Analysis of Small-Angle Scattering data from Colloidal Systems

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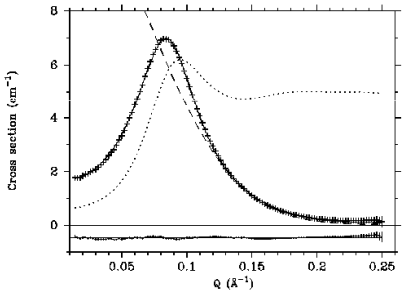
Julian Eastoe

Timescales (approximate)

idea

submit proposal

experiment



data analysis


Using Small-Angle Neutron Scattering to Study the Solution Conformation of *N*-(2-Hydroxypropyl)methacrylamide Copolymer−Doxorubicin Conjugates

submit paper

-6 months

8 months

18 months

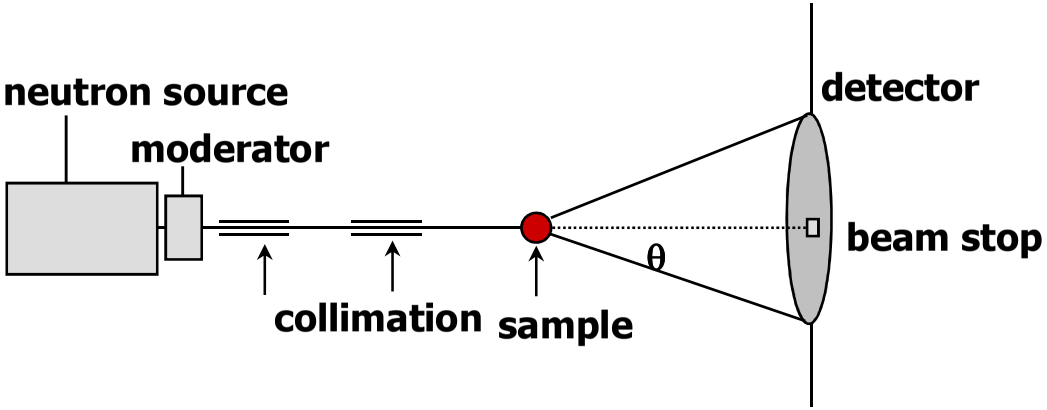
2 hours

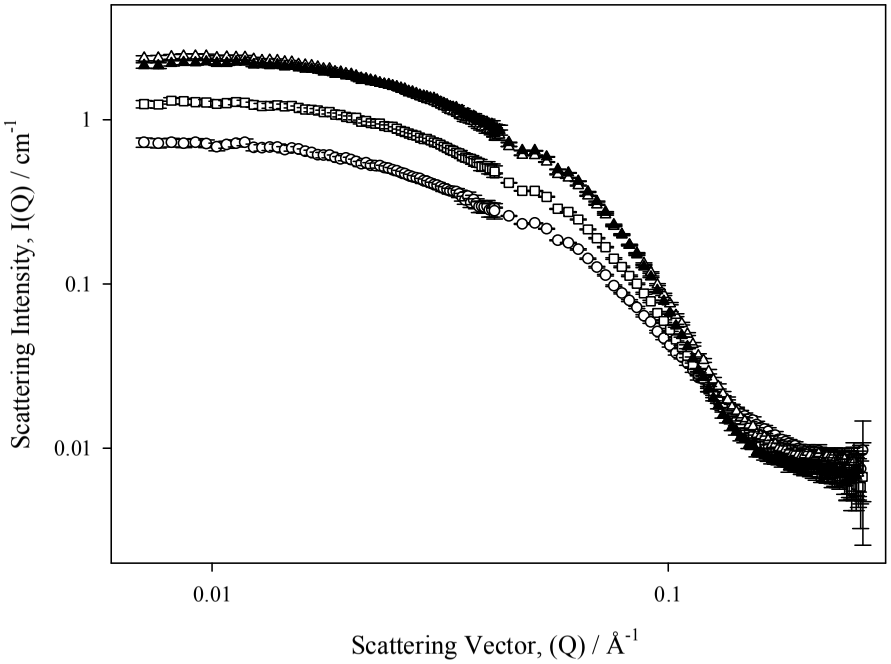
12 months

1 week

12 months

The easy bit…





LOQ Thu 8-MAY-2003 15:16 SAMPLE: 87752
EMPTY CAN: 87704 used /FLAT

Wav 2.20 > 10.00 Phi -90.0 > 90.0 Rad
38.0 > 419.0 Scaled* 0.975

122 0 0 0 1 122 0

0 0 0 0

3 (F12.5,2E16.6)

0.00700	1.298338E+00	2.832919E-01
0.00900	6.851087E-01	1.003761E-01
0.01100	5.462403E-01	5.673788E-02
0.01300	5.679009E-01	3.706261E-02
0.01500	5.380163E-01	2.699525E-02
0.01700	5.929618E-01	2.190137E-02
0.01900	6.539880E-01	1.881858E-02
0.02100	7.608917E-01	1.753074E-02
0.02300	8.432806E-01	1.670633E-02
0.02500	9.049114E-01	1.589828E-02
0.02700	9.514409E-01	1.538287E-02
0.02900	9.493540E-01	1.467021E-02
0.03100	9.125873E-01	1.392836E-02
0.03300	8.765299E-01	1.326172E-02
0.03500	8.499228E-01	1.272917E-02
0.03700	8.080100E-01	1.206244E-02
0.03900	7.885970E-01	1.161463E-02
0.04100	7.665921E-01	1.119541E-02
0.04300	7.416576E-01	1.081008E-02
0.04500	7.134403E-01	1.042103E-02

