, and indicates that stagnant layer conduction is affecting the electrokinetic behavior of the drops. Similar behavior was observed for emulsions prepared at  $\phi = 0.3$  (not shown).

For the most concentrated sunflower oil-in-D<sub>2</sub>O emulsion ( $\phi = 0.5$ ), the magnitude of the dynamic mobility increases with increasing frequency and the argument passes through a maximum, both features indicating high stagnant layer conductance.<sup>34</sup> High stagnant layer conduction also influenced the dynamic mobilities of sunflower oil-in-D<sub>2</sub>O emulsions prepared at 50 °C (not shown) and the bromohexadecane-in-D<sub>2</sub>O emulsions shown in Figure 1b.

The dynamic mobility data are fitted to a log normal drop size distribution, which has the probability density function

$$f(r) = \frac{1}{\sqrt{2\pi r} \ln \sigma_g} \exp\left[-\frac{(\ln r - \ln r_g)^2}{2 \ln^2 \sigma_g}\right] \quad (4)$$

where  $r_g$  is the geometric mean (the arithmetic mean of the logarithms of the radii) and  $\sigma_g$  is the geometric standard deviation of the distribution. Fit parameters are the arithmetic volume-average radius and a standard deviation that determines the radii

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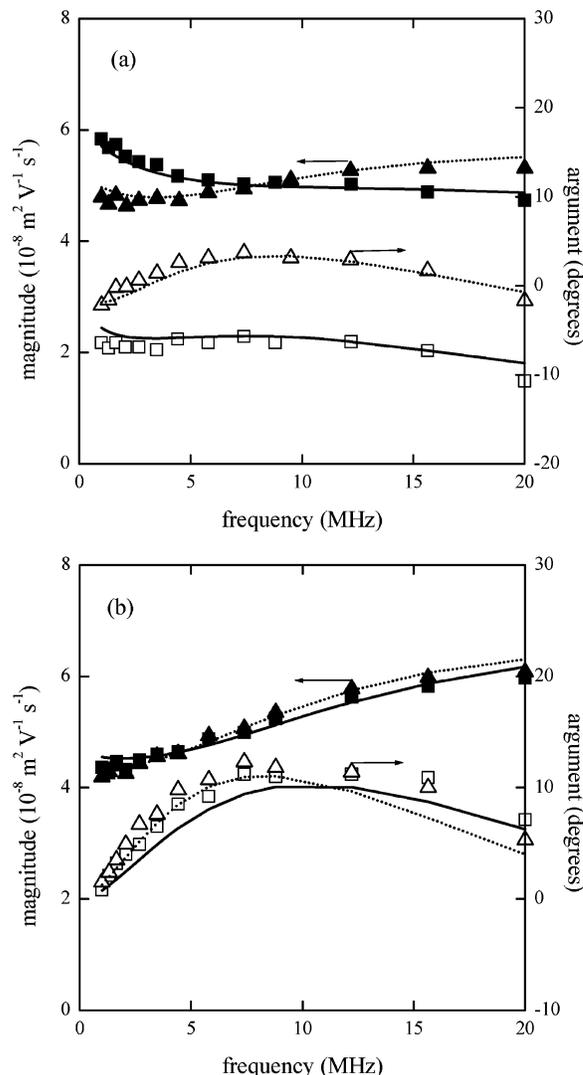
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**Figure 1.** Variation of the magnitude (left ordinate, filled symbols) and argument (right ordinate, open symbols) of the dynamic mobility with frequency for (a) sunflower oil-in-D<sub>2</sub>O emulsions stabilized by SDS and (b) bromohexadecane-in-D<sub>2</sub>O emulsions stabilized by SDS. The emulsions were prepared (at 25 °C) at oil volume fractions of 0.1 (■, □) or 0.5 (▲, △) and then diluted to an oil volume fraction of 0.02 for these measurements. The lines are theoretical fits incorporating surface conduction.

