Shape and size of highly concentrated micelles CTAB/NaSal by small angle neutron scattering

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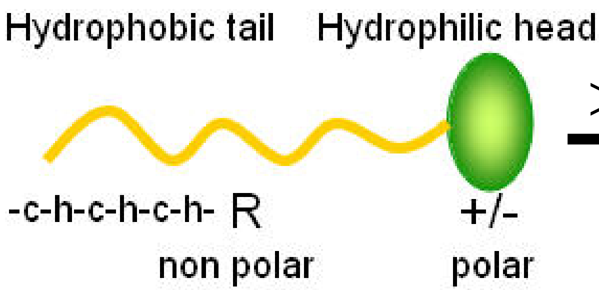
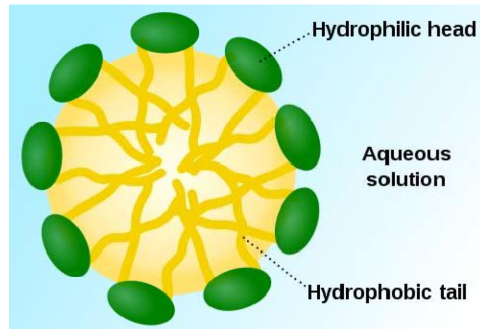
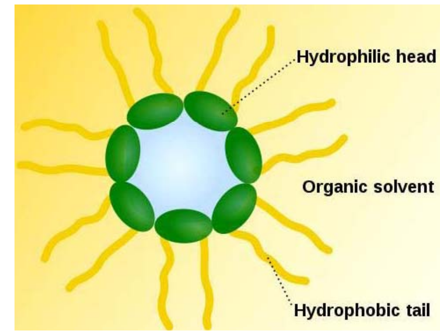
Surfactants and Micelles



> CMC →

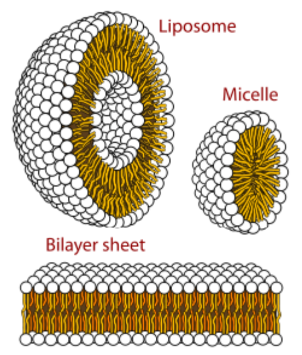


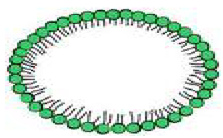
or



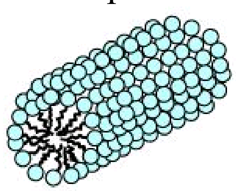
A surfactant molecule (organic amphiphilic)
= surface active agent

Aggregates of surfactant molecules
self-assembled in aqueous solutions → **micelles**

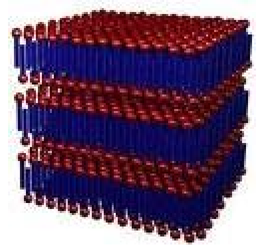




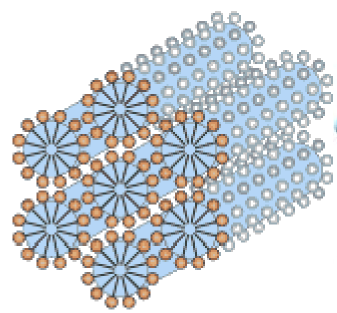
ellipsoidal



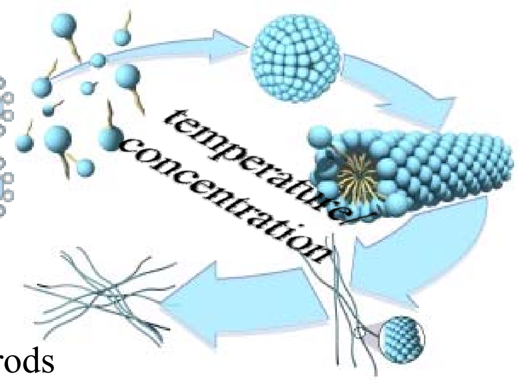
Cylindrical



Lamellae



Hexagonally packed rods



Size of head group; length and number of tails; charge on surfactant; temperature; concentration; pH; ionic strength; flow conditions

Applications of micelles

Oil field applications:

Viscoelastic type micelles used for fracturing fluids in the oil fields. Small molecule; recovers back; fewer additives req.

Hydrodynamic engineering (drag reducing agent):

Heating-cooling fluid. Warm-like micelles: dynamic associated structure-like living polymers

