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CHARACTERIZATION OF FULLERENES AND FULLERENE DERIVATIVES BY SMALL-ANGLE NEUTRON SCATTERING AND TRANSMISSION MEASUREMENTS

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ABSTRACT

Small-angle neutron scattering (SANS) has been shown to be an appropriate technique for the structural characterization of fullerenes (1) in solvents with strong SANS contrast (e.g. CS_2) and we have extended initial studies of C_{60} (1) to include C_{70} and C_{84} moieties. Deuterated solvents (e.g. toluene-d_8) have a high scattering length density (SLD), which is close to that of C_{60}, so there is virtually no SANS contrast with the solvent. Hence, these particles are practically "invisible" in such media, though the negative scattering length of hydrogen means that SLD of H^1 -containing materials is much lower, so they have strong contrast with toluene-d_8. Thus, SANS makes it possible to study the size and shapes of modified buckyballs and this paper describes the first results on cyclohexane-substituted fullerenes.

INTRODUCTION

The fullerenes and related nanoclusters possess unusual properties which make them well-suited for a variety of applications. Since the development of methods for production of these carbon-cage molecules in quantity, there has been great interest in the structural characterization of fullerenes and fullerene-based materials. Small-angle neutron scattering (SANS) is a proven tool for examining the structure of particles in solution, although the dimensions of backyballs are close to the lower resolution limit of the technique. However, the technique has been successfuly applied to characterize fullerenes and flagellenes (1,2) and other phenomena amenable to SANS are aggregation or polymerization mechanisms. These phenomena can be easily detected and resolved as clustering of as few as two molecules would cause increase in intensity of scattering of $\geq$ 100%. Also of considerable interest is the hydrogenation and dehydrogenation of fullerenes (3) as well as their interaction with solvents, all of which can be effectively studied by small-angle scattering techniques.

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In this paper we apply SANS for determining the radius of gyration R_g of C_{60}, C_{70} and C_{84} moieties as well as cyclohexane-substituted fullerenes, produced by γ-radiolysis of C_{60}/cyclohexane solutions. We also analyze a possibility of using the neutron transmission as a complementary tool for detetrmining the number of attached hydrogenated molecules.

EXPERIMENTAL

Pure C_{60} (99 wt.%), C_{70} (98 wt.%), and C_{84} (99 wt.%) were obtained from Texas Fullerenes Inc., Houston, Texas. CS_2 was reagent grade (99.98%). Two nominal concentrations of approximately 5 and 8 mg/ml were prepared to check that particle dimensions were independent of the concentration and that the scattering cross section scaled linearly with the concentration. Seventy-five milligrams of each fullerene were added to 7.5 ml CS_2 and the sample was stirred and then placed in an ultrasound cleaning bath for an additional 5 min. The sample was removed, placed in separate eppendorfs, spun (8000 rpm) for 2 min, and carefully decanted and inserted in a 20 mm path length quartz cell, leaving the sediment behind. The actual concentrations of each sample were measured after scattering experiments.

C_{60}-C_6H_{12} complexes were prepared using "Gold Grade" C_{60} obtained from Hoechst. 19.8 mg of the fullerene were dissolved in 10 ml toluene and after the C_{60} dissolved, the solution was put into a flask through wich argon was flushed to evaporate the toluene. C_6H_{12} was purified and collected in a flask with the C_{60} of the total volume 550 ml. Argon was bubbled through the solution during 20 min and left in dark for ~ 40 hours. After setting, the solution was sonicated for ~ 10 seconds to dissolve some undissolved C_{60} . The solution was bubbled with argon and irradiated to 50 krad producing brown turbid solution that was left setting in dark for ~ 30 hours. The C_{60}-C_6H_{12} was distilled off the remainder while sweeping the distillation flask/condenser with argon. After the volume was reduced to ~ 20 ml, the dark brown solution was transferred to the weighed vial in aliquots and evaporated to near dryness using argon and heating to ~ 60 ^{o}C. Three solutions of C_{60}-C_6H_{12} in toluene-d_8 (6.87, 3.38, and 2.61 mg/ml) were prepared and inserted in a 5 mm path length quartz cells. After scattering measurements, the cell with the solution of highest concentration was kept in dark at room temperature for ~ 3 month. After a lapse of time we obesrved gradual formation of a stable precipitant due to aggregation of C_{60}-C_6H_{12} complexes into a big particles. We repeated the scattering measurements for this solution after the aging.