Approximations – Q dependence

$$I(Q) = A\, V_p\, N_p^2\, (\Delta\rho)^2\, P(Q)\, S(Q) + B_{inc}$$

$$I(Q) \propto P(Q)$$

form factor

structure factor

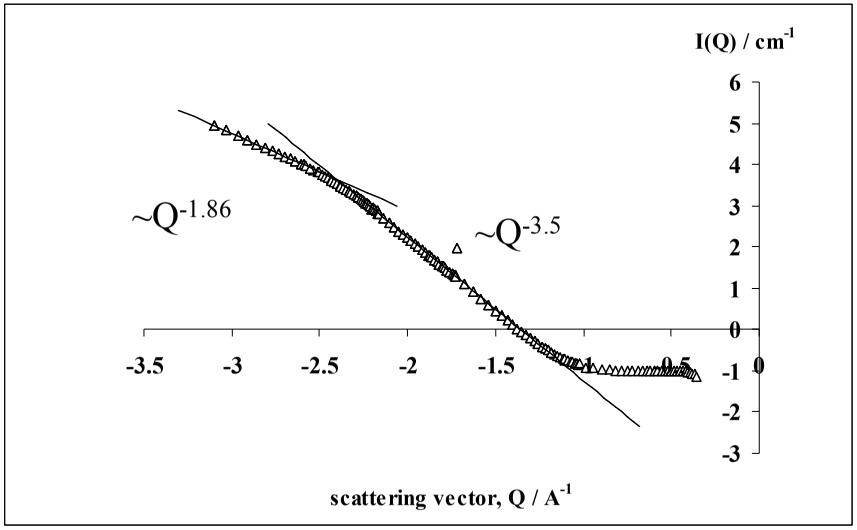
Q^0 = *spheres*

Q^{-1} = *rods*

Q^{-2} = *linear Gaussian chain*

Q^{-3} = *fractal surface*

Q^{-4} = *smooth interface*



Approximations – Guinier Plots

$$I(Q) \approx \phi_p \Delta\rho^2 V_p \exp\left(-\frac{Q^2 R_g^2}{3}\right)$$

$$P(Q,R) = 1 - \frac{Q^2 R_g^2}{3}$$

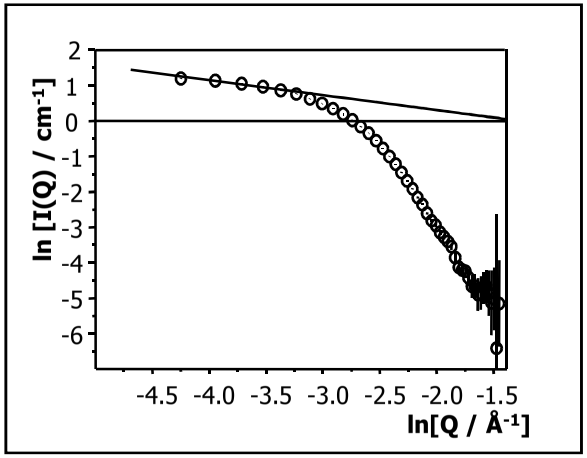
$$I(Q) \propto Q^{-D} \exp\left(-\frac{Q^2 R^2}{K}\right)$$

from the single particle form factor for dilute non-interacting spheres

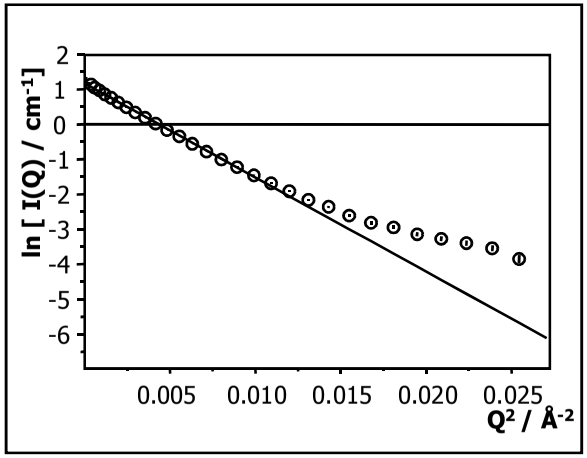
Rg relates to particle shape

- $\ln[I(Q)\cdot Q]$ vs. Q^2: cylinder radius $= \sqrt{\text{slope} \times 4}$
- $\ln[I(Q)\cdot Q^2]$ vs. Q^2: disk thickness $= \sqrt{\text{slope} \times 2}$
- $\ln[I(Q)]$ vs. Q^2 ($QR < 1$): sphere radius $= \sqrt{\text{slope} \times 5}$

