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1 – The SANS Technique

The NIST Center For Neutron Research
Small-Angle Neutron Scattering

\[ Q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \]

\[ \text{scattering angle} \]

Monochromatic Neutron Beam

Incident Beam

Source Aperture

Sample Aperture

Monochromation

Collimation

Scattering

Detection

Nanoscale Structures

Length Scale (Å)

Scattering Variable Q (Å⁻¹)

Polymers

Complex Fluids

Biology

USANS

SANS
SANS Cross Sections

\[ I(Q) = \frac{d\Sigma_{\text{coh}}(Q)}{d\Omega} + \frac{d\Sigma_{\text{incoh}}}{d\Omega} \]

COHERENT

\sim \text{ Contrast factor} = (\rho_A - \rho_B)^2

- Info. about structure

INCOHERENT

- Q-independent
- no info. about structure

Scattering length density: \( \rho_A = \frac{b_A}{v_A} = \frac{\text{scattering length}}{\text{volume}} \)

The Contrast Match Method

Finite contrast  Zero contrast

Multiple contrasts  Contrast match
2 – SANS Data Analysis

SANS Data Analysis

- Standard Plots (Guinier Plot, Porod Plot)
- SANS Models
- Inverse Fourier Transform
- Shape Reconstruction Method
### Guinier-Porod Regions

- **Cylinder with** $R_g^2 = 100 \, \text{Å}$ and $R_g^1 = 10 \, \text{Å}$
- **Scattering Variable** $Q (\text{Å}^{-1})$
- **Form Factor** $P(Q)$
- **Guinier Region**
  - $1/Q^0$
- **Intermediate-Q Guinier Region**
  - $1/Q^1$
- **Porod Region**
  - $1/Q^4$

### Guinier Plots
- Slope yields $R_g^2 = \frac{1}{12} \sum \frac{R_i^2}{2}$

### SANS Models

- **Macromolecules**
  - Form Factor $P(Q)$
  - Structure Factor $S_i(Q)$
- **Particles**
  - Form Factor $P(Q)$
  - Structure Factor $S_i(Q)$

**Random Phase Approximation**

\[
\frac{d\Sigma(Q)}{d\Omega} = \phi_A (\rho_A - \rho_B)^2 V_A P(Q) S_i(Q)
\]
Particle Structure Factor – The Ornstein-Zernike Equation

\[ \frac{d\Sigma(Q)}{d\Omega} = \phi_A (\rho_A - \rho_B)^2 V_A P(Q) S_I(Q) \]

Form Factor \( P(Q) \)

Structure Factor \( S_I(Q) \)

Fourier Transform

Density-density correlation function:

\[ P(Q) = \frac{\langle n(-Q)n(Q) \rangle}{n^2} = \frac{1}{V_P} \int \int \frac{n(r)n(r')}{n^2} \exp[-i\mathbf{Q} \cdot (\mathbf{r} - \mathbf{r}')] \]

Fourier transform:

\[ P(Q) = \int d^3r \exp[-i\mathbf{Q} \cdot \mathbf{r}] P(r) = \frac{1}{V_P} \int_0^\infty dr \int_0^\infty r'^3 \sin(Qr)' P(r) \frac{\sin(Qr)}{Qr} \]

Radial pair correlation function:

\[ P(r) = 1 - \frac{3}{4} \left( \frac{r}{R} \right) + \frac{1}{16} \left( \frac{r}{R} \right)^3 \]
3. SANS Research Topics

A- Phase Transitions in Pluronic P85 Solutions

B- Role of Chirality in Peptide Biogels

C- Structure of SDS Micelles
Pluronics

Dissolved Unimer (low temperature)

Formed Micelle (high temperature)

PEO
PPO

EO: CH₂CH₂-O-
PO: CH(CH₃)CH₂-O-

P85: EO₂₆PO₄₀EO₂₆

Pluronics Micelles

0.5 % P85 in d-Water

Scattering Intensity (cm⁻¹)

0.5 % P85 in d-Water

Scattering Variable Q (Å⁻¹)

0.01 0.1

1/Q⁴
1/Q⁵
1/Q⁶
1/Q⁷

spherical micelles
lamellar micelles
cylindrical micelles
unimers
Phase Diagram

Guinier Factor

Temperature (°C)

Core-Shell Spherical Particles Model

\[
\frac{d\Sigma(Q)}{d\Omega} = \frac{N}{V} \left[ (\rho_A - \rho_B) V_A \left( \frac{3 j_l(Q R_A)}{Q R_A} \right) + (\rho_B - \rho_C) V_{A+B} \left( \frac{3 j_l(Q R_B)}{Q R_B} \right) \right]^2 |

10% P85 Pluronic/D2O, 40 °C

Fits yield

\[
\rho_c = 6.4 \times 10^6 \text{ Å}^2
\]

\[
\rho_B = 5.9 \times 10^6 \text{ Å}^2
\]

\[
\rho_A = 1.7 \times 10^6 \text{ Å}^2
\]
Core-Shell Spherical Particles

Material Balance Equations:

\[
\frac{4\pi}{3} R_A^3 = N_{agA}[40v_{PPO} + 52f.v_{EO} + 52.f.v_{D_2O}.y_A]
\]

\[
\frac{4\pi}{3}(R_B - R_A)^3 = N_{agB}[52.(1-f).v_{EO} + 52.(1-f).v_{D_2O}.y_B]
\]

\[
\rho_A = \frac{N_{agA}[40v_{PPO} + 52.b_{EO}.f + 52.b_{D_2O}.f.y_A]}{\frac{4\pi}{3}R_A^3}
\]

\[
\rho_B = \frac{N_{agB}[52.b_{EO}.(1-f) + 52.b_{D_2O}.(1-f).y_B]}{\frac{4\pi}{3}(R_B - R_A)^3}
\]