The experiments were performed on the W. C. Koehler 30 m SANS facility at the Oak Ridge National Laboratory. The neutron wavelength λ was 4.75 Å ($\Delta\lambda/\lambda$ ~ 5%) and the beam was transported to a chosen source-sample distance (SSD) by means of moveable neutron guides. The SSD was 1.5 m for solutions of fullerenes in CS_2 and either 3.5 m or 7.5 m for solutions of C_{60}-C_6H_{12} complexes in toluene-d_8. The sample-detector distances were 1.55 m, 2.6 m, and 14 m, respectively. The area detector was a

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64x64 cm^2 proportional counter with element size ~ 1 cm^2. The data were corrected on a cell-by-cell basis for the detector efficiency and instrumental and solvent backgrounds prior to radial averaging over the appropriate range of the momentum transfer $Q=4\pi\lambda^{-1}\sin\Theta$, where 2Θ is the scattering angle. The net intensities were converted to an absolute (±4%) differential cross section per unit solid angle per unit sample volume [I(Q) in units of cm^{-1}] by comparison with precalibrated secondary standards (4).

The transmission of samples was measured in a separate experiment (5) by collimating the beam with slits (irises) ~ 1 cm in diameter, separated by a distance ~ 7.5 m. A strongly scattering sample, porous carbon, was placed at the sample position to spread the beam over the detector, placed at a sample-detector distance ~ 10 m. The total count summed over the whole detector ($>10^5$) was recorded in a time period ~ 1 min and the sample being measured was placed over the source slit, thus attenuating the beam. The count was repeated over the same time interval and the transmission T is given by the ratio of the two counts after minor correction (<0.1%) for the beam-blocked background due to electronic noise, cosmic rays, etc. All measurements were performed at room temperature (23 $^{\circ}$ C) and typical values of the transmission were $T_O \cong 0.95$, $T \cong 0.8$, and $T \cong 0.7$ for the empty quartz cell, 20 mm path cell with fullerene solutions, and 5 mm path cell with fullerene complex solutions, respectively.

RESULTS AND DISCUSSION

Solutions of C_{60}, C_{74}, and C_{84} in CS_2

In general, the differential scattering cross section I(Q) is given by

$$I(Q) = I(0)\, P(Q) \quad , \tag{1}$$

where P(Q) is the form factor describing the shape of the scattering entity [P(0)=1]. For independently scattering non-interacting particles (e.g. dilute solutions of buckyballs), the experimental scattering functions can be analyzed using the Guinier approximation(6):

$$I(Q) = I(0) \exp\left[-\frac{(Q^2 R_g^2)}{3}\right] \tag{2}$$

to extract I(0) and the radius of gyration (R_g). It should be emphasized that Eq.(2) is an approximation, which is only exact in the limit $Q \Rightarrow 0$. Thus for finite Q, the magnitude of R_g obtained may depend on the Q range covered in the experiment.

R_g can be extracted from the scattering function with higher accuracy if the shape (and thus the form factor) of the scattering object is known exactly. Analysis of the atomic coordinates shows that C_{60} can be modeled by a spherical shell of the vanishingly small thickness of the order of the dimensions of the carbon nuclei. The form factor of spherical shell is given by: (7,8):

$$P(Q) = \left(\frac{\sin QR_g}{QR_g} \right)^2 \quad . \qquad (3)$$

Hollow cages of C_{70} and C_{84} are slightly distorted, though we believe that the spherical shell model (SSM) remains a good approximation as the difference between the biggest D_{max} and the smallest D_{min} dimension of the buckyballs (9) is not large: $D_{min}/D_{max} \cong 0.9$.