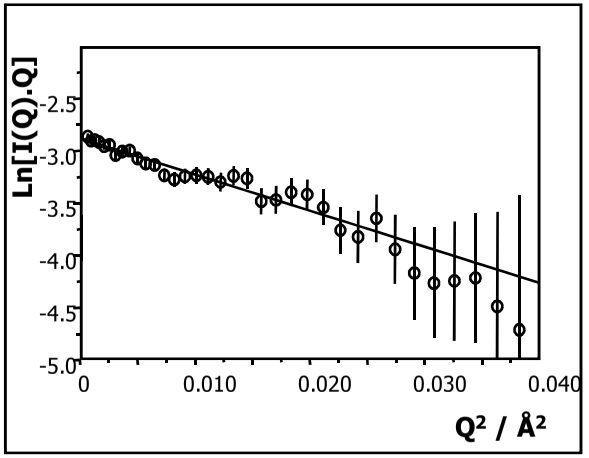
ln I (Q) vs Q



spheres = ln I (Q) vs Q²



cylinders = ln [I(Q).Q] vs Q²



Approximations – Porod plots

$$I(Q) = 2\pi\Delta\rho^2\left(\frac{S}{V}\right)Q^{-4}$$

At high Q values I(Q) is not sensitive to overall particle size, but to scattering from local interfaces

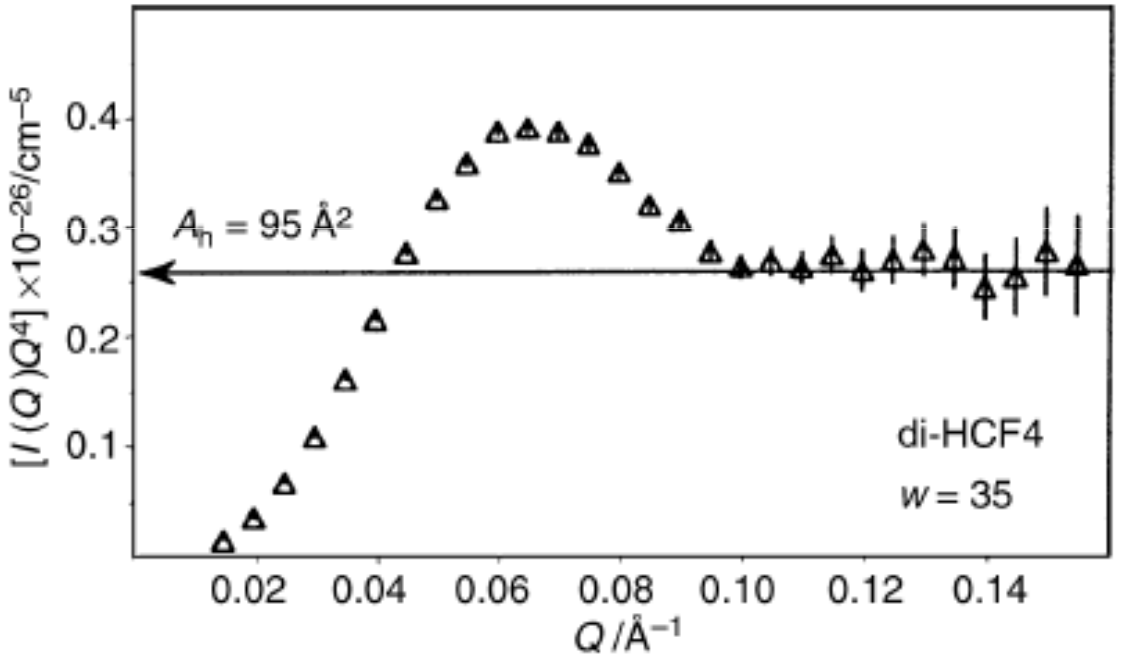


Fig. 7 Porod plot of SANS for di-HCF4 at $w = 35$, $T = 15\,^{\circ}C$, $P = 500$ bar and [surf] = 0.05 mol dm^{-3}. Error bars are shown.

