NEUTRON SCATTERING CHARACTERIZATION OF HOMOPOLYMERS AND GRAFT-COPOLYMER MICELLES IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Supercritical fluids are becoming an attractive alternative to the liquid solvents traditionally used as polymerization media[1]. As the synthesis proceeds, a wide range of colloidal aggregates form, but there has hitherto been no way to measure such structures directly. We have applied small-angle neutron scattering (SANS) to characterize such systems, and although SCF polymerizations are carried out at high pressures, the penetrating power of the neutron beam means that typical cell windows are virtually transparent. Systems studied include molecules soluble in CO_2 (e.g. polyfluoro-octyl acrylate or PFOA) and this polymer has previously[2] been shown to exhibit a positive second virial coefficient (A_2). Other CO_2-soluble polymers include hexafluoro-polypropylene oxide (HFPPO), which appears to have a second virial coefficient which is close to zero ($10^4 A_2 \simeq 0 \pm 0.2$ cm^3 g^{-2} mol). Polydimethyl-siloxane (PDMS), is soluble on the molecular level only in the limit of dilute solution and seems to form aggregates as the concentration increases ($c > 0.01$ g cm^{-3}). Other polymers (e.g. polystyrene) are insoluble in CO_2, though polymerizations may be accomplished via the use of PS-PFOA blockcopolymer stabilizers, which are also amenable to SANS characterization, and have been shown[3] to form micelles in CO_2. Other amphiphilic surfactant molecules that form micelles include PFOA-polyethylene oxide (PFOA-PEO) graft copolymers, which swell as the CO_2 medium is saturated with water. These systems have been characterized by SANS, by taking advantage of the different contrast options afforded by substituting D_2O for H_2O. This paper illustrates the utility of SANS to measure molecular dimensions, thermodynamic variables, molecular weights, micelle structures etc. in supercritical CO_2.

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DISCLAIMER

INTRODUCTION

Supercritical CO_2 presents an environmentally benign medium for polymerizations which minimizes the production of organic solvent and aqueous waste and facilitates isolation of the polymer product[1,4-6]. However, only two classes of polymeric materials have been shown to exhibit appreciable solubility at readily accessible temperatures and pressures: amorphous fluoropolymers and silicones. Thus, the relative insolubility of many industrially important polymers in supercritical CO_2 necessitates the use of heterogeneous polymerization techniques which employ stabilizing moieties to synthesize high molecular weight hydrocarbon polymers. The first successful dispersion polymerization in supercritical CO_2 involved the stabilization of poly(methyl methacrylate) particles by the homopolymer poly(1,1-dihydroperfluorooctylacrylate) (PFOA)[5]. In order to allow the synthesis of other polymers which are relatively insoluble in CO_2 (e.g. polystyrene), diblock copolymers have been synthesized for use as emulsifying agents in heterogeneous polymerizations. Because of their amphiphilic character, these stabilizers form micelles[2], which promote the polymerization of styrene and give rise to spherical particles in quantitative yields (>90 percent) in CO_2.

Small angle neutron and x-ray scattering (SANS and SAXS) methods allow the elucidation of the size and shape of both single polymer chains and supramolecular structures[7], and over the past two decades, SANS has emerged as the most powerful technique for studying polymer phase behavior[8] and the self assembly of amphiphiles in aqueous media[9,10] in the resolution range 5-2000Å. The first experiments to apply these techniques to study polymers in supercritical CO_2 have recently been undertaken[2,3,11-13],

and in this publication we review some of the first SANS data that have been taken to probe CO_2-soluble polymers and also to characterize of the micellar structures formed by amphiphilic molecules.

EXPERIMENTAL

The experiments were performed on the W. C. Koehler 30m SANS facility at the Oak Ridge National Laboratory[14]. The incident wavelength was $\lambda = 4.75$Å ($\Delta\lambda/\lambda \sim 5\%$) and several sample-detector distances were used to give a range of momentum transfer, $0.005 < Q = 4\pi\lambda^{-1}\sin\Theta < 0.2$ Å^{-1}, where 2Θ is the angle of scatter. The procedures used to correct for detector efficiency, instrumental backgrounds are described elsewhere[14,15]. The neutron intensities were converted to an absolute ($\pm$ 3%) differential cross section per unit sample volume [$d\Sigma/d\Omega(Q)$, in units of cm^{-1}] by comparison with pre-calibrated secondary standards[15]. The cross section of the corresponding "blank" cell filled with CO_2 formed only a minor correction to the "sample" data. The CO_2 cross section [fig. (1)] results from density fluctuations near the critical point[16], and amounts to $\sim$ 0.04 cm^{-1}, at the lowest Q-values, with a slight angular dependence which reflects the size of the density fluctuations ($\sim$ 5-10 Å). The experiments were conducted in the same cell that has been used extensively for polymer synthesis[1,4,5], and due to the high penetrating power of neutrons, the beam passed through two 1 cm. sapphire windows, with virtually no attenuation (cell transmission $\simeq$ 93%) or parasitic scattering.

RESULTS AND DISCUSSION (1): CO_2-SOLUBLE POLYMERS

For a homogenous polymer solution the methodology to extract the R_g, the radius of gyration (i.e. the r.m.s. distance of scattering elements from the center of gravity) and

the second virial coefficient (A_2), which indicates whether a polymer chain swells or contracts in the presence of a solvent is well established[3,8,17]. These parameters are related to the cross section via

$$Kc\left[\frac{d\Sigma}{d\Omega}(0)\right]^{-1} = \frac{1}{M_w} + 2A_2 c \qquad (1)$$

where A_2 the second virial coefficient, M_w is the (weight-averaged) molecular weight (MW), c is the concentration (g cm^{-3}) and $K = [\Delta(SLD)]^2/\rho_p^2 A_o$ is the contrast factor for neutron scattering. A_0 is Avogadro's number, ρ_p is the polymer density and we have assumed initially that the volume from which CO_2 is excluded by a PFOA chain in the supercritical fluid is the same as the molecular volume in the solid state. The factor in square brackets is the scattering length density (SLD) difference between PFOA (SLD = 0.0336 x10^{12} cm^{-2} in the solid state) and CO_2 (SLD = 2.498ρ_{CO2} x10^{12} cm^{-2}), giving K = 7.5 x 10^{-5} mol cm^2 g^{-2} at T = 65°C and P = 340 bar. SANS has previously been used[3] to measure A_2 and MW in the ranges $0.6 < 10^4 A_2 < 0.25$ and $114 < 10^{-3}MW < 1000$. To our knowledge, small angle scattering is the only method currently available for molecular weight determination in supercritical fluids.