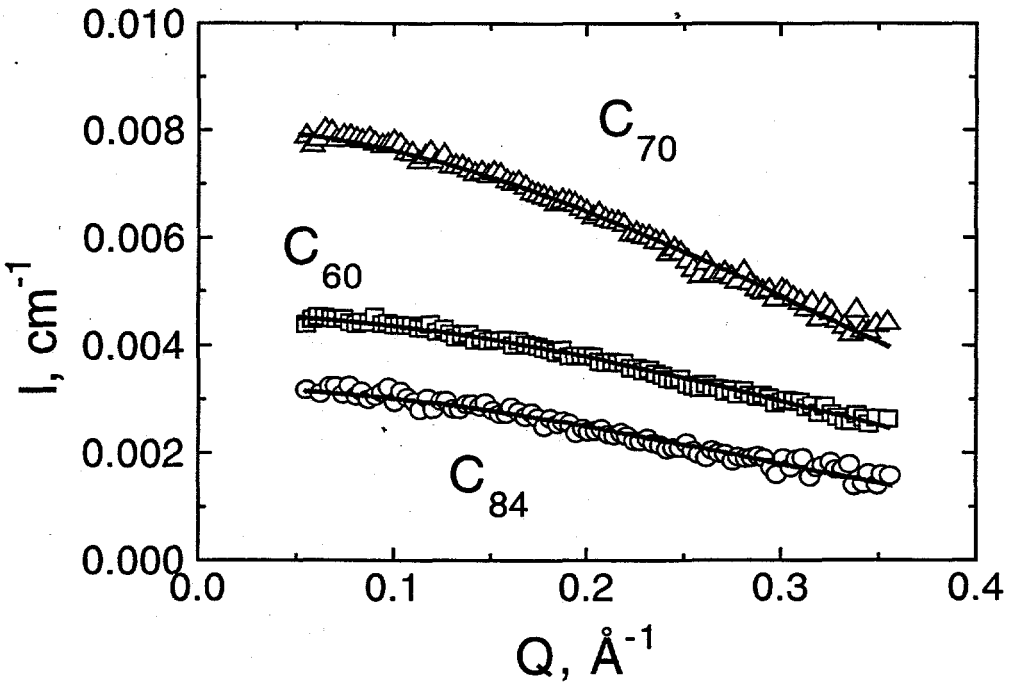

Figure 1. The scattering functions for solutions of C_{60} (5.45 mg/ml), C_{70} (7.59 mg/ml) (1), and C_{84} (2.67 mg/ml)in CS_2. Solid lines correspond to the nonlinear regression fits using the structure factor for a spherical shell (Eqs.1 and 3).

Figure 1 shows the representative scattering functions for C_{60}, C_{70}, and C_{84} in CS_2. The data obtained were processed in two different ways: a) by fitting functions I(Q) by the form factor of SSM (Eq.3) over the range of $0.05 < Q < 0.36$ Å^{-1} , and b) using the Guinier law (Eq.2) over the range of Q which satisfied the condition $Q_{max}R_g<1$. In the latter case, the cutoff values of Q_{max}=0.282, 0.258, and 0.351 Å^{-1} for C_{60}, C_{70}, and C_{84}, respectively were calculated for each fullerene using R_g determined from atomic coordinates (Table I). Å, (7)]

Table I. R_g of C_{60}, C_{70}, and C_{84} obtained experimentally via spherical shell model (SSM) and Guinier (G). Results of the calculation via the atomic coordinates (9) are also shown.

	C_{60} 7.75 mg/ml		C_{60} 5.45 mg/ml		C_{70} 7.59 mg/ml		C_{70} 4.78 mg/ml		C_{84} 2.67 mg/ml	
	SSM	G	SSM	G	SSM	G	SSM	G	SSM	G
R_g (Å), exp	3.64	3.80	3.71	3.85	3.94	4.14	3.91	4.10	4.27	4.68
R_g (Å), calc	3.54_6				3.86_5				4.19_5	