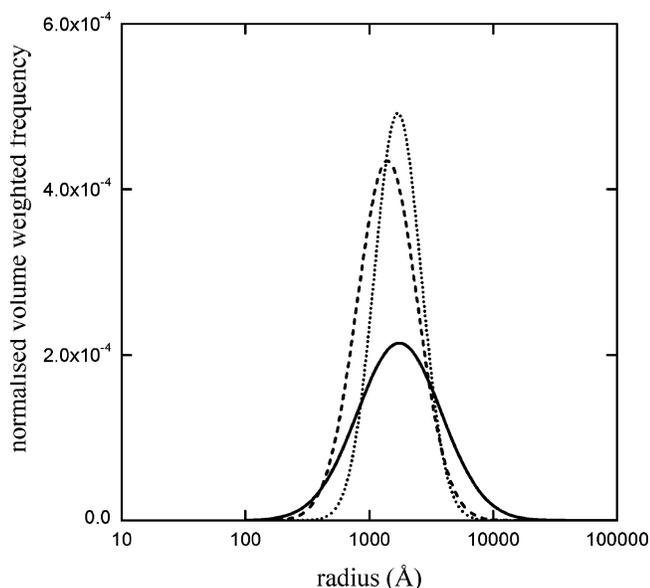
at the 15th and 85th percentiles of the distribution. The electrokinetics are characterized by the zeta potential and the Dukhin number, which is a measure of the relative surface conductance.<sup>33</sup> The zeta potential for dilute sunflower oil-in-water and hexadecane-in-water emulsions stabilized by SDS have previously been derived from electroacoustics measurements and the effects of stagnant layer conduction on their electrokinetic behavior investigated.<sup>33,34</sup> The zeta potentials and Dukhin numbers derived from those studies were used to guide the choice of the initial values used in the fitting process, and the variables describing the drop size distribution were adjusted to optimize the fit.

Table 2 shows the droplet size distributions derived from the electroacoustics data characterized by the volume-average drop radius ( $r_v$ ) and the polydispersity, the ratio of the standard deviation of the distribution,  $\sigma$ , to the mean radius. As expected, the drop size distributions of the emulsions prepared from bromohexadecane were relatively narrow and centered at smaller radii compared to those of emulsions prepared from the more

Table 2. Fitted Drop Size Distribution Parameters derived from Electroacoustic and USANS Measurements

$\phi$	electroacoustics			$\sigma/r_V$	$\phi_{\text{SANS}}$	USANS			
	$r_V$ (nm)	$r_S$ (nm)	$r_N$ (nm)			$r_{\text{Porod}}$ (nm)	$r_{\text{av}}$ (nm)	$\sigma/r_{\text{av}}$	
Sunflower Oil-in-D <sub>2</sub> O Emulsions Prepared at 25 °C									
0.1	360 ± 40	180 ± 40	40 ± 20	1.0 ± 0.1	0.1	250 ± 80 <sup>a</sup>	77 ± 5	0.98 ± 0.01	
0.3	360 ± 40	200 ± 30	60 ± 20	0.88 ± 0.07	0.02	20 ± 40	87 ± 7	0.99 ± 0.01	
					0.3	200 ± 10	<i>b</i>		
0.5	250 ± 20	120 ± 30	30 ± 20	1.0 ± 0.2	0.1	250 ± 30	70 ± 3	0.98 ± 0.02	
					0.5	134 ± 7	55 ± 5	0.95 ± 0.02	
					0.4	160 ± 20	50 ± 5	0.95 ± 0.02	
					0.1	160 ± 10	60 ± 5	0.94 ± 0.02	
Sunflower Oil-in-D <sub>2</sub> O Emulsion Prepared at 50 °C									
0.5	160 ± 40	140 ± 40	120 ± 50	0.6 ± 0.1	0.5	111 ± 5	<i>b</i>		
					0.1	120 ± 10	93 ± 3	0.44 ± 0.01	
Bromohexadecane-in-D <sub>2</sub> O Emulsions Prepared at 25 °C									
0.1	150 ± 20	120 ± 20	90 ± 20	0.47 ± 0.06	0.1	97 ± 8	85 ± 2	0.40 ± 0.01	
0.5	170 ± 20	140 ± 20	80 ± 20	0.51 ± 0.05	0.5	114 ± 7	80 ± 2	0.46 ± 0.01	
					0.1	110 ± 10	86 ± 4	0.48 ± 0.01	

<sup>a</sup> The large uncertainty in the Porod radius is due to the high signal:noise of this system. <sup>b</sup> No satisfactory fit could be achieved in these systems due to the low  $q$  scattering by aggregates.