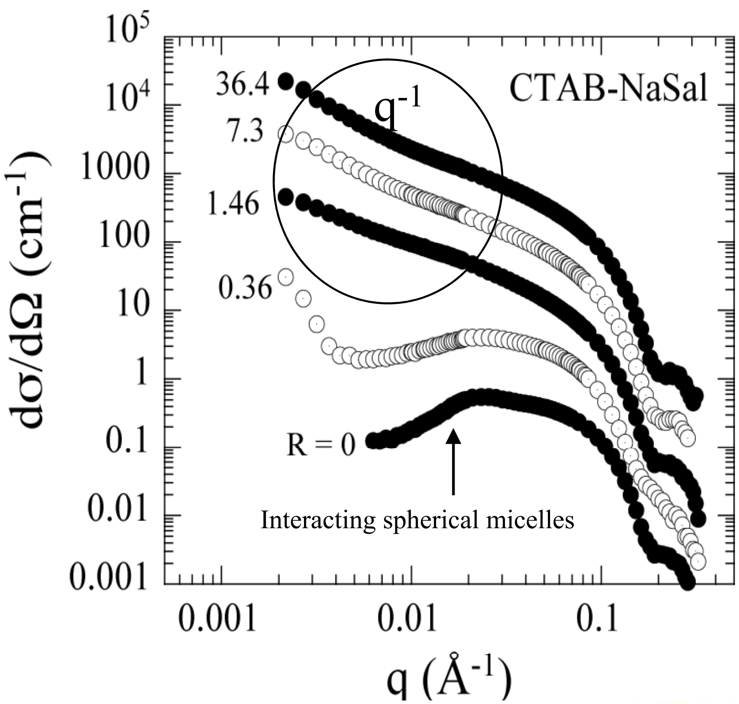
Rheological modifiers for paints, detergents, lubricant…

Home and personal cares:

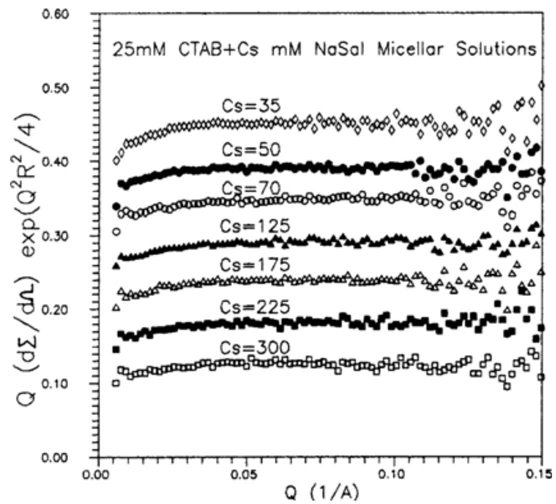
Viscoelastic property-Warm-like micelles. c.g., hard surface cleaners and drain-opener liquid plumber.

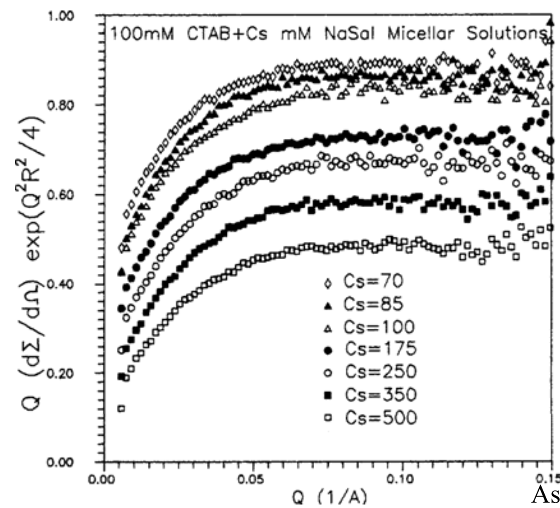
SANS about CTAB/NaSal

CTAB =0.2wt.% (5.5mM), R=[SAL^{-1}]/[$CTAB^{+1}$]



J F Berret Molecular Gels, 667, 2006





25mM CTAB
(x mM NaSal)
Long rod-like
Micelles (L>>r)

I(Q)~ exp(-(Qr)^2/4)/Q

r_b=22±1Å,
L=250±25Å

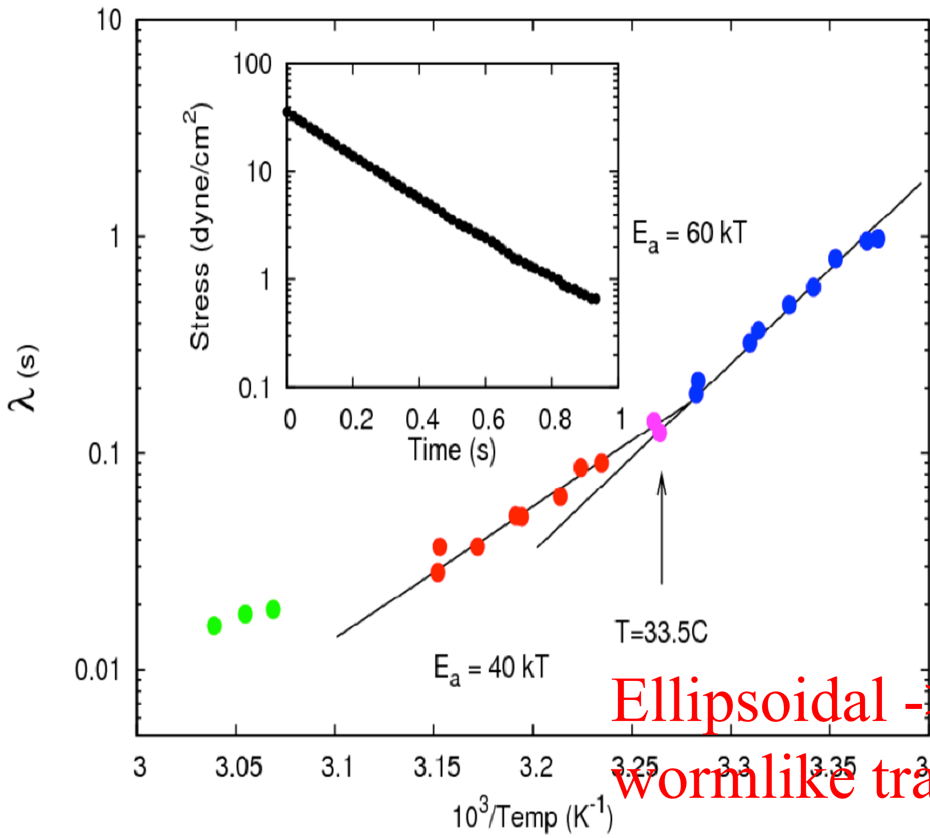
100 mM CTAB
(x mM NaSal)
Ellipsoid Micelles