The average values of the radius of gyration obtained via SSM are $R_g = 3.67 \pm 0.05$ Å (C_{60}), $R_g = 3.92 \pm 0.05$ Å (C_{70}), and $R_g = 4.27 \pm 0.06$ Å (C_{84}), where the error represents the sum of statistical and systematic errors. The experimental radii of gyration for C_{70} and C_{84} are in good agreement with the calculated numbers within the experimental errors (Table I). For C_{60} our measured R_g is ~ 3.5% higher than R_g calculated from the atomic co-ordinates though it agrees well with results of Spooner et al. [R_g=3.57±0.016 Å (7)] who used material from the same source. Thus, the discrepancy may be caused by contamination of this particular sample studied by higher order derivatives, as Gripon et al. measured a value of R_g=3.52±0.04 Å (8) for C_{60} in CS_2 and this result is in almost exact agreement with the radius calculated from the atomic coordinates [Table(I)].

As is seen in Table I, values of R_g obtained via Guinier law exceed systematically those being extracted by applying the model approach. To analyze the reason for the discrepancy, we calculated the scattering functions for C_{60} and C_{84} using the SSM [$I_{SSM}(Q)$, Eq.3] and the Guinier law [$I_G(Q)$, Eq.2] (see Fig. 2). The values of parameters used were I(0)=1, R_g=3.546 Å for C_{60}, and R_g=4.195 Å for C_{84}. Analysis shows that the relative deviation of I_G from I_{SSM} for both fullerenes exceeds 5% at $QR_g = 1$. Thus, interpolating the SSM (Eq.3) by the Guinier law (Eq.2) at $QR_g \leq 1$ gives should lead to overestimated values for R_g (10) which is really observed in the experiment (Table I).

Processing the scattering functions using Eqs.1,2,3 implies the absence of particle - solvent and/or particle - particle interactions which would otherwise introduce an extra concentration dependent term into Eq.(1) and give rise to a finite second virial coefficient A_2 (11). As is known, the value of A_2 can be determined using Zimm equation (12)

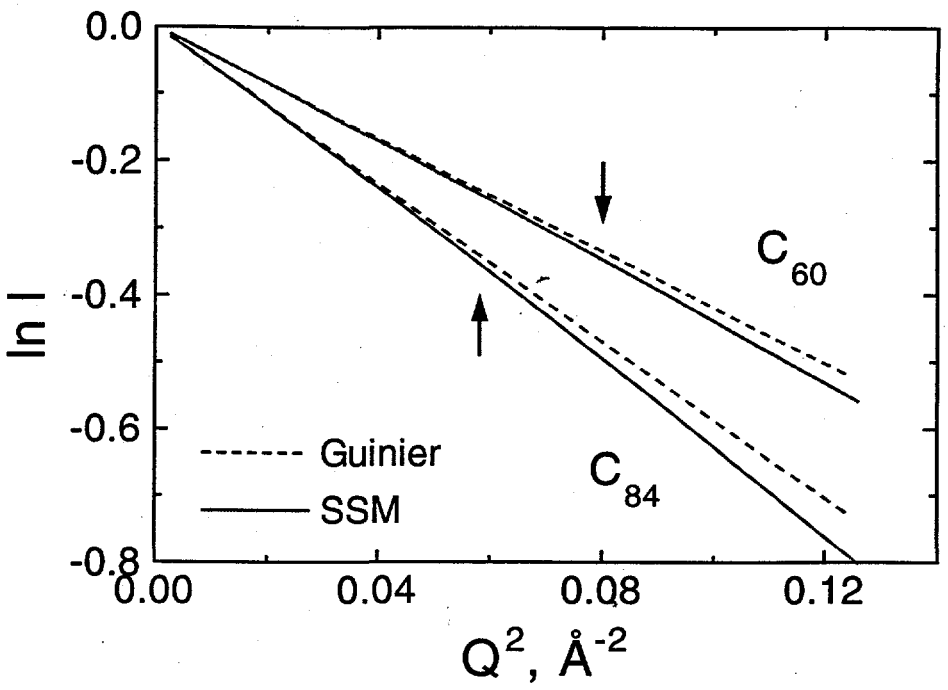

Figure 2. Simulated scattering functions for C_{60} and C_{84} in Guinier coordinates. Dashed and solid lines correspond to Guinier law and the SSM, respectively. Arrows show the $QR_g=1$ limit for each fullerene.

