

NMI - Amr - 9 Aug '24

$\frac{dn}{dc}$ = Differential Refractive Index

$$R_s = \frac{I_s r^2}{I_0 V} = \text{Rayleigh Ratio}$$

Light Scattered into detector at angle θ

I_s scattered Light Intensity

I_0 Incident Beam Intensity

V Illuminated Vol. & the scattering medium for which the detector at

θ collects light

r distance between V & detector

More generally,

$V = R I$, I = intensity, R = proportionality const V = Volts

$R = \frac{\text{Amp}}{\text{Watt}}$ for photodiode or $\frac{V}{\text{Watt}}$ if direct voltage output

$V \propto I$

MM from LS

Zimm Model, $\frac{dn/dc}{R^2} = 0.1849 \text{ ml/g}$

Peak 1 RM $r = 5.8 \pm 9.1 \text{ nm}$ slice 1811 @ 12.887 min

$$MM = (2.074 \pm 0.029) \times 10^6 \text{ g/mol}$$

$$R^2 = 0.2238$$

Peak 2 MM $(4.099 \pm 0.024) \times 10^6 \text{ g/mol}$ slice 1829 @ 15.601 min

$$r_{rms} = 8.1 \pm 2.1 \text{ nm}$$

$$R^2 = 0.2152$$

$$x\text{-axis} = \sin^2(\theta/2)$$

$$y\text{-axis} = k^* c / R(\theta)$$

What are all the angles?

Rh from DLS

corr. $x = t \text{ (sec)}$

func. graph $y = \text{correlation function.}$

control $x = \text{time (min)}$

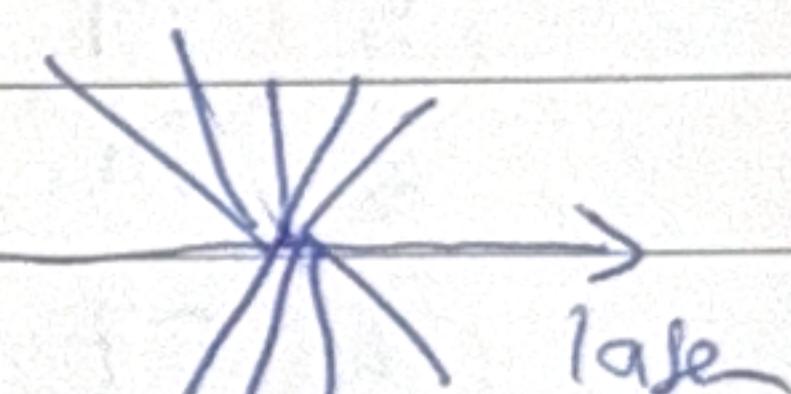
graph $y = \text{count rate (Hz)}$

Peak 1 $R^2 = 0.9684$

$$Rh = 3.19 \pm 0.12 \text{ nm}$$

$$Dt = (7.29 \pm 0.27) \times 10^{-7} \text{ cm}^2/\text{sec}$$

Detector #	Dt cm^2/sec	Relative Intensity
1	22.5	10 81.0
2	28.0	11 90
3	32.0	12 99
4	38.0	13 108
5	44.0	14 117
6	50.0	15 126
7	57.0	16 134
8	64.0	17 141
9	72.0	18 147



Conditioning $T = 23^\circ\text{C}$, Viscosity $\eta = 0.9324$

processing Parameters

Min Rh threshold (nm) Max Rh T. (nm)
1 300

Min fit delay (s)

$$2 \times 10^{-7}$$

Max fit delay (s)

1

DLS slice 407

(at 13.557 min)

Determining R_h

1. Equations

Dist Analysis

$x = g/mol \text{ MM}$

$y = \text{Cumulative Weight Fract.}$

$y_2 = \text{Differential Weight fraction} \left(\frac{g/mol}{g/mol} \right) (\text{mol/g})$

Cumulative Molar Mass y'

Linear Diff MM y_2

Detector Ref. Index	Corrected Scattering Angle	Normalisation coeff.
1 22.5° →	NAC (0.00°)	1.000
2 28.0° →	13.07°	1.719
3 32.0° →	20.68°	1.298
4 37° →	29.62°	1.263
5 44° →	37.48°	1.642
6 50° →	44.84°	0.757
7 57° →	53.07°	0.860
8 64° →	61.08°	0.932
9 72° →	70.07°	0.976
10 81° →	80.06°	1.018
11 90° →	90.00°	1.000
12 99° →	99.99°	0.963
13 108° →	109.93°	0.978
14 117° →	120.08°	1.026
15 126° →	120.43°	0.778
16 134° →	140.03°	0.725
17 141° →	149.02°	1.504
18 147° →	157.70°	1.524

$$\text{Calib Const} = 5.5088 \times 10^{-5} \text{ } ^1/\text{Vcm}$$

Conventional R_gms Determination, R_g vs $\sin^2(\Theta/2)$

Fit polynomial in $\sin^2(\Theta/2)$ to data, get intercept at

$\Theta = 0^\circ$, R_g , and slope at $\Theta = 0^\circ$.