The polymer chain dimensions were derived from the measured cross sections using both the Zimm approach (for the low-Q data points) and also by fitting the data to a Debye random coil model[8]. Good agreement (± 5%) was achieved between the two approaches [fig. (2)], and as the pressure is reduced the solubility decreases. At T = 65° PFOA falls out of solution [fig. (3)] at the critical point (P = 4350 psi, or 296 bar) as indicated by a zero intercept on the ordinate [$d\Sigma/d\Omega(0) \rightarrow \infty$].

The values of R_g are a function of molecular weight and may be summarized as $R_g = (0.10 \pm 0.02)M_w^{0.5}$. The second virial coefficient decreases with molecular weight, as is generally observed for polymer solutions, where $A_2(M_w)$ is empirically described by $A_2 \sim M_w^{-\delta}$, with $\delta \simeq 0.3$ in various systems[18]. From the two data points shown in Table (1) the exponent is $\delta = 0.4$ for PFOA in supercritical CO_2, showing that the variation of A_2 with M_w is reasonable, as the error in δ is probably $\pm$ 0.1. These results indicate that transport of monomers or initiators to the inside of the PFOA chains or aggregates would occur more efficiently for the low molecular weight polymer, for which A_2 is larger and hence the chains are more swollen than for high MWs.

It has been demonstrated[4] that PFOA can be used as a surface active agent to synthesize polymers that are otherwise insoluble in CO_2 (e.g. polymethylmethacrylate) and hence it is important to understand how the addition of methylmethacrylate (MMA) monomer to the CO_2 solvent affects the solution properties of PFOA. Initial studies indicate that the addition of 20 vol% (liquid) MMA to CO_2 (at T = 65° and P = 340 bar) leads to a concentration of 12 mole %, which increases the second virial coefficient by $\sim$ 350%. The reason for this increase is not understood, as presumably, A_2 will decrease for higher concentrations of added MMA. Measurements are currently in progress to explore the effect of added monomer in more detail.

Fig. 4(a) shows a plot of $Kc[d\Sigma/d\Omega(0)]^{-1}$ vs c for hexafluoropropylene-oxide (HFPPO) or Krytox™ and the values of A_2 and M_w are compared to the equivalent quantities for PFOA in Table 1. The magnitude of M_w measured by SANS is in good agreement with the nominal MW given by the manufacturer (16k) and A_2 is zero within the experimental

error, indicating that the polymer coil adopts the unperturbed chain dimensions in CO_2. Fig. 4(b) [plotting $\log_{10}(R_g)$ vs. $\log_{10}(C)$], shows that the observed variation in R_g with concentration is systematic ($R_g \sim c^{0.16}$). For $0.02 < c < 0.093$, values of R_g are in the range 30-37Å, giving $R_g/M_w^{0.5} \sim 0.29$, compared to 0.45 for polyethylene, 0.39 for polyethylene oxide and 0.35 for polypropylene. Thus, the size of a molecule for a given molecular weight becomes smaller as the size of the pendant group increases. The reason for the concentration dependence of R_g is not understood at present.

For polydimethylsiloxane (PDMS) in CO_2, fig (5) shows $Kc[d\Sigma/d\Omega(0)]^{-1}$ vs. concentration at T = 65°C and P = 340 bar. Above $c \simeq 0.02$ g cm^{-3}, both $d\Sigma/d\Omega(0)$ and R_g increase disproportionately with concentration and similar behavior is exhibited at T = 40°C. For molecules of this size (MW $\simeq$ 13k), the intercept in fig. (3) should be $\sim$ 73, indicating that there may already be some aggregation except possibly in the limit of infinite dilution ($c < 0.01$ g cm^{-3}). In this event, the SANS data do not yield accurate values of A_2 or M_w.

Thus, for the three species of "CO_2-soluble" molecules studied, CO_2 appears to be either a "good" solvent (PFOA), a theta solvent (HFPPO) or a "poor" solvent (PDMS).

RESULTS AND DISCUSSION (2): GRAFT COPOLYMER MICELLES

The first study of aggregation mechanisms of copolymer micelles in CO_2 was undertaken by Fulton and coworkers[11] on water-swollen PFOA-polyethylene oxide (PFOA-g-PEO) graft copolymers using SAXS, which was fitted to a core-shell model with inner and outer radii of 105 and 125Å respectively. The data were recorded in arbitrary, as opposed to absolute, units and thus it is possible that this model may be

consistent with the **shape** of the data without reproducing the intensity[15,18]. We have therefore repeated these measurements via SANS using absolute units, and taken advantage of the contrast opportunities afforded by substituting D_2O for H_2O. It will be seen that this allows a more stringent test of the model dimensions, though fortunately it does not alter the overall conclusions of the previous study. We have also examined this material in the absence of added water to show that the micelle dimensions are much larger in the presence of H_2O swelling.

The synthesis of the PFOA-g-PEO material has been described elsewhere[11], and the PEO grafts had a MW $\simeq$ 5000, with 3-5 grafts per chain and a wt. fraction of PEO is in the range 15-18%. Thus, the overall MW is estimated to be in the range 100-160k. Fig. (6) shows the dramatic differences in the SANS data introduced by H_2O and D_2O swelling, as the radius of gyration increases from $\sim$ 56Å to $\sim$ 82Å (H_2O-swollen) and 136Å (D_2O-swollen).

The SANS data were modelled as described previously[9,10], and the micellar solutions are represented as a two phase system in which core-shell micelles interact in a solvent medium. For a collection of polydisperse particles, assuming no orientational correlations the coherent differential scattering cross section is given by

$$\frac{d\sigma}{d\Omega} = N_p \left[\langle |F(Q)|^2 \rangle + |\langle F(Q) \rangle|^2 (S(Q) - 1) \right] + B \qquad (2)$$

where N_p is the number density of particles, S(Q) is the structure function arising from interparticle scattering and B is the coherent background from CO_2 [fig. (1)]. For the dilute solutions (e.g. c < 2% w/v) considered here, interparticle interactions may be

neglected, and the interparticle structure function in this case is similar to that of a dilute monatomic gas ($S(Q) \simeq 1$).. Spherical particles with a centrosymmetric distribution of scattering length density may be modelled by a set of concentric spherical shells[9,10], and for a core/shell micelle the intraparticle term in Equation (2) may be expressed as,

$$\langle |F(Q)|^2 \rangle = \int |F(Q,R_1)|^2 f(R_1)\, dR_1 \tag{3}$$

Where R_1 is the radius of a core, which occurs within the distribution of core radii with a normalized frequency of $f(R_1)$. The structure function of a particle with core radius R_1 and outer radius R_2 is given by,

$$\begin{aligned} F(Q,R) &= \frac{4\pi}{3}\left[R_1^3(\rho_1-\rho_2)F_0(QR_1) + R_2^3(\rho_2-\rho_s)F_0(QR_2)\right] \\ F_0(x) &= \frac{3}{x^3}(\sin x - x\cos x) \end{aligned} \tag{4}$$