Results for 10% P85 at 40 °C:

In the core:
- 2,795 PPO monomers
- 690 PEO monomers
- 490 D₂O molecules

In the shell:
- 2,943 PEO monomers
- 34,167 D₂O molecules

B- Role of Chirality in Peptide Biogels
**Faraday Rotation**

Substances rotate linearly polarized light to the left (L-type) or to the right (D-type).

**Chirality**

- A molecule is chiral if it is different from its mirror image.

- Human hands are chiral.

- Non-biological substances are heterochiral. They can be of the L-type or D-type.

- Biological substances are homochiral. They are either of the L-type or of the D-type.

- Proteins are of the L-type. Sugars are of the D-type. DNA is of the D-type.

The reason is still a mystery.
Proteins

- **Proteins** are responsible for most **biological function**. They are made out of **peptides**. Peptides are made out of **amino acids**. There are 20 amino acids.

- **Examples** of **amino acids** include Lysine (K), Glutamate (E), Tryptophan (W) and Alanine (A)

- **Most proteins rotate polarized light to the left**. They are left handed or **L-type**

DNA

- **DNA** is the blueprint for life. It is the **template for the synthesis of proteins**

- **DNA** is made out of **nucleotides**. There are 4 DNA nucleotides: A, C, T and G

- The **human genome** contains 6 billion nucleotides making up some 23,000 genes

- **Most DNA rotate polarized light to the right**. They are right handed or **D-type**

Peptide Biogels

- **Peptides** can be **synthesized to be L-type or D-type**

- **Series of L-type and D-type short peptide sequences** (11 amino acids) were synthesized.

- These were **combined** to give **L-D- or D-L- heterochiral mixtures** and **L-L- or D-D- homochiral mixtures**

- **The resulting gels** were **investigated** using **mechanical testing** (shear response) and **SANS measurements**
- Heterochiral samples gel faster. Homochiral samples are slow to gel.

- Homochiral gels are initially weaker then become stronger

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- Heterochiral gels scatter differently from homochiral ones

- They are all characterized by fibrilar structure
SANS Data Analysis

A

Heterochiral

\[ D-K/E \]
Fiber 50 Å
Web 18 Å
90 Å
D-K/D-E
Fiber 70 Å
Web 20 Å
160 Å

Homochiral

\[ L-K/D/E \]
Fiber 50 Å
Web 18 Å
90 Å
L-K/L-E
Fiber 70 Å
Web 20 Å
160 Å

Shape Reconstruction
Fiber cross sections

In reverse Fourier Transform

- Homochiral fibers are thicker and denser than heterochiral ones

Fiber-Web Structure

- Peptide biogel is formed of fibers joined by a web
Results

- Chirality plays a role in the mechanical properties and structure of biogels

- Homochirality confers higher strength (shear modulus) and yield stress value. **Right-right hand-shake is stronger.**

- Heterochirality confers faster gelation kinetics

- Biogel structure consists of main fibers held together by a web of cross fibers

- Fibers for homochiral biogels are thicker and denser

- Advantages conferred to homochirality lead to enhanced stability

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C- Structure of SDS Micelles
Micelle Formation

- Surfactants are formed of a hydrophilic head and a hydrophobic tail

- Micelles form when enough surfactants aggregate (above the critical micelle concentration or CMC)

- SDS surfactants form micelles in water (or deuterated water)

SANS from SDS Micelles

- Ellipsoidal micelles form
Ellipsoid Micelles Model Fit

\[ I(Q) = \frac{A}{Q^6} + \left[ \frac{d\Sigma(Q)}{d\Omega} \right]_{\text{ellipsoids}} + B \]

\[ \left[ \frac{d\Sigma(Q)}{d\Omega} \right]_{\text{ellipsoids}} = \phi \rho^2 V_r P(Q) S_r(Q) \]

- Power law (low-Q) + ellipsoidal micelles (high-Q) model fits well

Some Fit Results

- Micelles become smaller at higher temperatures and lower volume fraction
More Fit Results

- Salt addition affects lateral growth only

Material Balance Equations

- SDS surfactant fraction remains constant above the CMC
Phase Diagram

- SDS/water phase diagram from calorimetry

4. Final Points
Upgrade and VSANS

SANS, VSANS and USANS Ranges

4% PEO/d-Ethanol, 
$M_w = 42,900$ g/mole, $T = 25^\circ C$
SANS and USANS Data

Crosslinked CTVB Micelles

Scattered Intensity (cm$^{-1}$) vs. $Q$ (Å$^{-1}$)

- Red line: gel with no excess oil
- Blue line: gel with excess octane
- Black line: gel with excess toluene

Final Words

THE SANS PROGRAM AT NIST

200 experiments per year
15 theses per year
80 publications per year

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REFERENCES


http://www.ncnr.nist.gov/staff/hammouda/