Porod's limit of small angle x-ray scattering from AOT-H$_2$O isoctane micro-emulsions

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Abstract: Water-oil micro-emulsions consisting of AOT-H$_2$O isoctane of different water-surfactant, $W_0$, and oil-surfactant, $S_0$, ratios, have been studied by SAXS over a wide range of scattering vectors. The shape of the high angle portion of the scattered intensity is found to be independent of the micro-emulsion composition and furthermore, does not follow the classical $1/q^4$ Porod Law. Rather an additional $1/q^2$ contribution to the scattering curve is observed. These results are explained in terms of the distance correlation function for a pseudo two-phase system, water and oil, with a diffuse interface formed by a monomolecular layer of surfactant molecules. The observed $1/q^2$ behavior is shown to arise from a $1/r$ contribution to the correlation function. A quantitative analysis shows that the total interfacial area of the micro-emulsion is proportional to the total number of surfactant molecules in solution. Thus the average area per surfactant molecule is independent of the micro-emulsion composition.

Key words: X-ray scattering, micro-emulsion, interfacial area, surfactants, aerosol OT

Introduction

Micro-emulsions are mixtures of oil and water stabilized by surfactant molecules [1]. The mixtures form transparent, isotropic, fluid systems that are stable at room temperature for long periods. These systems are homogeneous dispersions of large amounts of two otherwise immiscible liquids. Variation of the water-oil ratio can induce dramatic changes in the macroscopic properties of the micro-emulsion similar to critical phase transitions in single component systems. For example, a conductivity threshold and a maximum in the permittivity as a function of water concentration or temperature, or both, is observed in the Aerosol OT-H$_2$O-iso-octane micro-emulsion [2, 3]. The behavior of the dielectric properties of this Aerosol OT-H$_2$O-iso-octane micro-emulsion can be well understood within the framework of percolation theory [2]. This, however, gives a description of the micro-emulsion only on a macroscopic scale.

On a microscopic scale it has been shown that at low water-oil ratio the water is dispersed in small spherical droplets ($R = 5 - 70$ Å) in the oil phase [4–6]. The average droplet size, $R$, is determined by the area per surfactant molecule, $\Sigma_\sigma$, and the molar ratio of water to surfactant, $W_0$. The molar ratio of oil to surfactant, $S_0$, then determines the droplet concentration or micro-emulsion concentration. A concentration increase can induce different types of structural transitions [4–8]. The micro-emulsion can change from a droplet structure at low concentration to a bicontinuous structure with irregular regions of water interspersed in oil regions of a similar arbitrary shape. But the micro-emulsion may retain its droplet nature at higher concentrations where large aggregates of droplets exist. The type of transition will most probably be governed by the geometry of the surfactant molecule and the way it is incorporated in the water-oil interface [9].

Techniques such as light, neutron, and x-ray scattering provide information concerning the shape, size, polydispersity, and particle interactions in inhomogeneous systems [10, 11]. Particularly interesting is the high-angle portion of the scattered intensity of x-rays or neutrons. This part, governed by Porod's Law, contains information about variations in the electron density (x-ray scattering) or scattering-length density (neutron scattering) over small distances. Importantly, fluctuations across the water-oil interface...
contribute to the scattered intensity. Porod formulated a $1/q^4$ dependence of the scattering curve at high angles for a two-phase system with a sharp interface (vide Eq. 3) [12–14]. This behavior, however, is not observed in the x-ray scattering of the Aerosol OT-H$_2$O-isooctane micro-emulsion.

We shall consider here the origin of this deviation from Porod's Law and show that it can be explained using a model of a pseudo two-phase system, oil and water, with a diffuse interface formed by a monomolecular layer of surfactants. It is shown that quantitative information about the surfactant structure in the interface as a function of micro-emulsion concentration can be obtained from the experimental data.