**Figure 2.** Volume-weighted log normal drop size distributions derived from electroacoustic measurements on diluted samples of 50 vol % sunflower oil-in-D<sub>2</sub>O emulsions stabilized by SDS prepared at 25 °C (—) or at 50 °C (---) and a 50 vol % bromohexadecane-in-D<sub>2</sub>O emulsion stabilized by SDS prepared at 25 °C (···).

viscous sunflower oil. All the emulsions were quite polydisperse, with the sunflower oil-in-D<sub>2</sub>O emulsions prepared at 25 °C having the largest polydispersity of about 1 and the bromohexadecane-in-D<sub>2</sub>O emulsions having the smallest polydispersity of 0.5. The uncertainty associated with drop sizes derived for the sunflower oil-in-D<sub>2</sub>O emulsions prepared at 25 °C was relatively large since there was no unique fit between the theoretical predictions and the measured dynamic mobility data. In contrast, there was a smaller range of possible fits to the variation in the magnitude and argument of the dynamic mobility with frequency for the sunflower oil-in-D<sub>2</sub>O emulsions prepared at 50 °C and the bromohexadecane-in-D<sub>2</sub>O emulsions.

Examples of volume-weighted log-normal drop size distributions calculated from fitting the dynamic mobility data for the emulsions are shown in Figure 2. The log normal distribution has the unique property that if one of the number, surface, and volume distributions is log normal, then all the distributions will be log normal with the same geometric standard deviation and

polydispersity. This facilitates comparison with USANS data. Hence, following the method described by Allen,<sup>6</sup> the geometric mean of the number-weighted distribution ( $r_{gN}$ ) can be calculated from the known geometric mean of the volume-weighted distribution ( $r_{gV}$ ) and  $\sigma_g$  using the relationship

$$\ln r_{gV} = \ln r_{gN} + 3.0 \ln^2 \sigma_g \quad (5)$$

Thus, the mean of the surface- and number-weighted distributions ( $r_S$  and  $r_N$ , respectively) can be calculated using the equations of Hatch and Choate<sup>37</sup>

$$\ln r_S = \ln r_{gN} + 2.5 \ln^2 \sigma_g \quad (6)$$

$$\ln r_N = \ln r_{gN} + 0.5 \ln^2 \sigma_g \quad (7)$$

The mean drop radii thus calculated for the surface- and number-weighted drop size distributions of the sunflower oil-in-D<sub>2</sub>O and bromohexadecane-in-D<sub>2</sub>O emulsions are given in Table 2. The decrease in the mean drop radius from the volume-weighted distribution to the number-weighted distribution was more dramatic for the sunflower oil-in-D<sub>2</sub>O emulsions compared to that for the bromohexadecane-in-D<sub>2</sub>O emulsions. Indeed, the predicted number-average radii for some of the sunflower oil-in-D<sub>2</sub>O emulsions seem too small to be physically realistic (<500 Å), and this is a measure of the limitations of the transformation of drop sizes in such polydisperse systems.

**Neutron Scattering.** The drop size distributions were next determined by neutron scattering. The scattered intensity,  $I(q)$ , from a dispersion of identical homogeneous emulsion drops is typically represented as contributions from scattering centers within each particle known as the form factor,  $P(q)$ , and those from the spatial arrangement of the particles throughout the continuous phase, or structure factor,  $S(q)$ .<sup>38–40</sup> Assuming that the interactions between particles do not depend on the particle orientations and that all orientations of the scattering centers are equally probable, the variation in the scattered intensity with the

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scattering vector,  $q = (4\pi/\lambda)\sin(\theta/2)$ , is given by

$$I(q) = nV^2\Delta\rho_s^2P(q)S(q) \quad (8)$$

where  $n$  and  $V_{\text{drop}}$  are the number density and volume of drops, respectively, and  $\Delta\rho_s$  is the scattering length density difference between the dispersed (droplet) and continuous phases. For a dilute dispersion, the form factor is sufficient to describe the scattered intensity as  $S(q) \rightarrow 1$  at infinite dilution. At higher concentrations, however, interactions between particles can significantly modify the scattered intensity leading, for example,<sup>41</sup> to a scattering peak.

It is common to numerically desmear USANS data in order to directly compare it with point-collimated SANS. While quite reliable for dilute systems, where a low  $q$  ( $q < 1/r$ ) Guinier regime exists, this approach is known to be less reliable in strongly interacting and concentrated systems. Here we take two separate approaches. First, a “model-free” approach, using the high  $q$  ( $> \pi/r$ ) scattering is used to determine the surface-area-weighted droplet size, and second, the line-collimated USANS spectra are fitted directly to a model of interacting, homogeneous, polydisperse spheres.