Figure from Eastoe , Paul et al, JACS, 2000

Valid for sharp, smooth interfaces and where Q>>>1/R

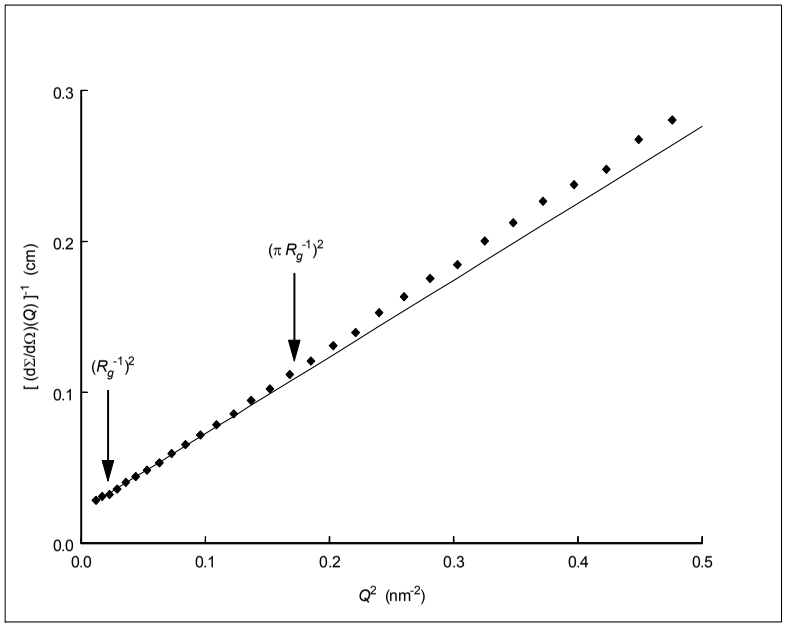
Approximations – Zimm plots

plot of

1/I(Q) vs. Q²

$$intercept = \frac{1}{M} \times \frac{N_A \delta^2}{c(\Delta\rho)^2} = \frac{1}{M} \times \frac{N_A \delta}{\phi(\Delta\rho)^2}$$

$$gradient = \frac{R_g^2}{3} \times intercept$$



The scattering from a homogeneous blend of perdeuterated and hydrogenous polystyrene (M_{dPS} ~ 69200 g mol^{-1}, ϕ_{dPS} ~ 0.2) plotted according to the Zimm approximation.

The fit gives M_w ~ 72100 g mol^{-1}, R_g ~ 8.4 nm.

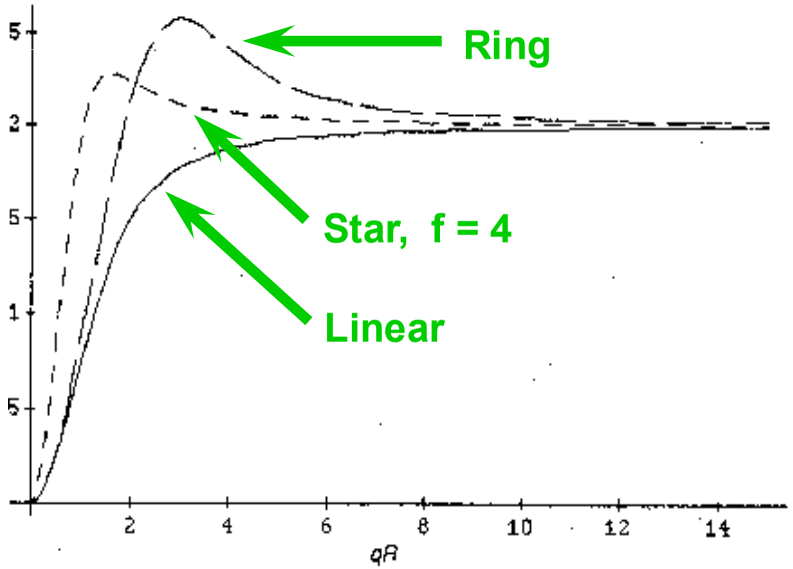
Data courtesy of Dr R K Heenan

Zimm B, *J Chem Phys*, (1948), 16, 1093

Kratky plots

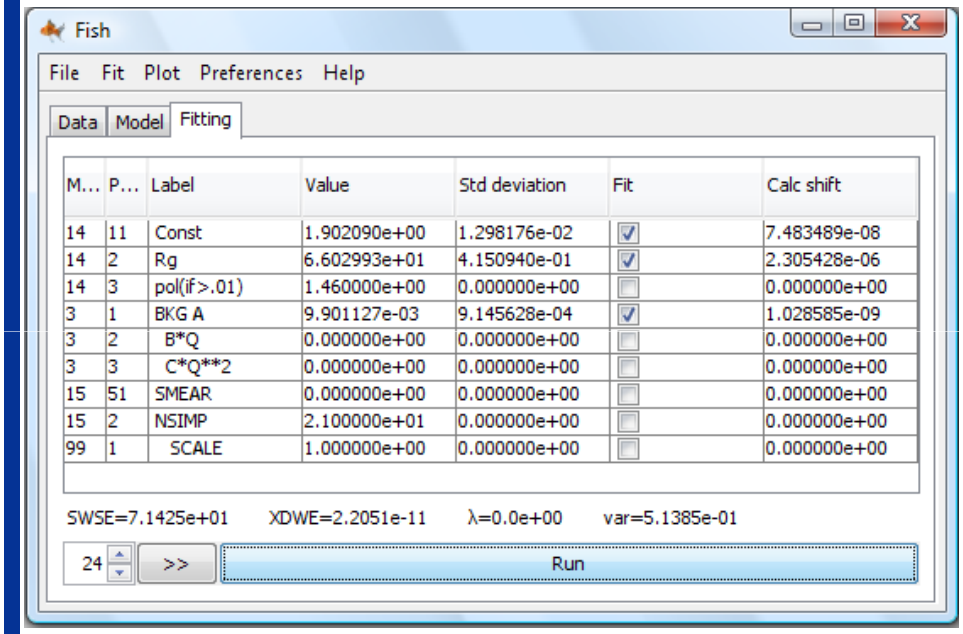
Indication of shape/conformation of scattering body