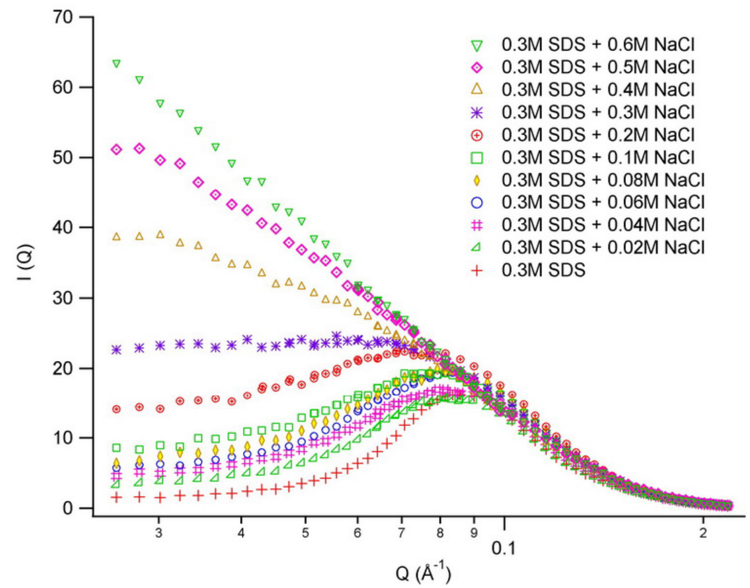
r_b=22±1Å,
r_a=44+5Å

Aswal et al. J. Phys. Chem. B, 102, 2469, 1998

Motivation and Objective

Rheological Relaxation time measurements





Ellipsoidal -> wormlike transition?

Major axis: 22 →250Å
(ellipsoidal → worm like micelles)

Ref: Small Angle Neutron Scattering BATAN

Joseph (Josh) Gladden, Dept. of Physics, University of Mississippi

Low Energy Neutron Source at Indiana University

Accelerator	13 MeV
Moderator	Coupled < 20 K solid methane
Wavelength Range	4 Å - 14 Å
Q Range	0.005 to 0.3 A $^{-1}$
Pulse Width	600us
Source Frequency	10 to 30 Hz
Collimation	Circular pinhole collimation
Area Detector (^{3}He 2D ORDELA)	
Active Volume	64 x 64 cm^2, 4.4 cm thick
Pixel Size	1 x 1 cm^2
Detector Efficiency	71% for 5 Å neutrons, 52% for 3 Å neutrons
Count-Rate Capability	10^4 n/s for 10% coincidence losses (10^5 n/s max.)
Integrated Flux on Sample	$2*10^4$ n/cm^2/s (at full accelerator power of 13 kW)

SANS Science Applications

Polymers

Molecular self-assembly and interactions in complex fluids; Colloids and microemulsions; Micelles;