For drops with (surface-weighted) radii of 140 nm and higher, the scattering at  $q \geq 0.001 \text{ \AA}^{-1}$  is determined by the interface between the dispersed droplets and the continuous phase (Porod regime). Figure 3 shows USANS spectra for several sunflower oil-in- $\text{D}_2\text{O}$  emulsions as prepared at 25 °C at different volume fractions, together with various dilutions. All exhibit Porod scattering at high  $q$  with a power-law slope of  $-3$ , characteristic of a sharp interface.

Using Porod’s asymptotic approximation,<sup>42,43</sup> it can be shown that the absolute value of line smeared scattered intensity,  $I_s(q)$ , at large scattering vectors depends only on the total interfacial area per unit volume of emulsion,  $\Sigma$

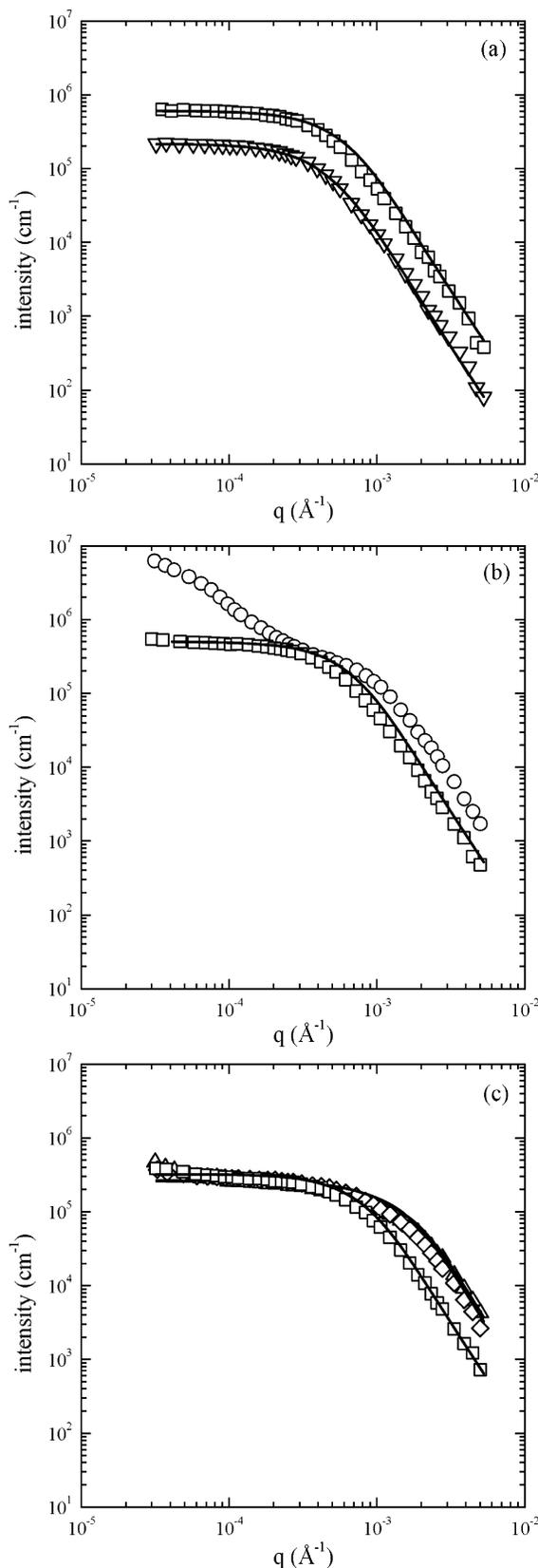
$$\lim_{q \rightarrow \infty} I_s(q) = \frac{2\pi^2\Delta\rho_s^2\Sigma}{4\Delta\rho_v q^3} \quad (9)$$

Since  $I_s(q)q^3$  is an oscillatory function of  $q$ , it is preferable to measure the Porod scattering by USANS rather than SANS which has a lower scattering angle limit of  $0.005 \text{ \AA}^{-1}$ . The scattering length densities for bromohexadecane and  $\text{D}_2\text{O}$  are  $-2.02 \times 10^{-7} \text{ \AA}^{-2}$  and  $6.33 \times 10^{-6} \text{ \AA}^{-2}$ , respectively.<sup>44</sup> The sunflower oil was assumed to be a 1:3 mixture of oleic and linoleic acid and the scattering length density estimated as  $1.87 \times 10^{-7} \text{ \AA}^{-2}$ . The order of magnitude difference between the scattering length densities of the fatty acid components in sunflower oil and  $\text{D}_2\text{O}$  means that variation in the oil composition would not affect the contrast significantly.