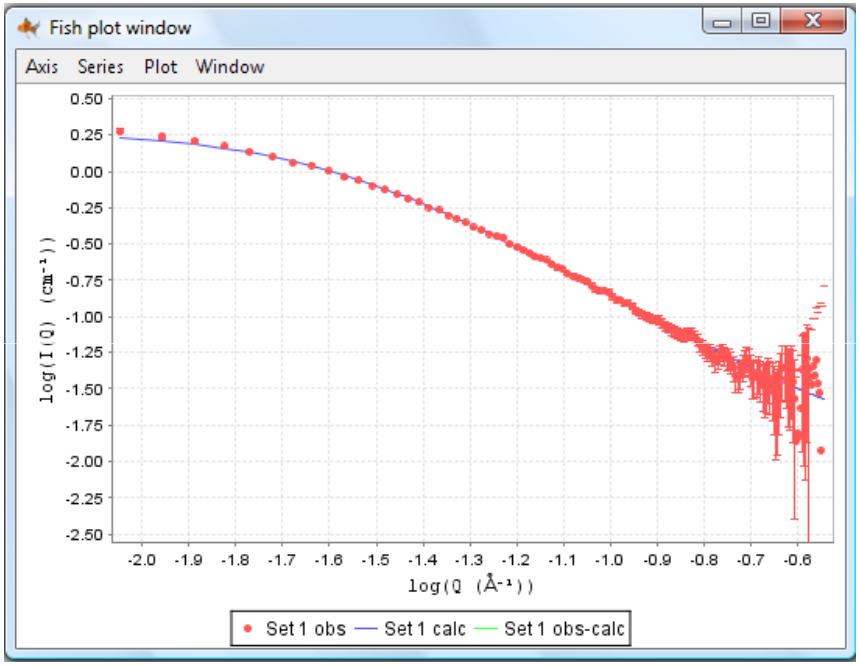
plot of $I(Q).Q^2$ *vs.* Q



Data Modelling

$$I(Q) = A\, V_p\, N_p^2\, (\Delta\rho)^2\, P(Q)\, S(Q)$$

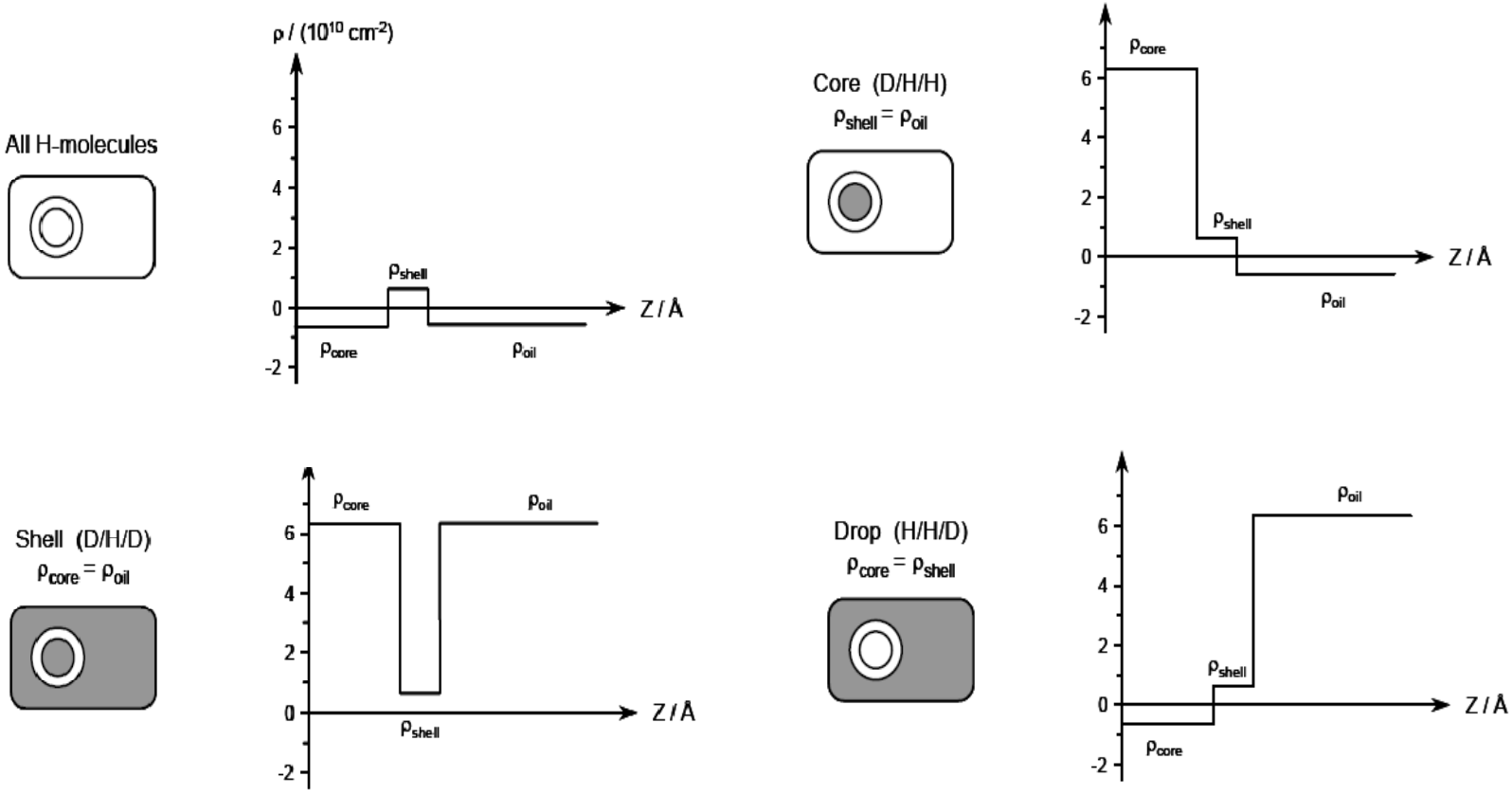




parameterised models for P(Q), S(Q) etc

iterative least squares fit