$$S = \frac{d[R_g]}{d[\sin^2(\Theta/2)]}_{\Theta=0}$$

$$\langle r_g^2 \rangle = -3S \lambda^2$$

$$16 \pi^2 R_g$$

Determining Molar Mass (M)

1. Calibrate Detectors

- Using standard sample with known Rayleigh Ratio $R_{std}(\theta)$ and concentration c_{std}
- Measure voltages for standard $V_{std}(\theta)$

2. Calculate Detection Constant (k)

$$K_{det} = \frac{R_{std}(\theta)}{V_{std}(\theta)}$$

3. Calculate Sample R_s

$$R(\theta) = K_{det} \times V_{sample}(\theta)$$

4) Determine Sample Concentration (c)

Use UV data & Beer - Lambert Law $(\text{L mol}^{-1} \cdot \text{cm}^{-1})$

$$A = Ecl \Rightarrow c = \frac{A}{E l} \quad A = \text{Absorbance}, E = \text{molar extinction coeff.}$$

$A = \text{Path Length of the cuvette (cm)}$ (typically 1cm)

5) calculate Optical Const. (K) - ~~use diff symbol~~

$$K = \frac{4\pi^2 \cdot n^2 (\Delta n / \Delta c)^2}{N_A \lambda^n} \quad n = \text{ref. i. \& solvent} \quad \Delta n / \Delta c = \text{ref. i. increment} \quad (\text{mL/g})$$

$N_A = \text{Avogadro Number. } \lambda \text{ in cm}$

6. Use Rayleigh Eqn to get M

$$\text{Small Particles (how small!)} \quad R(\theta) = k_c M \Rightarrow M = \frac{R(\theta)}{k_{opt} c}$$

~~Larger Particles~~ ↑

$$\text{incorporate form factor } P(\theta): \quad R(\theta) = k_{opt} c M P(\theta)$$

$$\text{for spherical particles, } P(\theta) = \exp\left(-\frac{(2R_g)^2}{3}\right)$$

$R_g = \text{Radius of Gyration}$

7. Plot $\frac{k_{opt} c}{R(\theta)}$ vs. c & Extrapolate

Prepare Zimm Plot: Plot $\frac{k_c}{R(\theta)}$ vs. $\sin^2\left(\frac{\theta}{2}\right) + c$ for multiple $\theta \neq 90^\circ$

Extrapolate to

$\theta = 90^\circ$ conc. and θ angle to obtain $\frac{1}{M}$ from intercept

8 - for sol. where interactions are significant, account for Second Viral

$$\text{coeff (A}_2\text{)} \cdot \frac{k_{opt} c}{R(\theta)} = \frac{1}{M} + 2A_2 c, \quad A_2 \text{ determined from slope.}$$

Determining R_h

1. Extract Raw Intensity Data

2. Calculate $g_2(\tau)$ - Autocorrelation function - Explain what'

$$g_2(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2}$$

$I(t)$ = Intensity at time t
 τ = Delay Time - Explain
 $\langle \cdot \rangle$ = Time avg.

3. Relate $g_2(\tau)$ to Electric Field Autocorr. Function - Exp.

$$\cancel{g_2(\tau)} = \frac{1}{2} e^{-\Gamma \tau}$$

$$g_2(\tau) = 1 + \beta |g_1(\tau)|^2$$

β = coherence factor.
 exp.

4. Fit $g_2(\tau)$ to get Decay Rate (Γ) < exp.

Model for Monodisperse Particles

$$g_1(\tau) = e^{-\Gamma \tau} \Rightarrow g_2(\tau) = 1 + \beta e^{-2\Gamma \tau}$$

Γ in User guide, this is B .

B = baseline of corr. Function at $\tau=0$ delay

5. Calculate Scattering Vector for each detector \ominus

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

n = ref. index & solvent θ = Scat. angle
 λ = wavelength of incident light in Vacuum

6. Calculate Diffusion Coefficient

$$\Gamma = D q^2 \Rightarrow D = \frac{\Gamma}{q^2}$$

7. Calculate R_h

$$\text{Stokes-Einstein eqn. } D = \frac{k_B T}{6\pi\eta R_h} \Rightarrow R_h = \frac{k_B T}{6\pi\eta D}$$

k_B = Boltz const.
 T in Kelvin

η = viscosity of sample
 (Pa.s)

Size Determination

- \bar{M}_n / \bar{M}_w need not be known
- particle concentrations are low enough that there are no interactions or consequences between them
- Above means second virial coefficient = 0
- Assumed that particles have been fractionated (each slice contains identical size particles)

Calculating M_w using DLS typically requires \bar{M}_n / \bar{M}_w .

Can get around by assuming 100% mass recovery.