Figure 3 also shows the effect of dilution on the total interfacial area, and hence on the scattered intensity at high  $q$ . For a dispersion of spherical drops, it can be shown that the total interfacial area per unit volume depends on the ratio of the oil drop volume fraction ( $\phi$ ) to the drop radius, which is known as the Porod radius, given by

$$r_{\text{Porod}} = \frac{3\phi}{\Sigma} \quad (10)$$

The Porod radius is thus the ratio of the total drop volume to the



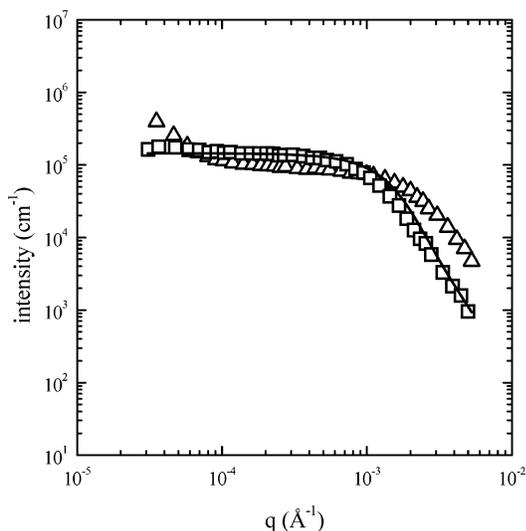
**Figure 3.** USANS spectra of SDS-stabilized sunflower oil-in- $\text{D}_2\text{O}$  emulsions (a) prepared directly at an oil volume fraction of 0.1 ( $\square$ ) and then diluted to an oil volume fraction of 0.02 ( $\nabla$ ), (b) prepared directly at an oil volume fraction of 0.3 ( $\circ$ ) and then diluted to an oil volume fraction of 0.1 ( $\square$ ), and (c) prepared directly at an oil volume fraction of 0.5 ( $\triangle$ ) and then diluted to oil volume fractions of 0.4 ( $\diamond$ ) and 0.1 ( $\square$ ). The emulsions were prepared at 25 °C. Only every third data point is shown for clarity. Solid lines are theoretical fits to the data.

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**Figure 4.** USANS spectra of SDS-stabilized sunflower oil-in-D<sub>2</sub>O emulsions prepared at 50 °C directly at an oil volume fraction of 0.5 ( $\Delta$ ) and then diluted to an oil volume fraction of 0.1 ( $\square$ ). Only every third data point is shown for clarity. The lines are theoretical fits to the data.

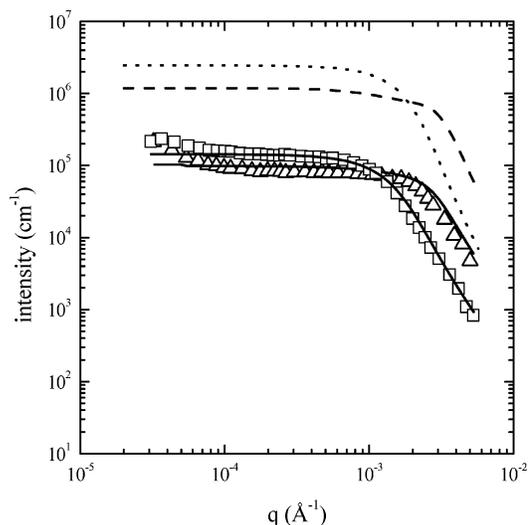
total drop surface area, which is the same as the surface-weighted average radius. Regardless of the polydispersity or drop volume fraction, Porod radii were typically consistent with the surface-weighted mean radii,  $r_s$ , obtained from electroacoustics on the diluted emulsions, as shown by the data given in Table 2.