Contrast Variation – *partial deuteration*

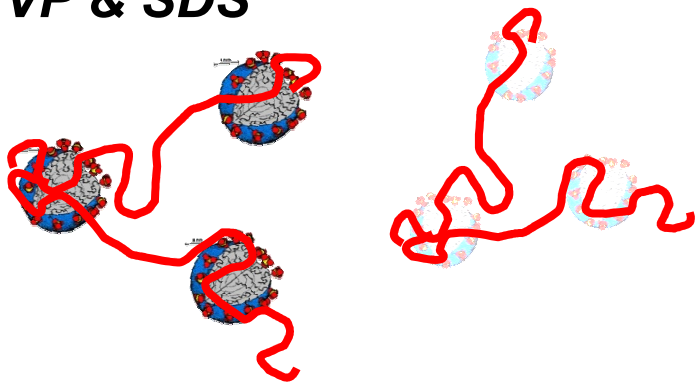


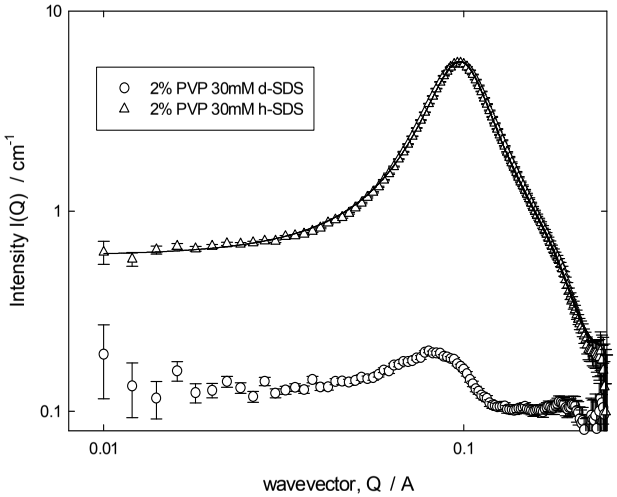
simultaneous fitting…

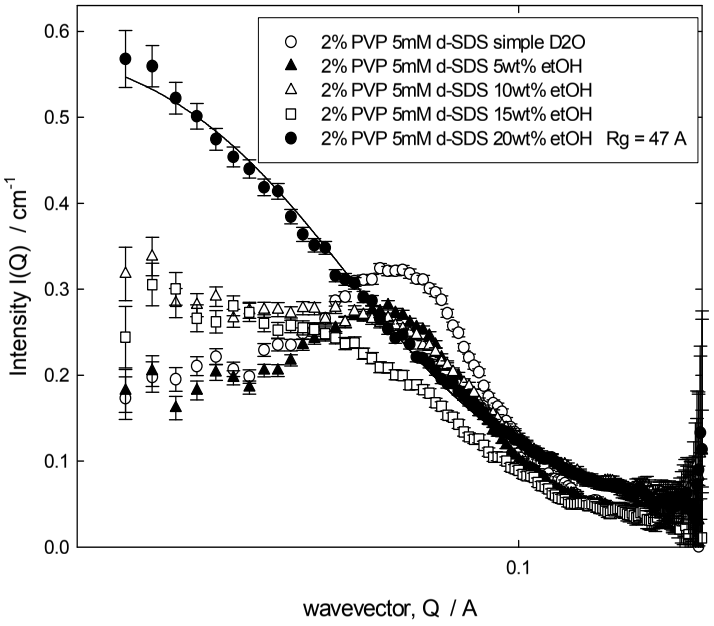
Figure from J Eastoe,

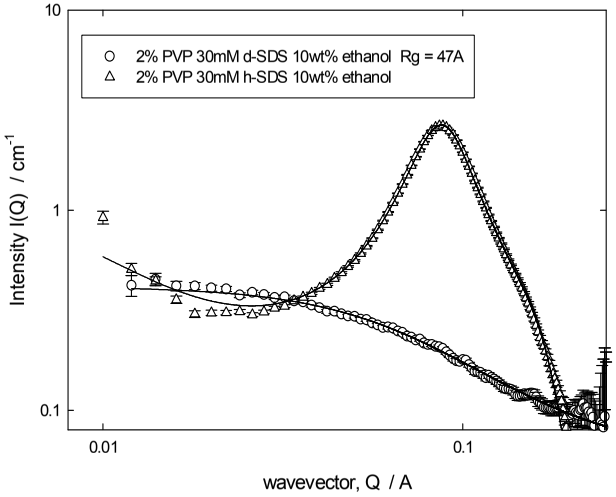
Contrast Variation – *partial deuteration*