Several particle shapes were used to calculate P(Q), and the best fits were given by a spherical core-shell model with a Schultz distribution[9,10] of particle sizes

$$\begin{aligned} f(R_1) &= \frac{(Z+1)^{Z+1} X^Z \exp[-(Z+1)X]}{\overline{R_1}\,\Gamma(Z+1)} \\ Z &= \frac{1 - \left(\frac{\sigma}{\overline{R_1}}\right)^2}{\left(\frac{\sigma}{\overline{R_1}}\right)^2} \\ X &= \frac{R_1}{\overline{R_2}} \end{aligned} \tag{5}$$

where σ^2 is the variance of the distribution, Z is the breadth parameter and ρ_1, ρ_2 are the core/shell SLDs.

Figure (7) shows the fit to the SANS data, using the parameters derived from the initial

SAXS data[11]. It may be seen that the simulation differs from the SANS data by a substantial factor, thus illustrating the point made by Hayter and Penfold[18] that the cross section is extremely sensitive to the particle dimensions ($d\Sigma/d\Omega \sim R^6$), and that even an approximate calibration ($\pm$ 25%) is desirable to avoid such discrepancies. In principle, the SANS simulation should be different for the H_2O- and D_2O-swollen micelles. However, Fulton et al., gave no quantitative estimate as to the location of the aqueous species, and assumed that the core (the probable location of the absorbed water) had the bulk (unswollen) PEO density. We have therefore calculated the core SLD on this basis. Although the different isotopes would have had the same SAXS contrast, it may be seen that the SANS patterns are quite different [fig. (7)].

Figs. (8) and (9) show fits to the SANS data using core-shell model and changing only the contrast between the H_2O- and D_2O-swollen systems. The inner and outer radii are $\simeq$ 86Å and $\simeq$ 128Å respectively, with an aggregation number (i.e. the number of molecules per micelle) of $N_{agg} \simeq 83$, compared to $N_{agg} \simeq 120$ derived from the SAXS study, and $N_{agg} \simeq 3$ for the unswollen micelle. Thus, the basic overall picture remains the same as in the initial study, though the advantage of absolute calibration and the extra information provided by the contrast variation studies allows a more precise description of the system.

The SLDs for the core and shell respectively are 1.93 and 1.87 x 10^{10} cm^{-2} (for D_2O) and 1.50 and 2.17 x 10^{10} cm^{-2} (for H_2O-swollen micelles). These values may be compared with 2.12 and 0.7 and 3.36 x 10^{10} for CO_2, bulk PEO and PFOA respectively, indicating that there must be considerable mixing of the components in both regions.

The shell SLD is higher when the micelle is swollen by D_2O, indicating that water swells not only the core but also the shell, which must therefore be penetrated by PEO in addition to CO_2. The fact that the shell SLD is less for the D_2O- swollen micelle as compared to the equivalent H_2O-swollen system is puzzling, though the CO_2 solvent is saturated with water, and thus it is not certain that each sample has absorbed the same amount of fluid.

These comparisons indicate the extra information available from the combination of absolute calibration and isotopic labelling, though it is still insufficient to independently determine all the details of the micelle structure (partitioning of water/CO_2 between the core/shell etc.). It should be noted that the combination of absolute SAXS and SANS data, each highlighting different features of the system via the particular contrast factors, would provide an even more precise description of the system. We are currently exploring the possibility of combining these techniques on the same set of micelle-forming amphiphiles (e.g. polystyrene-PFOA blockcopolymers). These systems were described in an initial publication[2], and will also be the subject of future paper containing detailed model simulations.

ACKNOWLEDGEMENTS

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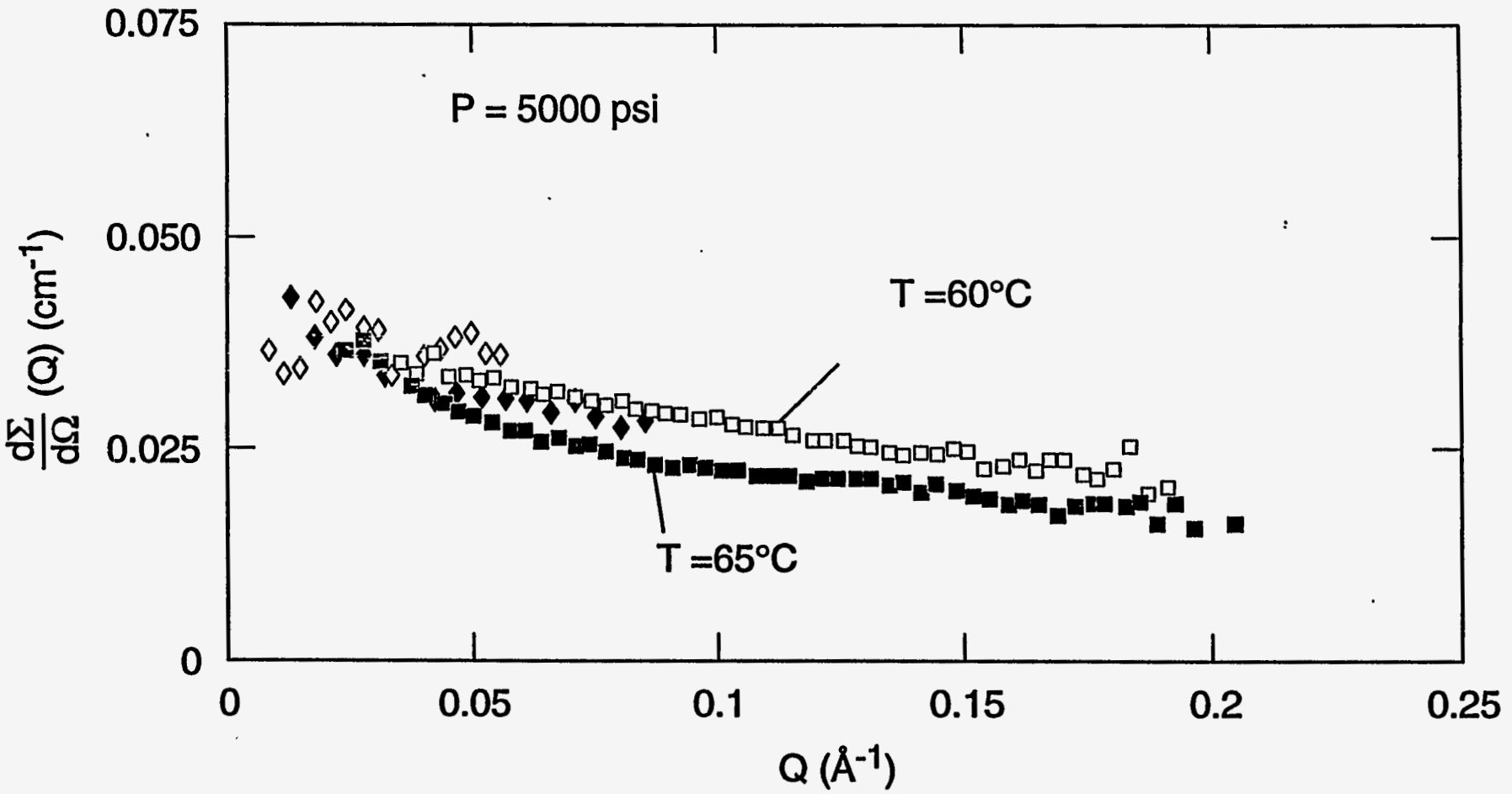
Polymer	10^{-3}M (g/mol)	10^4A_2 ($cm^3\ g^{-2}$ mol)	R_g (Å)	$R_g/M^{1/2}$ (Å $g^{-0.5}$)
HMW-PFOA	1000 ± 400	0.25 ± 0.05	100 ± 9	0.10 ± 0.02
LMW-PFOA	110 ± 20	0.6 ± 0.1	34 ± 5	0.10 ± 0.02
HFPPO	13 ±1	0.0 ± 0.2	30 - 37	