which in the limit of $Q \Rightarrow 0$ can be reduced to:

$$I(0) = \frac{KC}{\frac{1}{M} + 2A_2C} \quad , \tag{4}$$

where K is a constant composed of instrumental parameters and other factors, C and M are the concentration and the molecular weight of scattering objects, respectively. To obtain the value of A_2, we investigated the variation of I(0) with the concentration of C_{60} in CS_2 in a separate experiment using successive diluting of the initial solution with C~5.5 mg/ml down to ~0.5 mg/ml. The results are shown in Figure 2. As is seen, whithin experimental errors the value of A_2 is equal to zero which supports the assumption (1,9) that particle - solvent interactions in diluted solutions of fullerenes in CS_2 may be neglected to a good approximation.

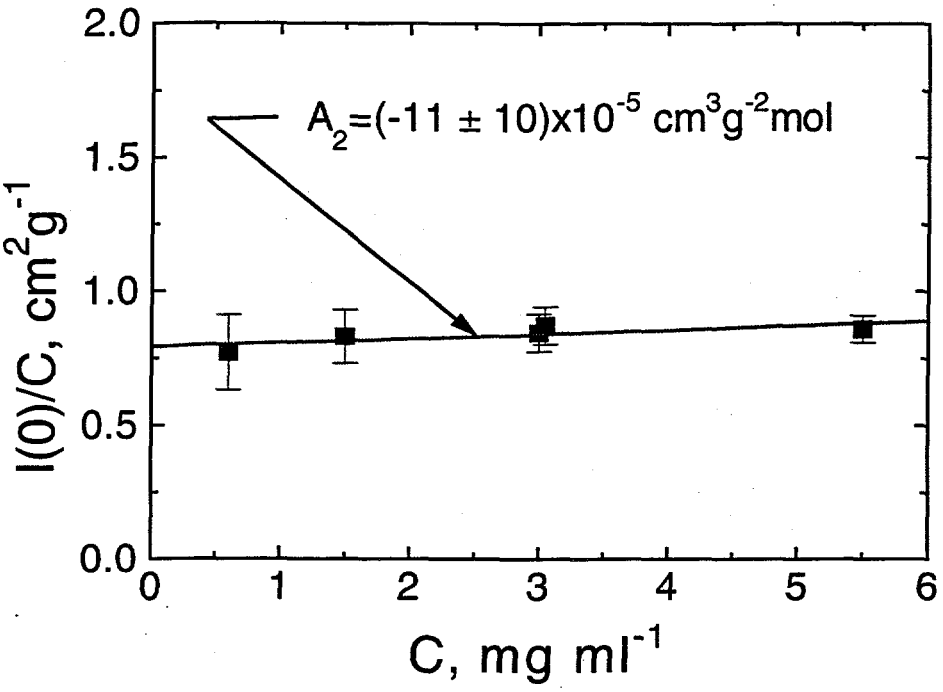

Figure 3. I(0)/C vs. the concentration of C_{60} in CS_2. The slope of the straight line gives the value of the second virial coefficient (see Eq.4) which is shown in the Figure.

C_{60} - cyclohexane complexes

Previous ion mobility, mass specrometry and small-angle X-ray scattering studies have suggested that the γ-radiolysis of C_{60} dissolved in organic solvents can generate a radical addition to the fullerenes and/or dimerization products (13,14). Specifically, the γ-radiolysis products of C_{60} in cyclohexane most likely form cyclohexyl adducts $C_{60}/(C_6H_{12})_X$ with X≅10 (14). Figure 4 shows the scattering functions obtained for three solutions of $C_{60}/(C_6H_{12})_X$ in d-toluene in the Guinier representation. As is seen, within experimental errors all scattering intensities normalized to the concentration of the solute fall onto a single curve which is indicative of negligible interparticle interactions. Thus, each of the I(Q) functions can be used for independent evaluation of R_g. Applying Guinier law (Eq. 2) gives an average $R_g \cong 11.7$ Å which exceeds the radius of gyration $R_g \cong 7.2$ Å calculated