The intense scattering of the  $\phi = 0.3$  sunflower oil-in-D<sub>2</sub>O emulsion at low  $q$  (Figure 3b) indicates the presence of even larger structures. This was attributed to the presence of aggregates of drops rather than large or coalesced drops, as the scattering disappeared after dilution. No aggregates were detected by electroacoustics measurements on further diluted systems. The presence of such aggregates also reduces the interfacial area (and hence the scattering at large angles), causing the Porod radius to be underestimated somewhat.

The USANS spectrum of the sunflower oil-in D<sub>2</sub>O emulsion prepared at 50 °C and  $\phi = 0.5$  are shown in Figure 4, together with that after dilution to  $\phi = 0.1$ . These smaller and much less polydisperse emulsions also show characteristic Porod scattering, and a Porod radius that is independent of volume fraction and agrees well with  $r_s$  derived from electroacoustics (Table 2). A slight upturn at low  $q$  indicates that some flocculation has occurred during sample preparation, and in this case is not entirely eliminated by dilution to  $\phi = 0.1$ .

Figure 5 shows the USANS spectra of bromohexadecane-in-D<sub>2</sub>O emulsions prepared at  $\phi = 0.5$  and 0.1. The  $\phi = 0.5$  bromohexadecane emulsion shows a small amount of very low  $q$  scattering, although much less than in Figure 3b, that also disappeared upon dilution (data not shown). The Porod radius is again independent of volume fraction and agrees well with electroacoustics results.

The drop size distribution in these emulsions was also determined by directly fitting the data with a distribution of polydisperse spheres with excluded volume interactions. In a system of polydisperse spheres, the form factor is an average of the scattering of all the spheres in the distribution, and the structure factor depends on all the correlations between particles of different sizes.<sup>45</sup> For systems with moderate polydispersity, the structure factor may be approximated by an average, one-component structure factor,<sup>46</sup> but this approach fails as the polydispersity or



**Figure 5.** USANS spectra for SDS-stabilized bromohexadecane-in-D<sub>2</sub>O emulsions prepared directly at oil volume fractions of 0.5 ( $\Delta$ ) and 0.1 ( $\square$ ). Only every third data point is shown for clarity. Solid lines are theoretical fits to the data, and the dashed and dotted lines show the calculated point-collimated scattering curves for  $\phi = 0.5$  and 0.1, respectively.

the concentration of particles increases.<sup>47</sup> Because of the high polydispersity of these emulsions, we have used here an exact, multicomponent solution for scattering by a system of polydisperse spheres with excluded volume interactions using the Percus–Yevick closure, where the size distribution is described using the Schulz distribution.<sup>48,49</sup> Although these emulsions are stabilized by SDS, the drop size and salt concentration make these thin double layer systems, so electrostatic repulsions are expected to have a negligible effect on the scattering. The probability density function of the Schulz distribution<sup>49,50</sup> is given by

$$f(r) = \frac{(z+1)^{z+1}}{r_{av}\Gamma(z+1)} x^z \exp[-(z+1)x] \quad (11)$$

where  $z = (r_{av}^2/\sigma^2) - 1$ ,  $x = r/r_{av}$ ,  $\sigma^2$  is the variance of the distribution, and  $r_{av}$  is the number-average radius. The polydispersity is again given by the ratio  $\sigma/r_{av}$ . The Schulz distribution was used for the exact, multicomponent solution of the scattering since, unlike the log normal distribution, it is mathematically tractable.

The qualitative effect of interactions between drops can be seen directly in Figures 3–5. Dilution of a sunflower oil-in D<sub>2</sub>O emulsion from  $\phi = 0.1$  to  $\phi = 0.02$  (Figure 3a) has little effect on the shape of the scattering curve. To a good approximation, the intensity is simply reduced by a factor of 5. However, dilution of a sunflower oil-in D<sub>2</sub>O emulsion from  $\phi = 0.5$  to  $\phi = 0.4$  and 0.1 (Figure 3c) causes a proportional decrease in intensity only in the Porod region, whereas the low  $q$  intensity is almost unaffected. The effect of concentration on the less polydisperse emulsions shown in Figures 4 and 5 is even more noticeable. In these systems, the intensity in the low  $q$  plateau region is higher for the more dilute emulsions, as expected for repulsions between droplets. Although no peak is observed even at  $\phi = 0.5$ , the structure factor increases the abruptness of the shoulder. The