**Theory**

X-rays are scattered at small angles by fluctuations in electron density of the medium. The fluctuations can be described using the distance correlation function [11, 15]

$$\gamma(r) = \langle \eta(x + r) \eta(x) \rangle / \eta^2$$

with $\eta(x) = \bar{\eta}(x) - \bar{\eta}$, where $\bar{\eta}(x)$ is the electron density at point $x$, and $\eta^2$ is the average of the squared electron density about some average value $\bar{\eta}$. For solutions and other centro-symmetric systems $\gamma(r)$ is a function of $r$ only. If no long-range order exists, $\gamma(r)$ will decay to zero for a large $r$. The scattered intensity, can then be given in terms of $\gamma(r)$ as

$$I(q) = I_e V \eta^2 \int 4 \pi r^2 \gamma(r) \frac{\sin(qr)}{qr} dr$$

with $q = 4\pi/\lambda \sin(\theta/2)$, $V$ the volume irradiated and

$$I_e = 7.9 \times 10^{-26} I_0 \frac{(\cos^2 \theta + 1)}{2 R_s^2}$$

where $I_0$ is the incident radiation intensity of wavelength $\lambda$, $R_s$ the sample to detector distance, and $\theta$ the scattering angle. $I_e V$ can be taken as arbitrarily equal to unity. We note that $qI(q)$ and $r\gamma(r)$ form a sine Fourier pair [10, 16].

Porod has derived an expression for $I(q)$ in the limit for large $q$, known as Porod's Law, for a system composed of two phases with a difference in electron density

$$I(q) = 4\pi \eta^2 \frac{S}{q^4}$$

with $S$ the total interface between phases. Equation (3) is, however, valid only for two-phase systems with an ideal interface at which the electron density changes discontinuously.

In the case of AOT micro-emulsions it is doubtful whether this condition is satisfied. The AOT surfactant is made up of an SO$_4$ headgroup attached to two hydrocarbon chains. These chains will have approximately the same electron density as iso-octane and therefore will not contribute to an electron density fluctuation. The sulfate polar headgroup however has a relatively high electron density compared with either water or iso-octane. There will thus be a strong variation in electron density across the oil-water interface over a distance of approximately 1–5 Å. Consequently we do not expect to find the $q^4$ decay of the scattering curve at high angles as described by Eq. (3) [17].

An expression for the scattered intensity at high $q$ can nevertheless be obtained for a general pseudo two-phase system. In this system arbitrarily shaped regions of electron densities $\rho_1$ and $\rho_2$ are separated by a small layer, $\delta$, of electron density $\rho_0$. The value of $\gamma(r)$ can now be calculated using Eq. (1) analogous to the way of Weigel et al. [18]. For a two-phase system with a radius of curvature, $R$, we find

$$\eta^2 \gamma(r) = a'r^3 - b'r + c' \quad \text{for} \quad r < \delta \quad (4a)$$

$$\eta^2 \gamma(r) = ar^3 - br + d + c' \quad \text{for} \quad \delta < r < 2R \quad (4b)$$

with

$$a' = \eta^2$$

$$b' = \frac{S}{4V} \left( (\rho_0 - \rho_2)^2 + (\rho_0 - \rho_1)^2 \right)$$

$$c' = \frac{S}{4V} \frac{(\rho_0 - \rho_2)^2 + (\rho_0 - \rho_1)^2}{12 R^2}$$

and

$$a = \eta^2$$

$$b = \frac{S}{4V} (\rho_2 - \rho_1)^2 \left( 1 + \frac{\rho_0 + \rho_2 - 2\rho_0}{R} \frac{(\rho_2 - \rho_1)^2}{4 R^2} \right)$$

$$c = \frac{S}{4V} \frac{(\rho_0 - \rho_2)^2 + (\rho_0 - \rho_1)^2}{12 R^2}$$

$$d = \frac{S}{4V} \frac{(\rho_0 - \rho_2)^2 + (\rho_0 - \rho_1)^2}{12 R^2}$$