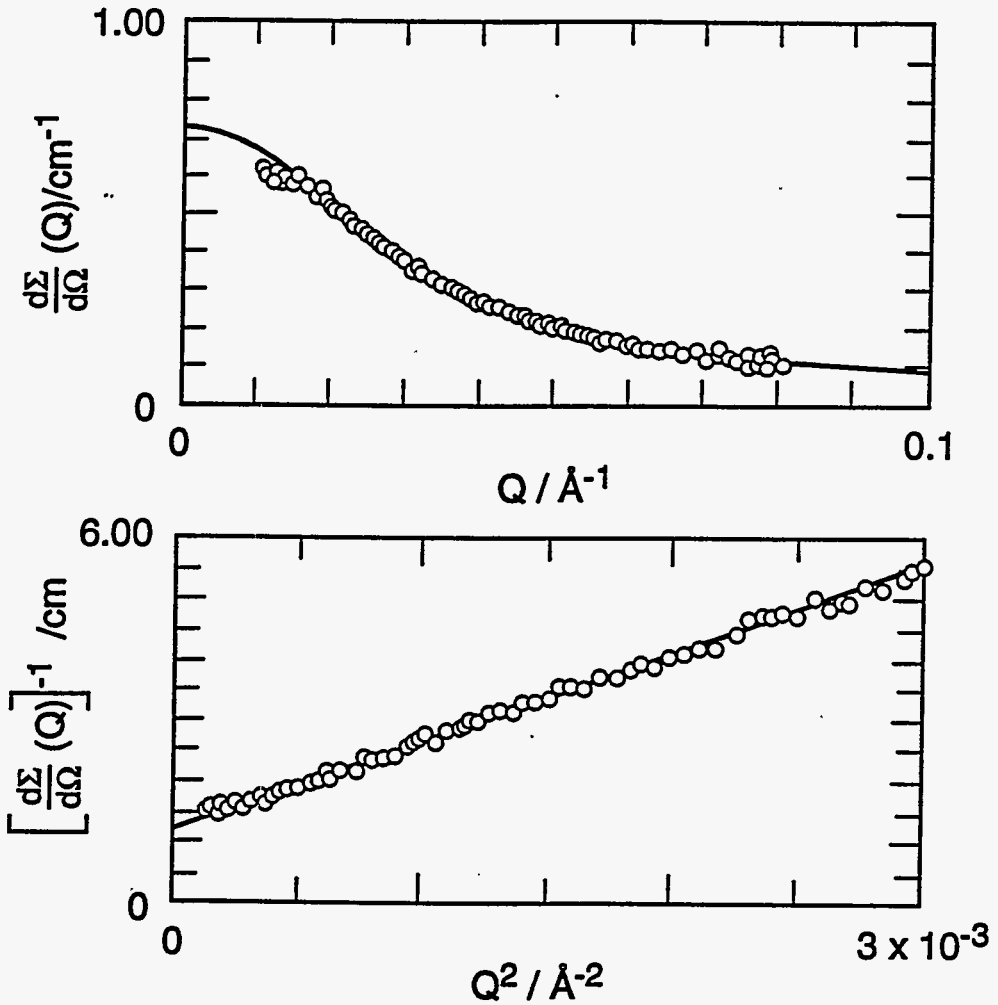
Table 1 - Molecular weight (M), second virial coefficient (A_2), radius of gyration (R_g), and $R_g/M^{1/2}$ for PFOA and fluorinated polypropylene oxides.