PVP & SDS

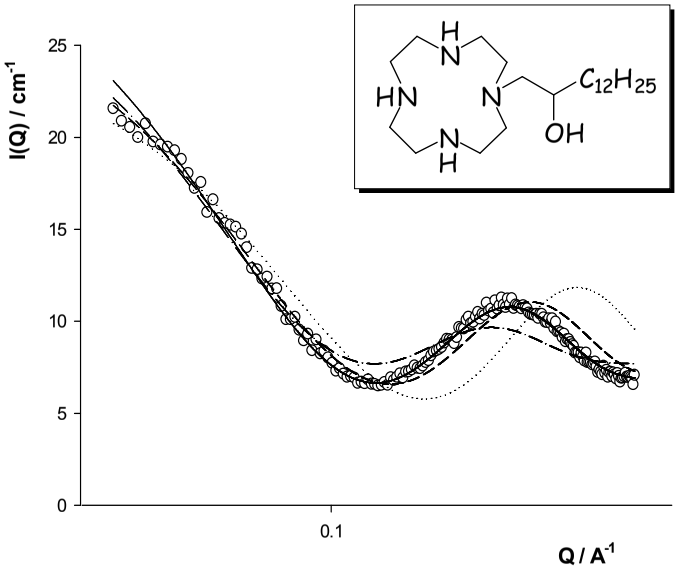








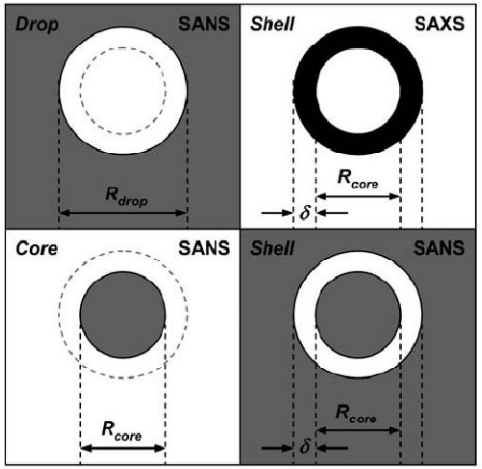
Combined SANS and SAXS



micelles and microemulsions of metallosurfactants

distinguish between oblate and prolate micelles

estimate shell thickness and thereby calculate head-group hydration

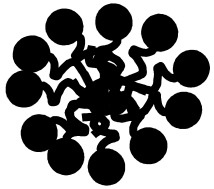


confirm location of metal ions

→ *shell thickness*

→ *alcohol content of shell*

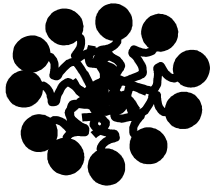
Constraining fits



$L_c \rightarrow R_{core}$

$L_c = 0.125 + 0.1265\ n_c$

Constraining fits



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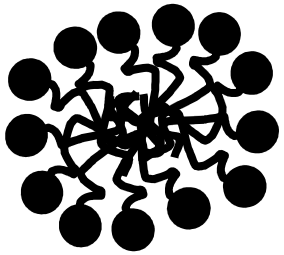
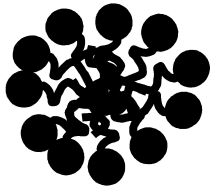


Nagg →→ shape

core volume = Nagg * V_{hc}

$V_{core} = 4/3\ \pi\ R_{core}\ X$

Constraining fits



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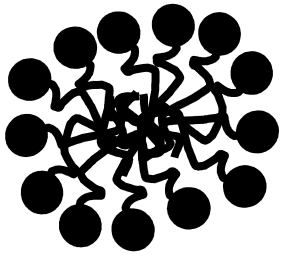

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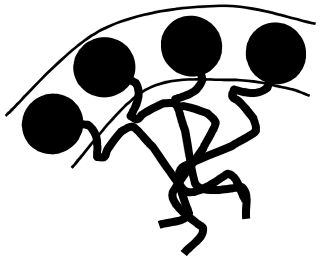