Materials Science

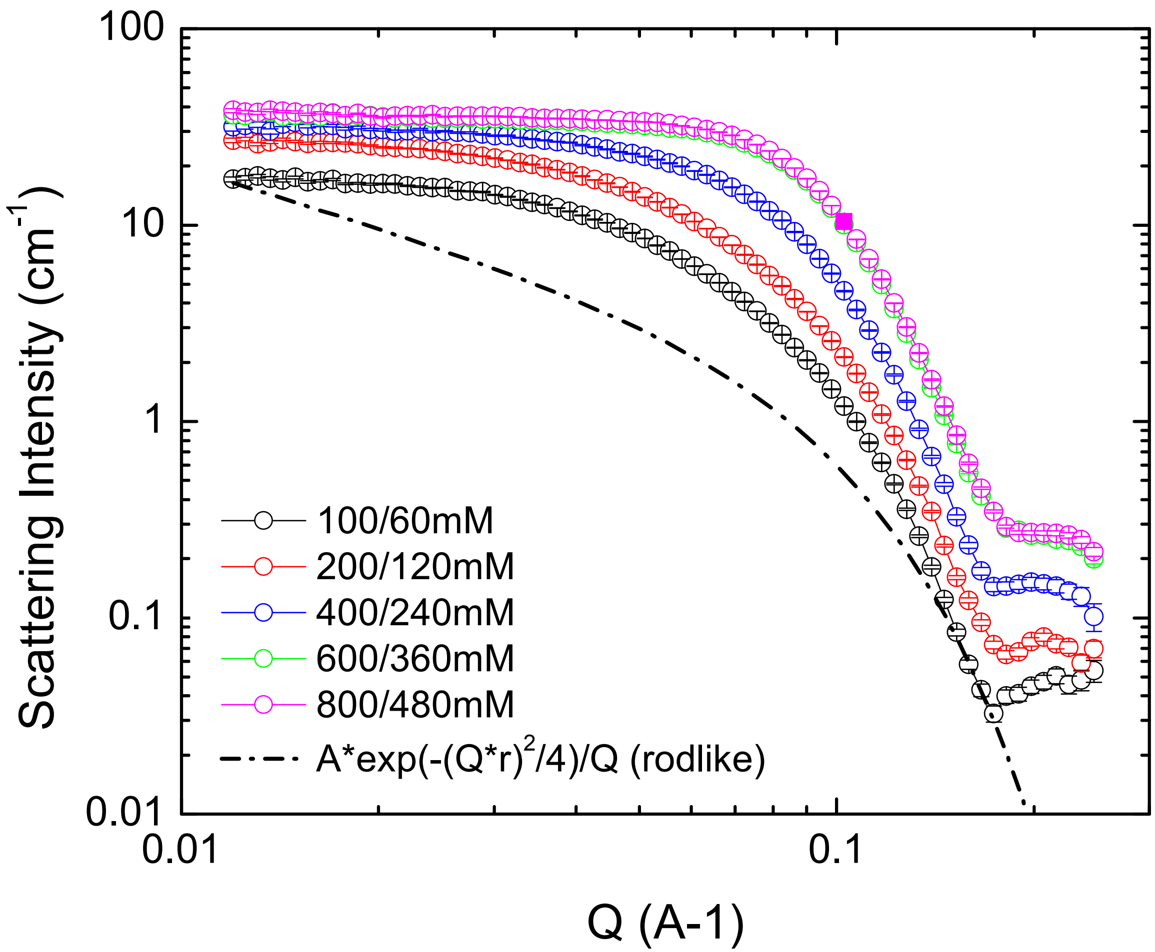
Phase separation in alloys and glasses; Morphologies of superalloys; Nanocomposites

Biological Macromolecules

Size and shape of proteins; macromolecular complexes
Hierachical biological structures; Biomembranes

Preliminary Evaluation of Micelles Structures

Micelles CTAB/NaSal (=0.60), T = 293^0C



Possible Shapes:

- Spheres
- Ellipsoid

SANS Data Modeling

$$\frac{d\Sigma}{d\Omega} = n_m(\rho_m - \rho_s)^2 V_m^2 \langle F(Q) \rangle^2 S(Q) + bkgd$$

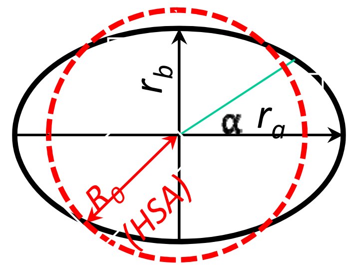
❖Particles F(Q,x)– Ellipsoid

Density-n_m Volume-$V_m(b) = 4\pi r_b r_a^2/3$

Neutron Contrast-$(\rho_m - \rho_s)^2$

Form factor-

$$F(Q,x) = 3(\sin u - u\cos u)/u^3, u = Qr_b[1 + x^2(\gamma^2 - 1)]^{1/2}, u = \cos\alpha \qquad \gamma = r_a / r_b$$



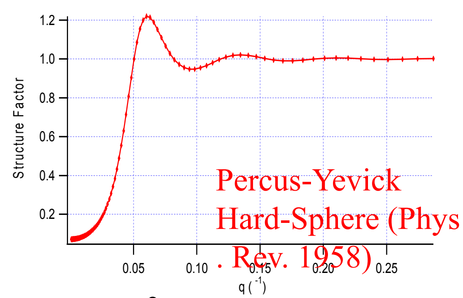
❖Size Distribution – Gaussian

$$f(r_b) = \frac{1}{\sqrt{2\pi\delta^2}} \exp(-(r_b - \bar{r}_0)^2 / 2\delta^2)$$