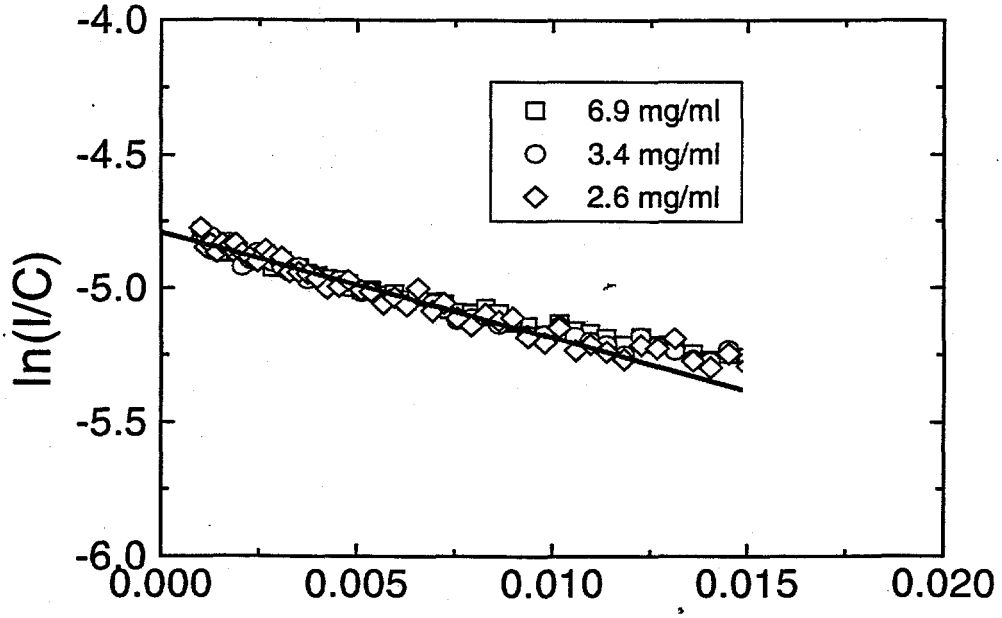

Figure 4. Scattering functions of solutions of $C_{60}/(C_6H_{12})_X$ in d-toluene at different concentration C of the complex. A slope of the solid line corresponds to R_g=11.7 Å.

(9) from the atomic coordinates of the monomer for the [$C_{60}/(C_6H_{12})_X$, X=10] model suggested in (14). The difference between calculated and measured R_g can be attributed to dimerization of a portion of the $C_{60}/(C_6H_{12})_X$ units. The degree of dimerization can be evaluated from weighed contribution into zero angle intensity of scattering from monomers and dimers of $C_{60}/(C_6H_{12})_X$ which gives the mole ratio of dimer to monomer ~0.3. The latter number is in good agreement with the result of small-angle X-ray scattering (≈0.33) (14). The distribution of the cyclohexyl adducts on the monomer and dimer species as extracted from SANS experiments represents a seprate important problem and we plan to explore this issue in more detail in a future publication.

Number X of cyclohexyl adducts per C_{60} can also be estimated from independent measurements of the neutron transmission vs. the concentration of $C_{60}/(C_6H_{12})_X$. As is seen in Fig.5, in good agreement with theoretical calculations (15), natural logarithm of the transmission of the solution is proportional to the concentration of the solute expressed in weight fraction of $C_{60}/(C_6H_{12})_X$. For a set of blank d-toluene and three solutions of $C_{60}/(C_6H_{12})_X$ of known concentration and transmission one can write (15):