ORNL-DWG 95M-8407

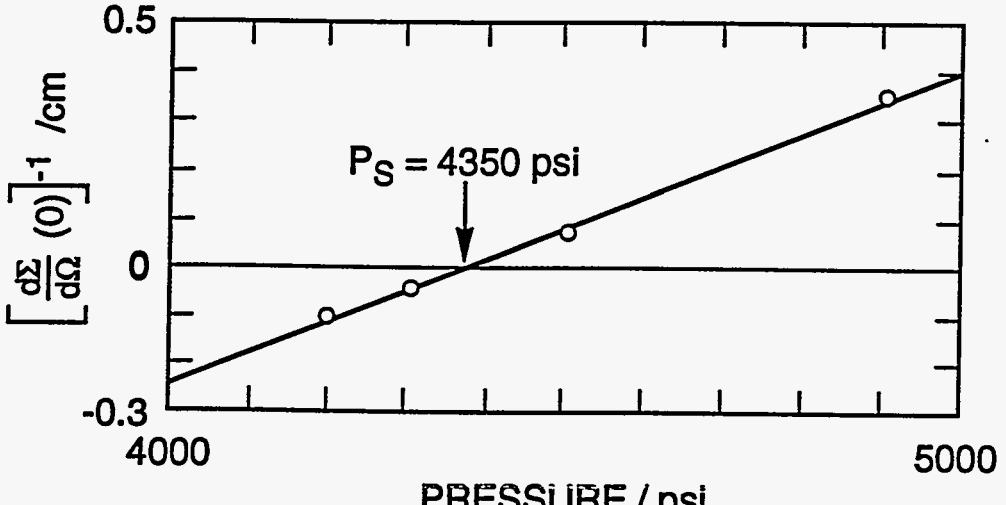


BACKGROUND SCATTERING FROM CO_2 BLANKS AT T = 60°C AND T = 65°C

PFOA in CO_2



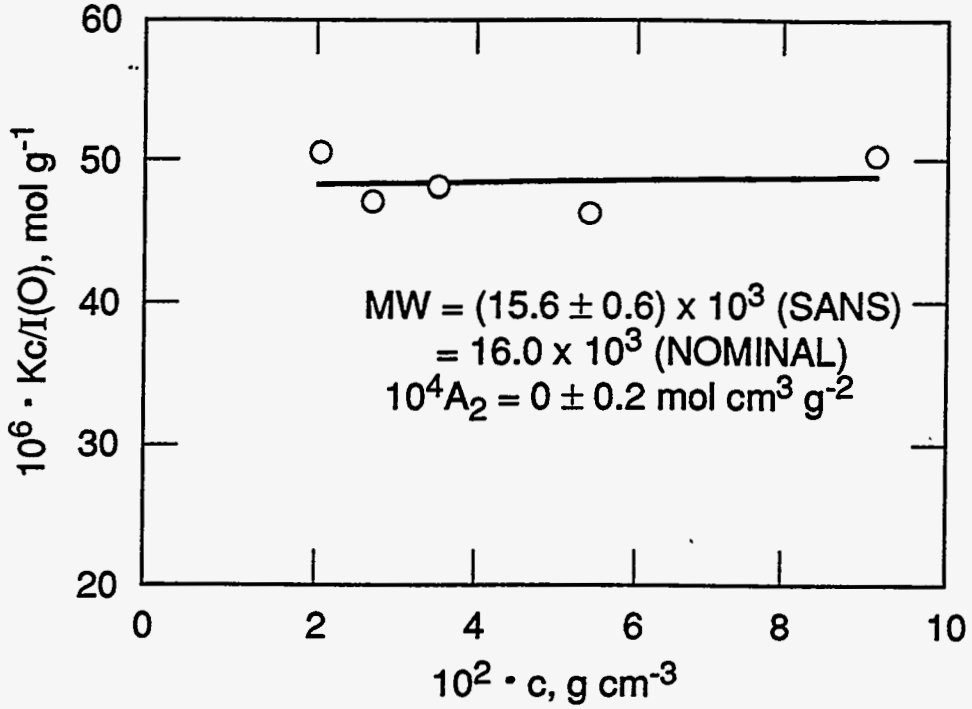
DEBYE AND ZIMM FITS TO SANS DATA. 10% (W/V) HIGH MOLECULAR WEIGHT POLYFLUOROOCTYL ACRYLATE IN SUPERCRITICAL CO_2



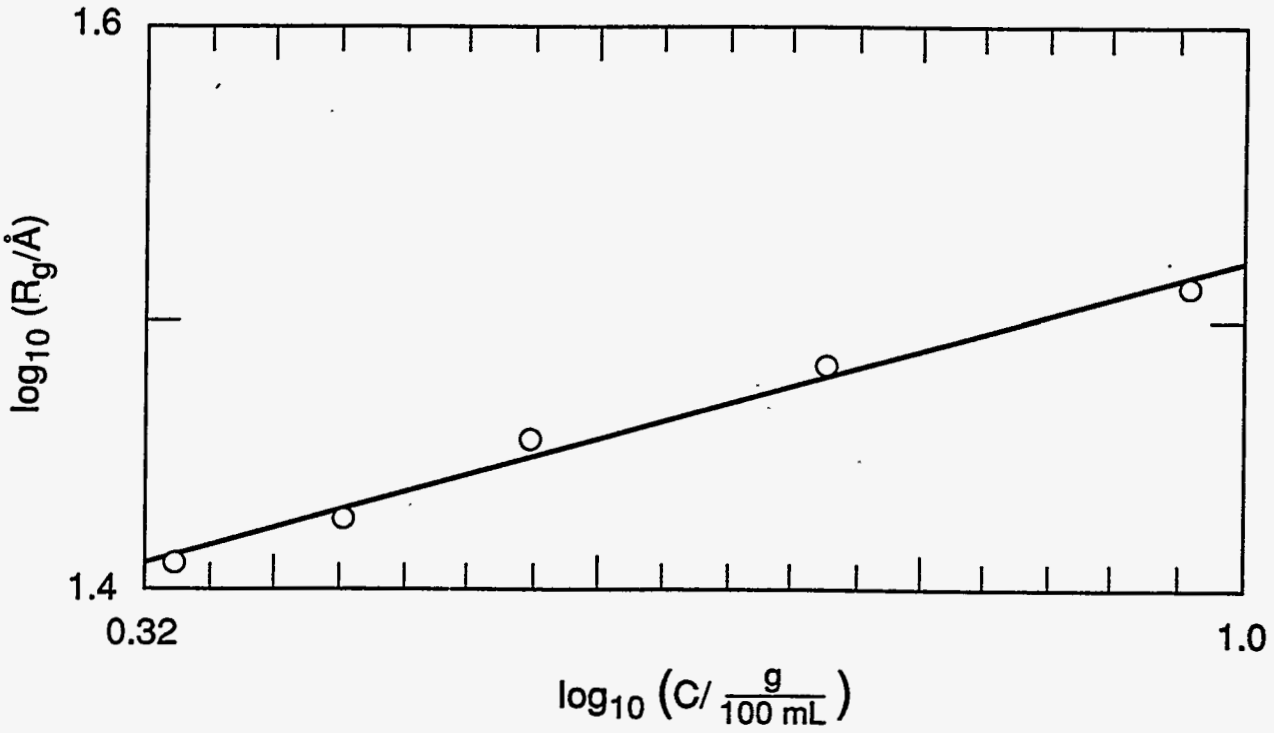
SOLUBILITY DETERMINATION USING SANS. 3% (W/V) POLYFLUOOCTYL ACRYLATE (PFOA) IN CO_2 AT 65°