❖Structural Factor S(Q) – Hard Sphere Model

$$u(r) \begin{cases} 0, & r \geq 2R_0 \\ \infty, & 0, r < 2R_0 \end{cases}$$

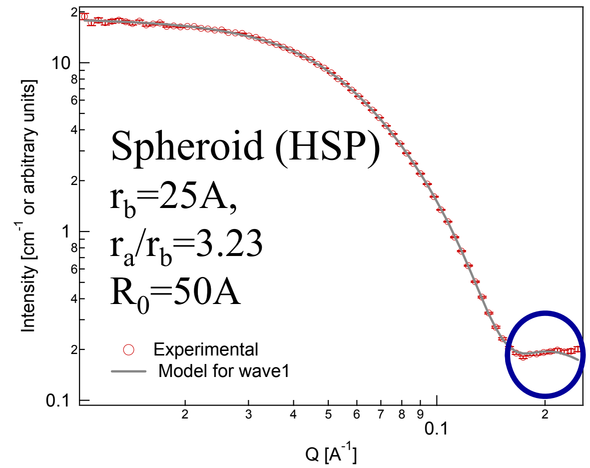
Interparticle potential

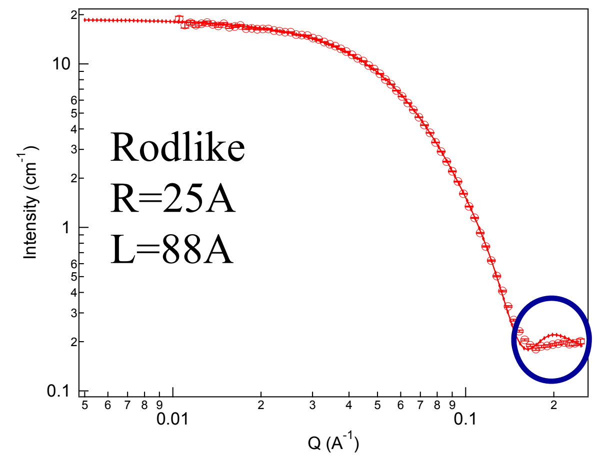


In solution the single particle form factor must be averaged over all angles to give the form factor:

$$\frac{d\Sigma}{d\Omega} = n_m(\rho_m - \rho_s)^2 \int V_m^2(r_b) f(r_b) dr_b \int_0^1 [F(Q,x)]^2 S(Q) dx + bkgd$$