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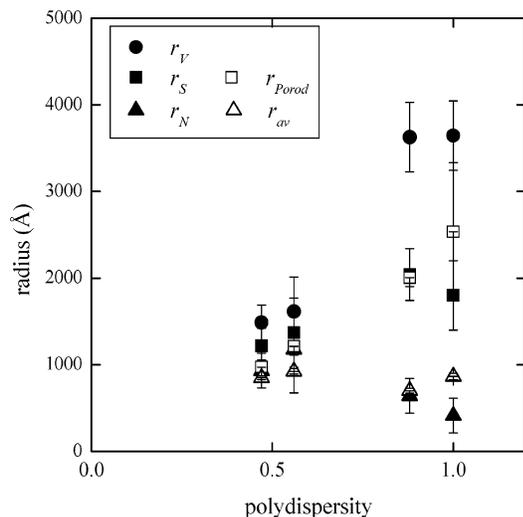
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**Figure 6.** Comparison between the volume-, surface-, and number-weighted mean radii from electroacoustics with those derived from the neutron scattering measurements for 10 vol % oil-in-D<sub>2</sub>O emulsions.

absence of a scattering peak in these systems is a consequence of the high polydispersity, and not of smearing due to line-collimation. This is illustrated in Figure 5, which shows calculated point-collimated scattering spectra corresponding to the best-fit parameters for  $\phi = 0.5$  and 0.1 emulsions.

USANS data were fitted by optimizing the mean drop radius and polydispersity, using contrast fixed by the scattering length densities of sunflower oil, bromohexadecane, and D<sub>2</sub>O, and the volume fraction set by the emulsion composition as prepared or after dilution ( $\phi_{SANS}$ ). The continuous phase does not contribute significantly to the incoherent scattering ( $0.136 \text{ cm}^{-1}$  for D<sub>2</sub>O<sup>44</sup>). For the concentrated emulsions, however, the incoherent scattering by the oil phase ( $5.3 \text{ cm}^{-1}$  for sunflower oil and  $5.47 \text{ cm}^{-1}$  for bromohexadecane) leads to a background between about 0.7 and  $3 \text{ cm}^{-1}$  depending on the volume fraction of the emulsion.

Table 2 lists the best-fit results for all the emulsions except the most flocculated, where the scattering at low  $q$  prevented satisfactory fits to the data. Unfortunately, models for polydisperse spheres with attractive interactions have yet to be developed. The best-fit radii and polydispersity derived from USANS are identical, however, within experimental error for dilution series of all the disperse emulsions studied. This suggests that USANS accurately reports average size and polydispersity even in concentrated emulsions, but also that these emulsions do not change their size distributions on dilution (except for flocculation). This gives us further confidence in the electroacoustics results obtained on diluted emulsions.

The fitted USANS radii agree remarkably well with the number-average radii derived by transforming the volume-weighted electroacoustics results. Only in the  $\phi = 0.1$  sunflower oil-in-water system is the difference greater than experimental uncertainty, and this small discrepancy is an understandable consequence of propagating the high polydispersity.

The situation is summarized in Figure 6 where the radii derived from the electroacoustics measurements (filled symbols) are compared to the radii derived from the neutron scattering measurements (open symbols). Since the neutron scattering measurements were performed on emulsions at various drop volume fractions, for consistency, data are shown only for the 10 vol % oil-in-D<sub>2</sub>O emulsions.

## Conclusions

Concentrated oil-in-water emulsions were prepared with polydispersities ranging from about 0.5 to 1 at drop volume fractions between  $\phi = 0.1$  and 0.5. The volume-weighted drop size distributions of the emulsions obtained from electroacoustics measurements on diluted emulsions, and the derived surface-area- and number-weighted drop size distributions, yielded excellent agreement with size distributions obtained from fitting USANS spectra to a model of interacting polydisperse hard spheres and Porod limit scattering on the concentrated emulsions. In these systems, the drop size distribution was found not to change with dilution on the experimental time scale, which was up to several days.

The consistency between the mean radii calculated from fitting the USANS data with those derived from electroacoustics confirms the validity of using models which include the effects of stagnant layer conduction when analyzing the electrokinetic behavior of dispersions.

USANS thus shows great promise for in situ determination of drop size distributions in concentrated emulsions under a variety of situations. It is likely that USANS could be used to investigate less stable emulsions, where drop size does depend on dilution, as well as for more strongly interacting and less polydisperse emulsions, where structure factor effects would be more evident.

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