FLUORINATED POLYPROPYLENE OXIDE ($C_3 F_6 O$) IN CO_2

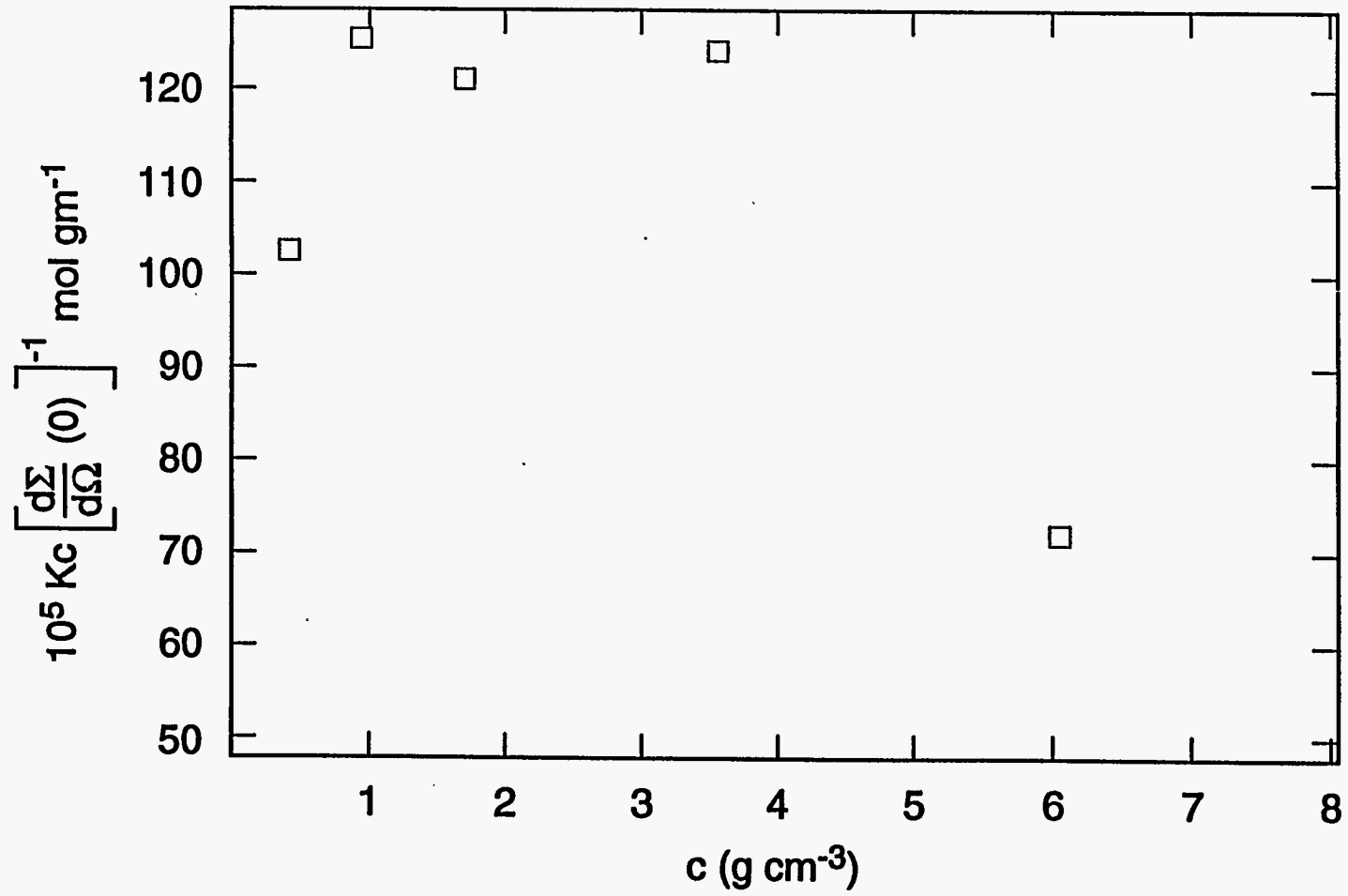
4 (a)



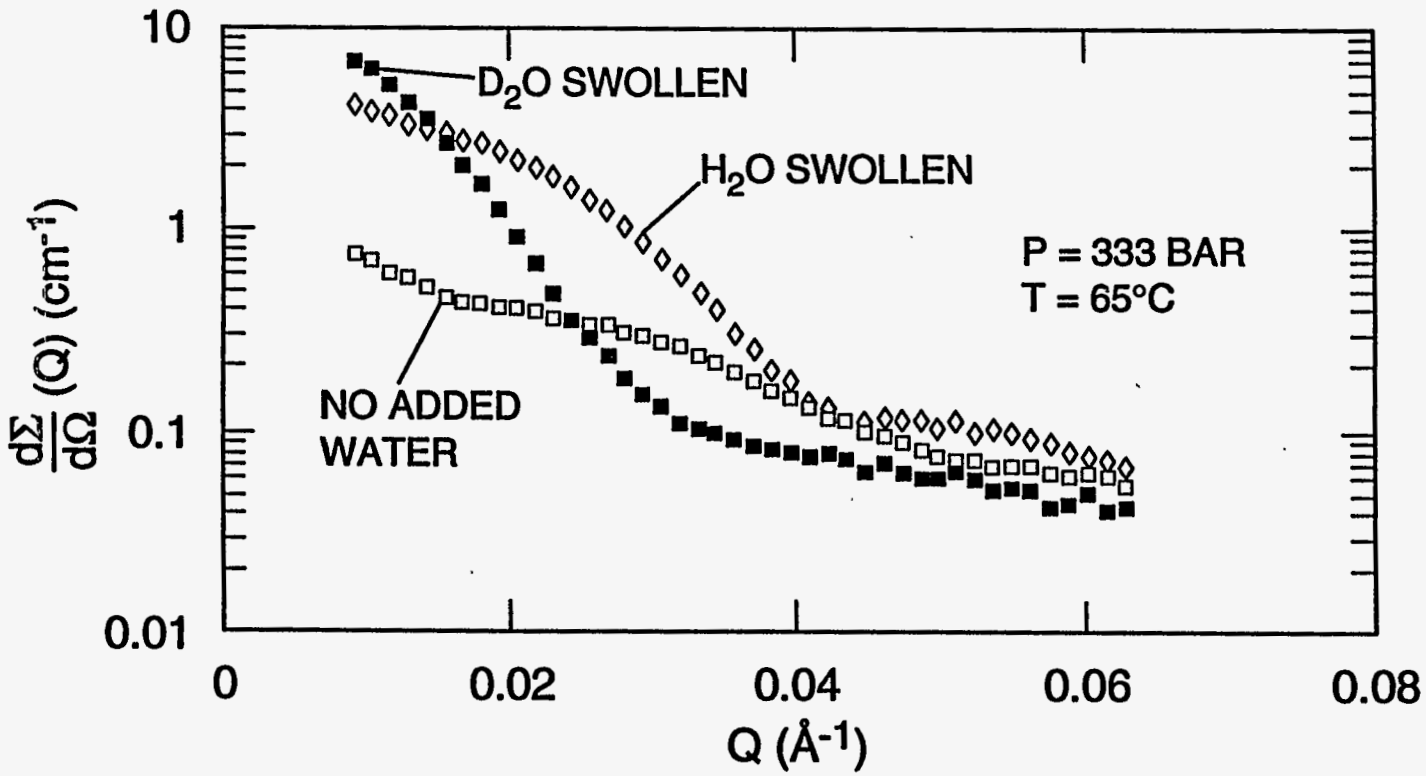
4 (b)