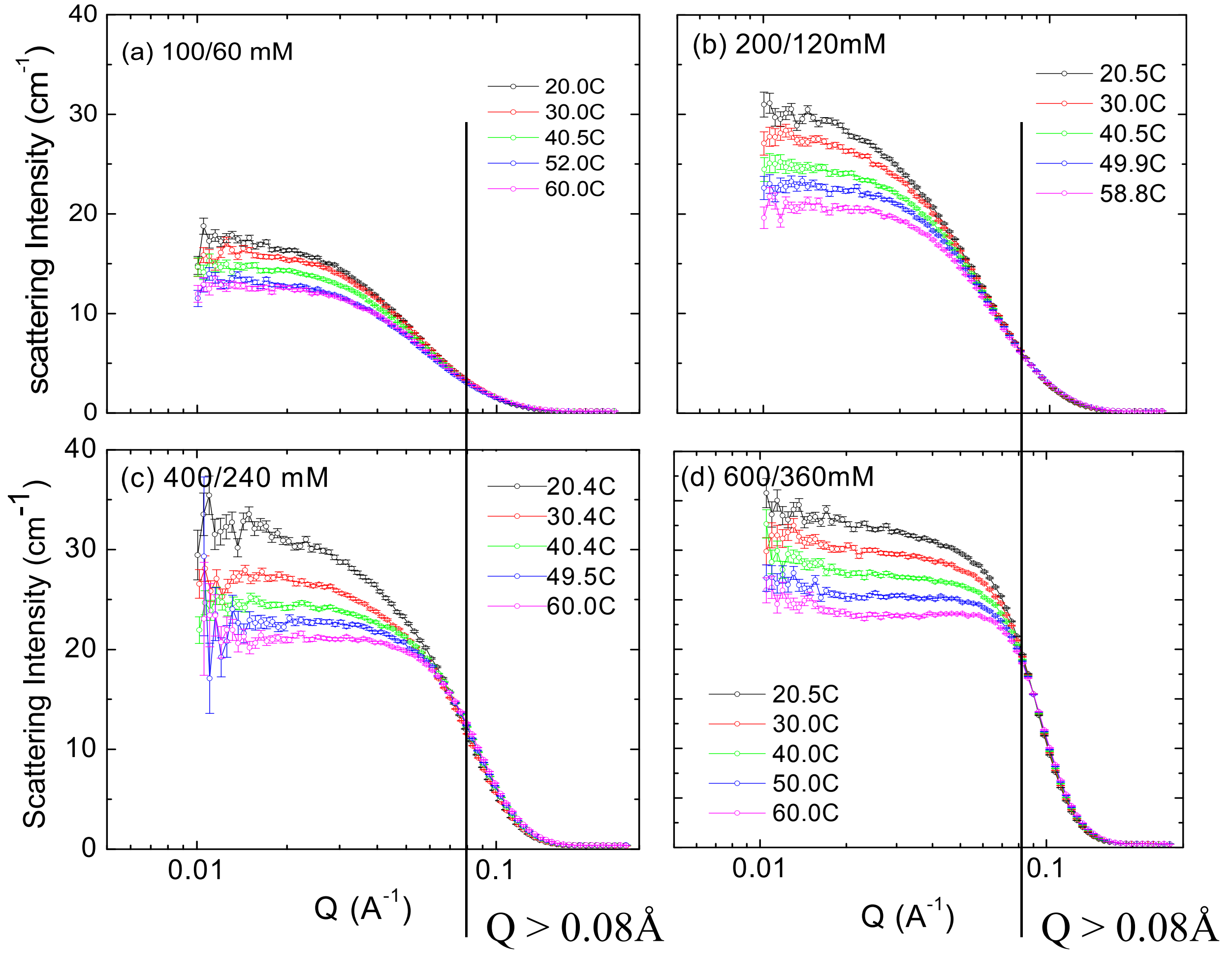
100/60mM CTAB/NaSal, 20^{0}C





1. Irena Package from the USAXS at APS, ANL: http://usaxs.xor.aps.anl.gov/staff/ilavsky/irena.html
2. SANS Igor Pro from SANS at NCNR, NIST: http://www.ncnr.nist.gov/programs/sans/data/red_anal.html

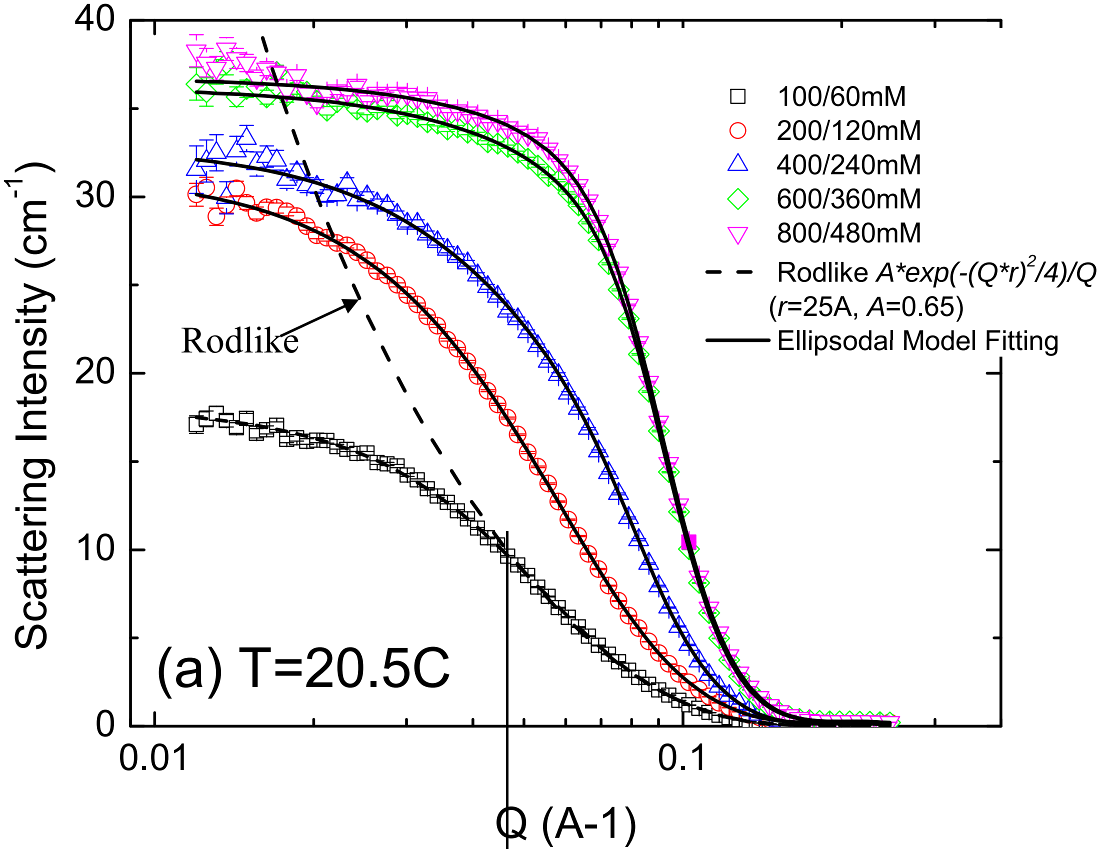
Temperature dependence of scattering intensity