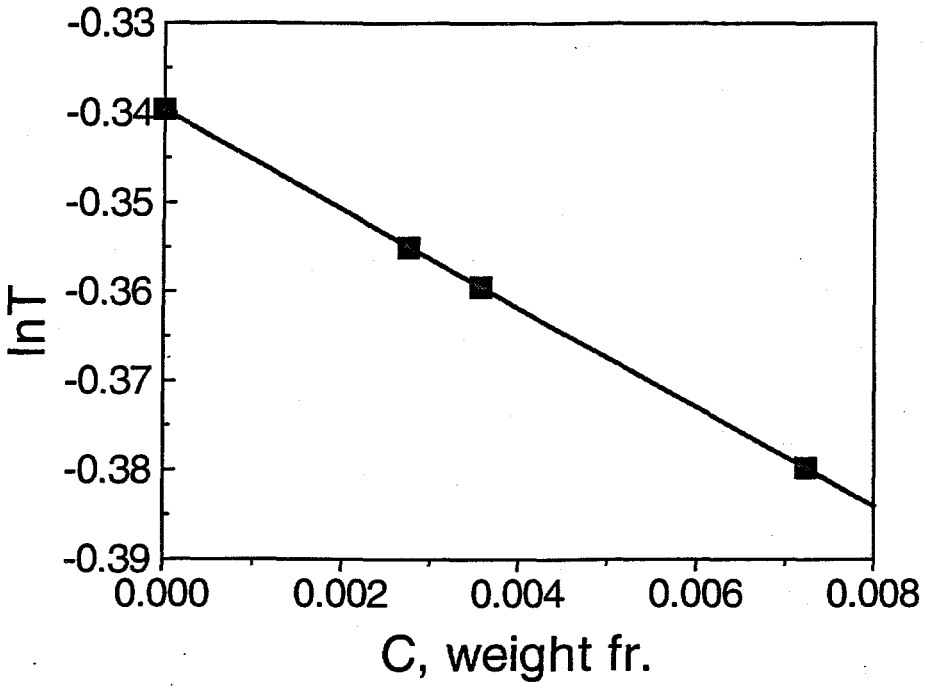

Figure 5. Natural logarithm of the neutron transmission of solutions of $C_{60}/(C_6H_{12})_X$ in d-toluene as a function of the weight concentration of the solute. The intersect with y- axe corresponds to the transmission of the empty quartz cell $\ln T_O$

$$\ln T_0 = -N_0\sigma_0 L = -0.3397$$
$$\ln T_1 = -N_0\sigma_0 L - N_1 L\left(\sigma_{C_{60}} + X\sigma_{C_6H_{12}}\right) = -0.3798$$
$$\ln T_2 = -N_0\sigma_0 L - N_2 L\left(\sigma_{C_{60}} + X\sigma_{C_6H_{12}}\right) = -0.3592 \qquad (5)$$
$$\ln T_3 = -N_0\sigma_0 L - N_3 L\left(\sigma_{C_{60}} + X\sigma_{C_6H_{12}}\right) = -0.3552$$

where T_i and N_i are the transmission and the number density of the $C_{60}/(C_6H_{12})_X$ complex in the i-th solution, respectively; $\sigma_{C_{60}}, \sigma_{C_6H_{12}}$ are the total neutron crossection of C_{60} and cyclohexane, respectively; L is the thickness of the solution. Using Eq.(5) and taking σ of carbon $\cong 5.51\times10^{-24}$ cm^2 (16) and σ of hydrogen $\cong 91\times10^{-24}$ cm^2 (17), one

arrives at the average value of cyclohexane molecules per buckyball equal to X≅12. The estimated number of C_6H_{12} adducts is in a reasonable agreement with the estimate of X≅10 reported in (14). The 20% discrepancy may be associated with possible dissociation of $C_{60}/(C_6H_{12})_X$ groups. Evidently, dissociated molecules of cyclohexane will contribute into the total transmission of the solution, however they will not give rise to small-angle neutron scattering from the solution.

CONCLUSIONS

1. SANS can resolve fullerenes in solution with as few as 60 atoms (1). Larger particles (dimers, flagellenes) are progressively easier to study.
2. Different features of the structure can be highlighted by varying the particle-solvent contrast. SANS is well suited to locate light atoms (e.g. hydrogen, pendant polymer chains); SAXS is well suited to locate heavy atoms (e.g. metal-carbon clusters).
3. The Q=0 cross section I(0) is a function of the number of adducts, so SANS can be used to assess the number of cyclohexane molecules (10-12) which are attached to the fullerene "shpere".

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