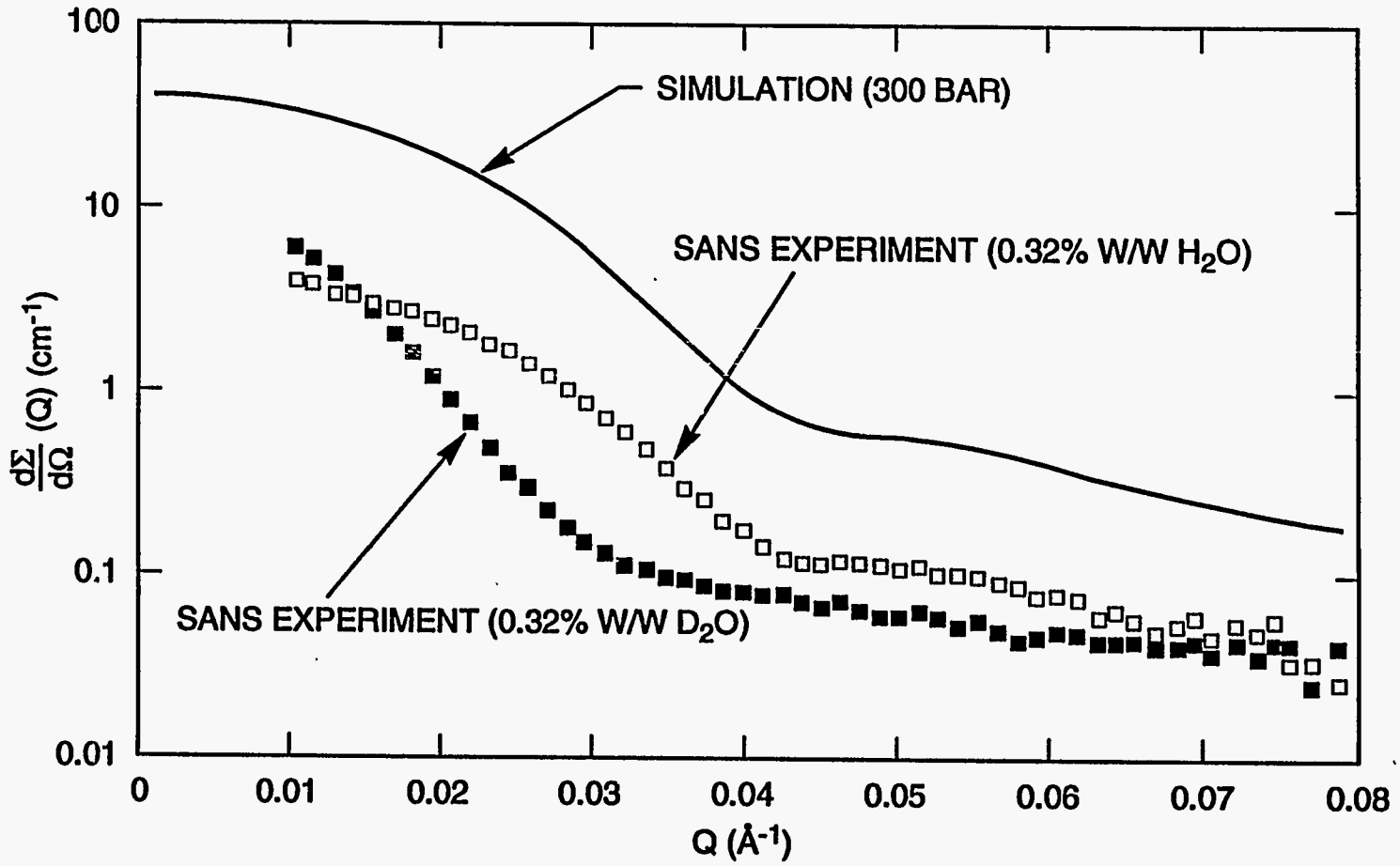
RADIUS OF GYRATION VARIES SYSTEMATICALLY WITH CONCENTRATION



INVERSE (Q = 0) CROSS SECTION AS A FUNCTION OF THE CONCENTRATION OF POLYDIMETHYLSILOXANE IN CO_2

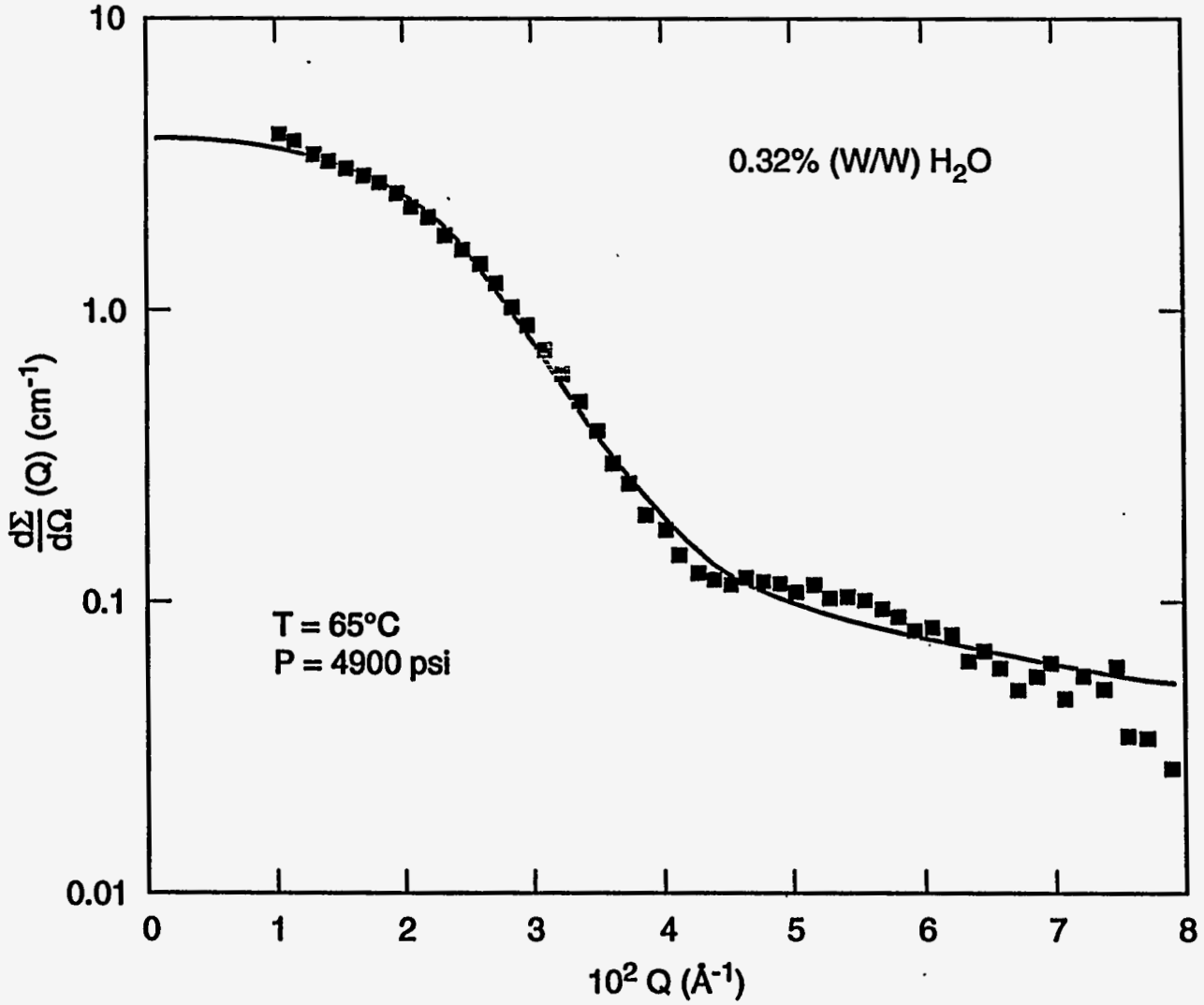


$\frac{d\Sigma}{d\Omega}$ (Q) FOR PFOA–g–PEO GRAFT COPOLYMER IN CO_2 BEFORE AND AFTER SWELLING WITH H_2O AND D_2O



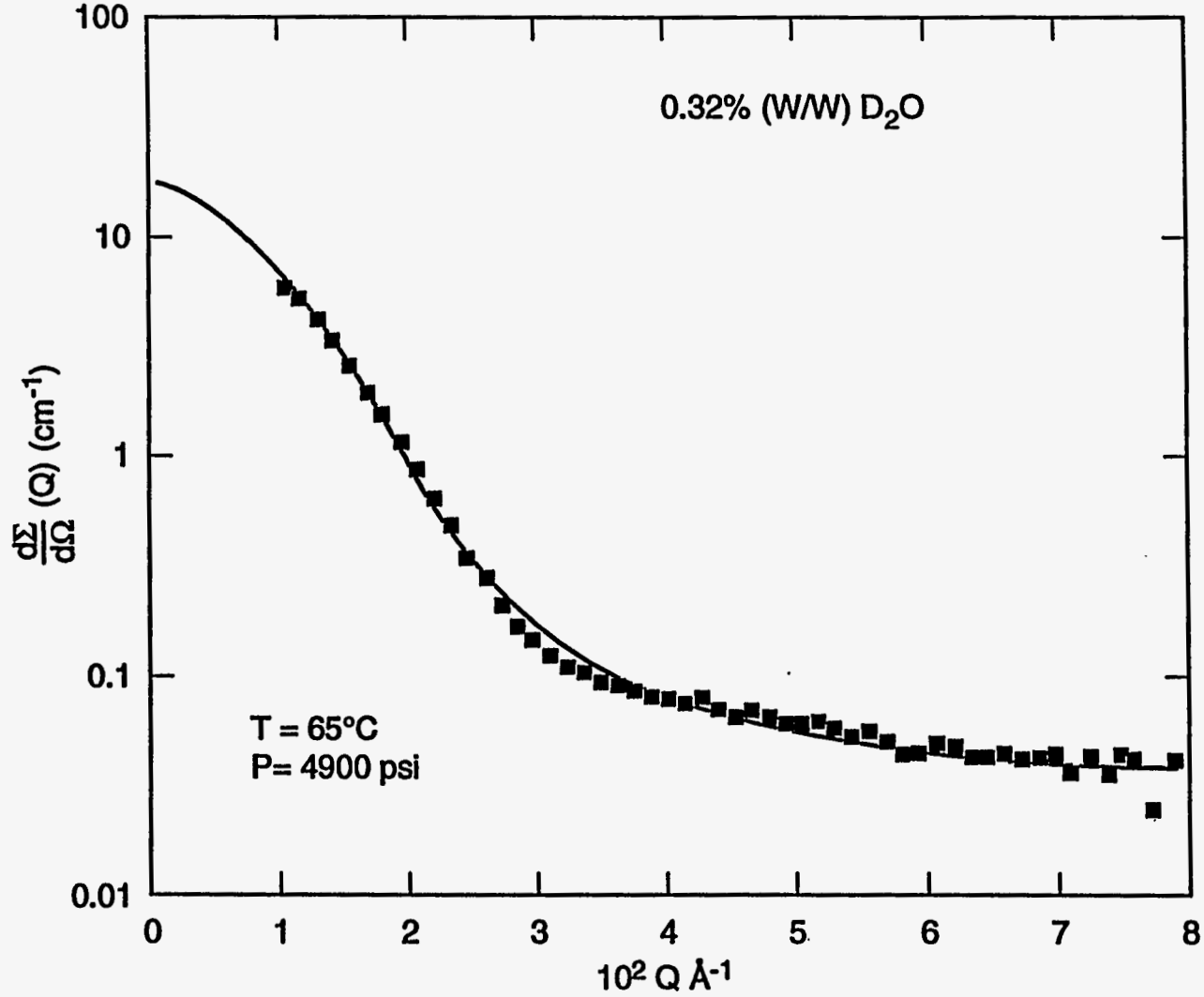
SANS DATA FOR 1.9% PEO–GRAFT COPOLYMER IN SUPERCRITICAL CO_2 (SATURATED WITH WATER) COMPARED TO SIMULATION USING PARAMETERS FROM FULTON *et al.*, LANGMUIR,1995

(2)



8

SANS DATA FROM 1.9% (W/V) PFOA–PEO GRAFT COPOLYMER IN H_2O–SATURATED SUPERCRITICAL CO_2 COMPARED TO POLYDISPERSE CORE–SHELL MODEL



SANS DATA FROM 1.9% (W/V) PFOA–PEO GRAFT COPOLYMER IN D_2O–SATURATED SUPERCRITICAL CO_2 COMPARED TO POLYDISPERSE CORE–SHELL MODEL