Q > 0.08Å
Short axis remain constant

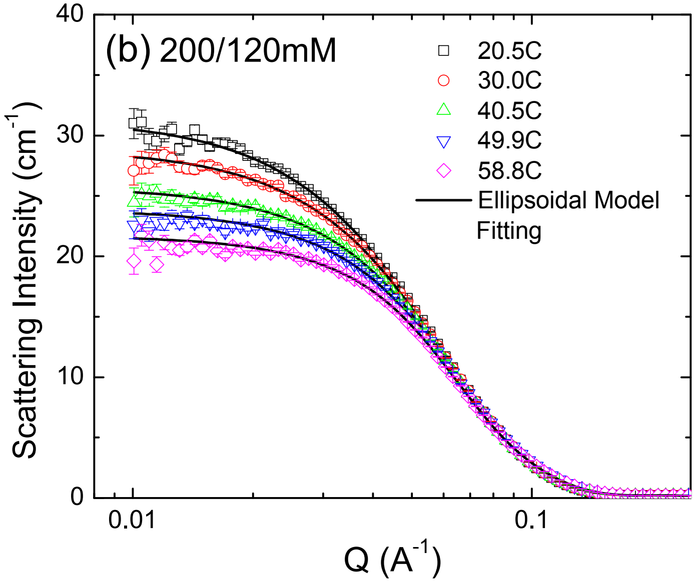
Q < 0.08Å
Long axis change with temperature
↓
shorter with temp.

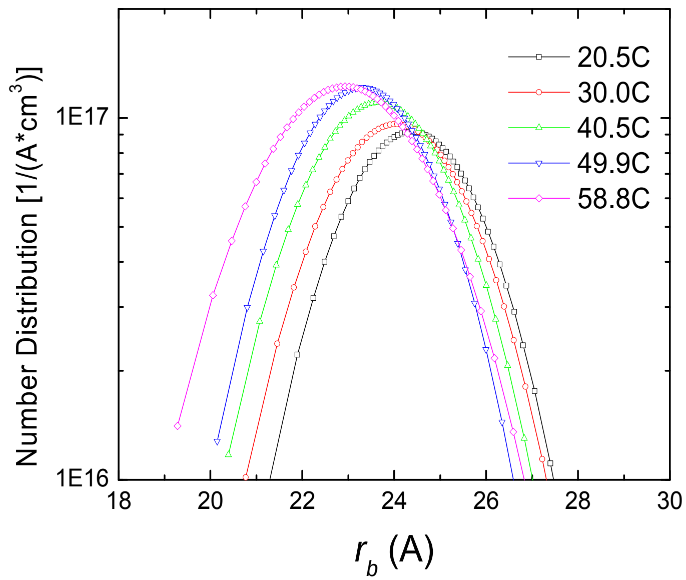
Temperature dependence of scattering intensity



Short ellipsoidal axis ~
length of the surfactant molecule (20~26Å)

Model fitting



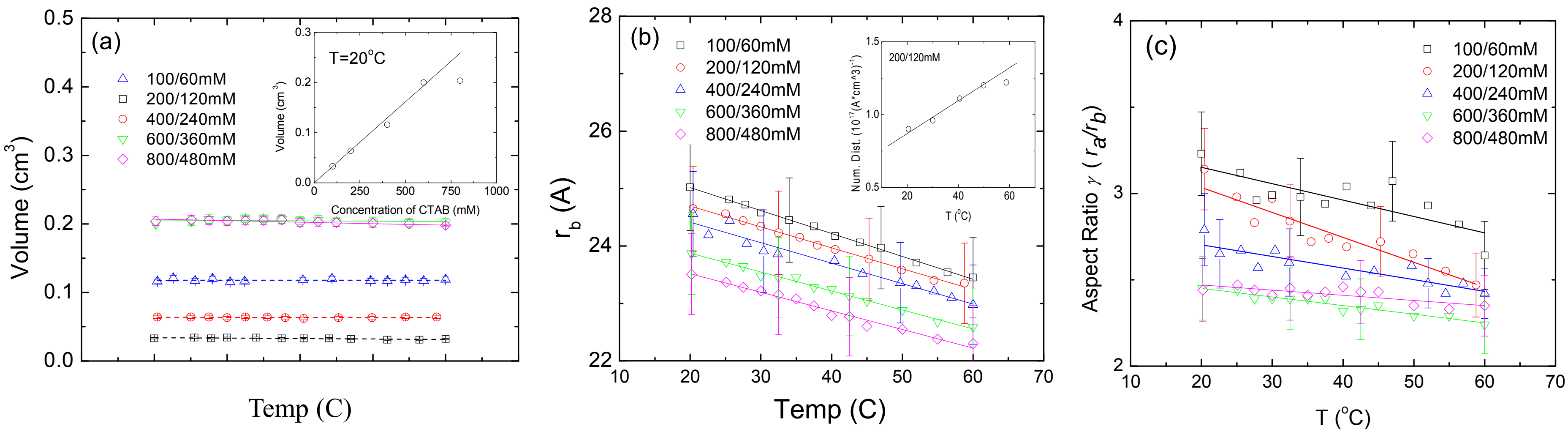


Model: Ellipsoid form, a hard sphere structure factor and Gaussian size distribution

Fitting parameters (7): total scattering volume of micelles, the semiminor axis r_b, width of Gaussian function (δ), aspect ratio ($\gamma=r_a/r_b$), the radius (R_0) and volume fraction ($\eta=4\pi R_0^3 n_m/3$) of hard sphere, and background (*bkgd*).