EPR →→ shell thickness

hydration → ϕ_{H2O} in shell

$V_{hg} * Nagg = (1- \phi_{H2O})$

$V_{micelle} = V_{core} + V_{shell}$

Constraining fits

SDS / C12E4

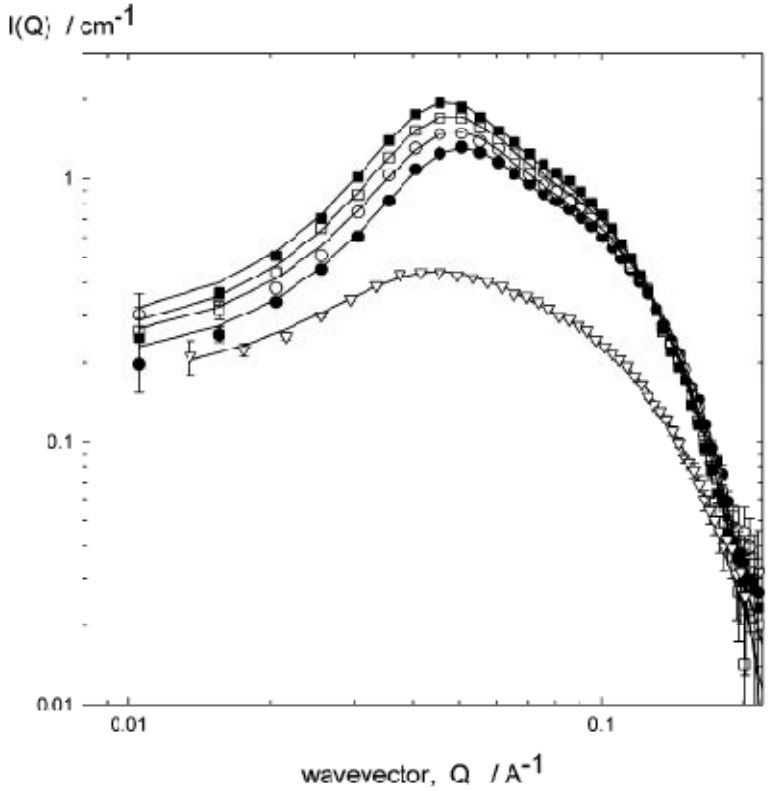


Figure 1. Intensity of scattered radiation as a function of wavevector, Q (linear-linear representation), for binary surfactant micelles comprising SDS and $C_{12}E_4$ in D_2O. (■) $\alpha_{SDS} = 1.0$ (25 mM); (●) $\alpha_{SDS} = 0.95$ (50 mM); (○) $\alpha_{SDS} = 0.90$ (50 mM); (□) $\alpha_{SDS} = 0.85$ (50 mM); (▽) $\alpha_{SDS} = 0.80$ (50 mM). The solid lines drawn through the data points correspond to the fits to the constrained model as described in the text.

Griffiths et al, J Phys Chem B, 2005

TRFQ, EPR and eNMR constrained fits

↓

calculate P(Q)

TABLE 1: Sodium Dodecyl Sulfate SDS/Tetra(ethylene oxide) Dodecyl Ether SANS Analysis, Constrained Core–Shell Fit[a]

x_{SDS}	aggregation no. ± 3	δ_{shell}/Å ± 0.1	R_{core}/Å ± 0.1	axial ratio ± 0.1	α_{Na^+} ± 0.05
1.00	65	3.6	16.7	1.2	n/a
0.95	85	3.7	16.7	1.5	0.27
0.90	88	3.8	16.7	1.6	0.28
0.85	91	3.9	16.7	1.6(5)	0.29
0.80	95	4.2	16.7	1.7	0.29

[a] δ_{shell}, R_{core}, and axial ratio are all constrained from the aggregation number.

Decrease in ϕ_{H2O} as $X_{nonionic}$ increases

Replacing water with ethyene glycol in shell region of micelle

Scale factors

$$I(Q) = \phi V_p (\Delta\rho)^2 P(Q,R)\, S(Q) + B_{inc}$$

Calculate how much scattering we expect based on the fit parameters

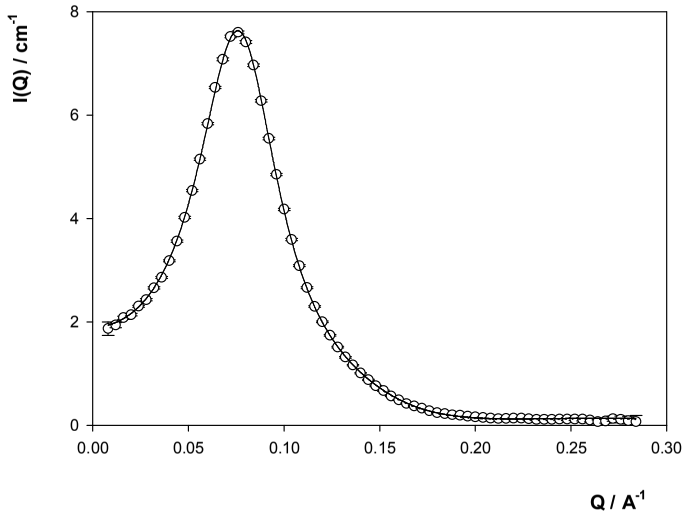
e.g. calculate Vp based on P(Q) parameters and multiply by concentration

take into account the appropriate contrast and should be within 10% of fitted scale

physically reasonable

parameters

scale factor



Summary & Limitations

Approximations often apply

- ***only under certain conditions***
  e.g. – dilute non-interacting systems, in a theta solvent
- ***only over certain Q ranges***
  e.g. – QRg <1 (Guinier) or $Q>5.Rg^{-1}$ (Kratky)
- ***only after accurate background subtraction***

Combination of methods is usually required to obtain a robust fit

scale factors
constraints

physically reasonable representation of the data

CARDIFF UNIVERSITY
PRIFYSGOL CAERDYDD

Polymers & Neutron Scattering
Higgins & Benoit

The SANS Toolbox
B Hammouda

The FISH manual
R K Heenan