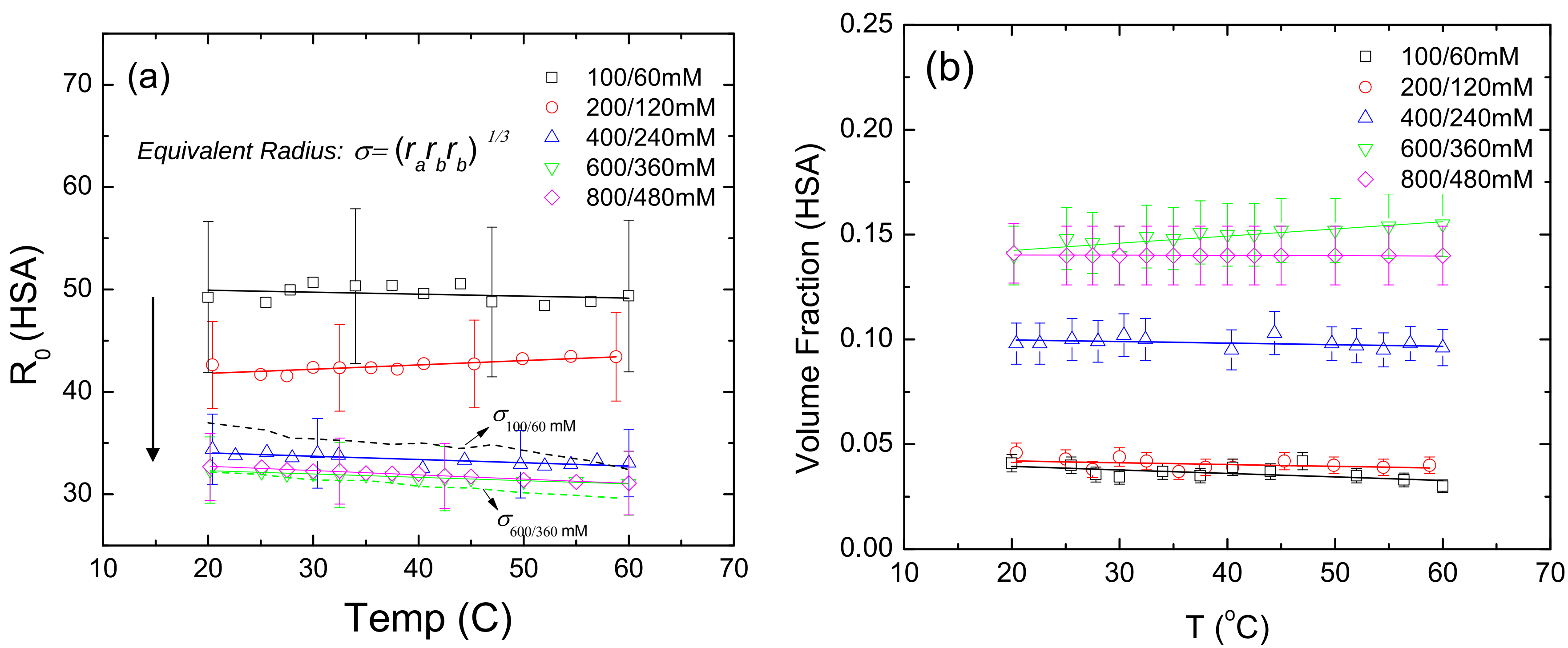
Width (δ) of Gaussian function ~ 0.001 Å, the semiminor length of the ellipsoidal particle might be simply equal to the length of the surfactant molecule and these ellipsoidal particles could be monodispersed

Temperature dependence of fitting parameters of Micelles



Linear decrease in both the semiminor axis r_b and aspect ratio (r_a/r_b)
: Micelles begin to condense with increase in temperature
: 100/60 mM shows the largest particle size
:r_a (growth direction) shortens faster than r_b
: Volume remains constant-micelles break- and extra broken begin to recombine
: number density increases with heating

Temperature dependence of fitting parameters of Micelles



$R_0 \rightarrow$ 50 to 33Å (100/60 to 400/240 mM)
HAS works well for ellipsoidal or more spherical micelles

Volume fraction: $4\pi R_0^3 n_m/3$

Temperature effect on size of micelles and number density

Summary

- ❖ Highly concentration CTAB/NaSal formed ellipsoidal micelle. Ellipsoidal micelles have been investigated by small angle neutron scattering.
- ❖ SANS results suggests that this micelles solution fall in the ellipsoidal regime and micelles shape are independent on the concentration and temperature.
- ❖ Micelles size decreases with concentration and temperature whereas total volume of micelles remain constant, indicating that long micelles start to break on heating and broken surfactant molecules coalesce again to form more micelles.
- ❖ No structural transitions (linear change) in the studied temperature range for highly concentration CTAB/NaSal.