# Experimental methods for Quantifying Counterion Condensation

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Slides:

Pre-print:

American Physical Society March Meeting 2026, Denver

# Experimental methods for Quantifying Counterion Condensation

**01 Theory**

Counterion condensation

**02 Challenge**

Quantifying methods and their challenges

**03 Solution**

Light scattering
viscometry

**04 Closing**

Case study on Polyglutamic acid

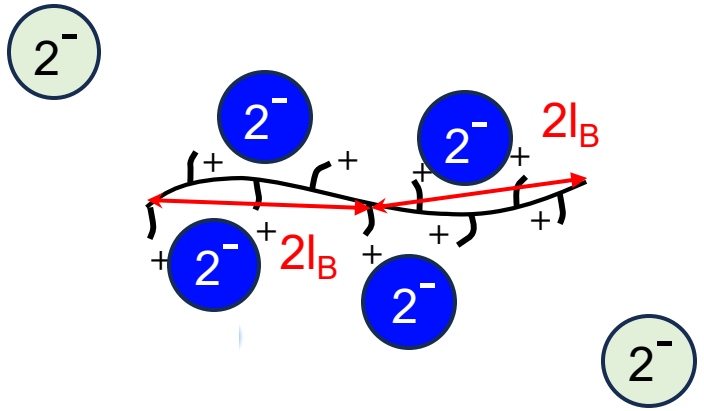
Slides:

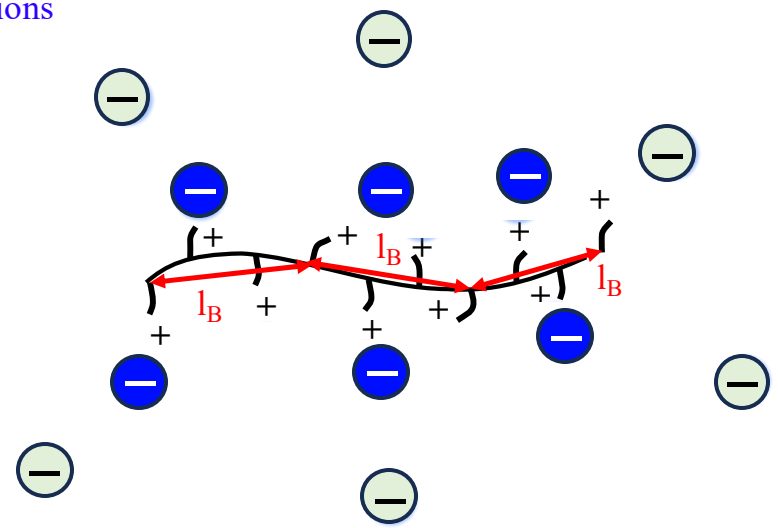
Pre-print:

# Oosawa-Manning theory of condensation

Counterions will condense onto the chain until the charge density decreases to a value of $e/l_B$.

I. Condensed counterions
II. Free counterions

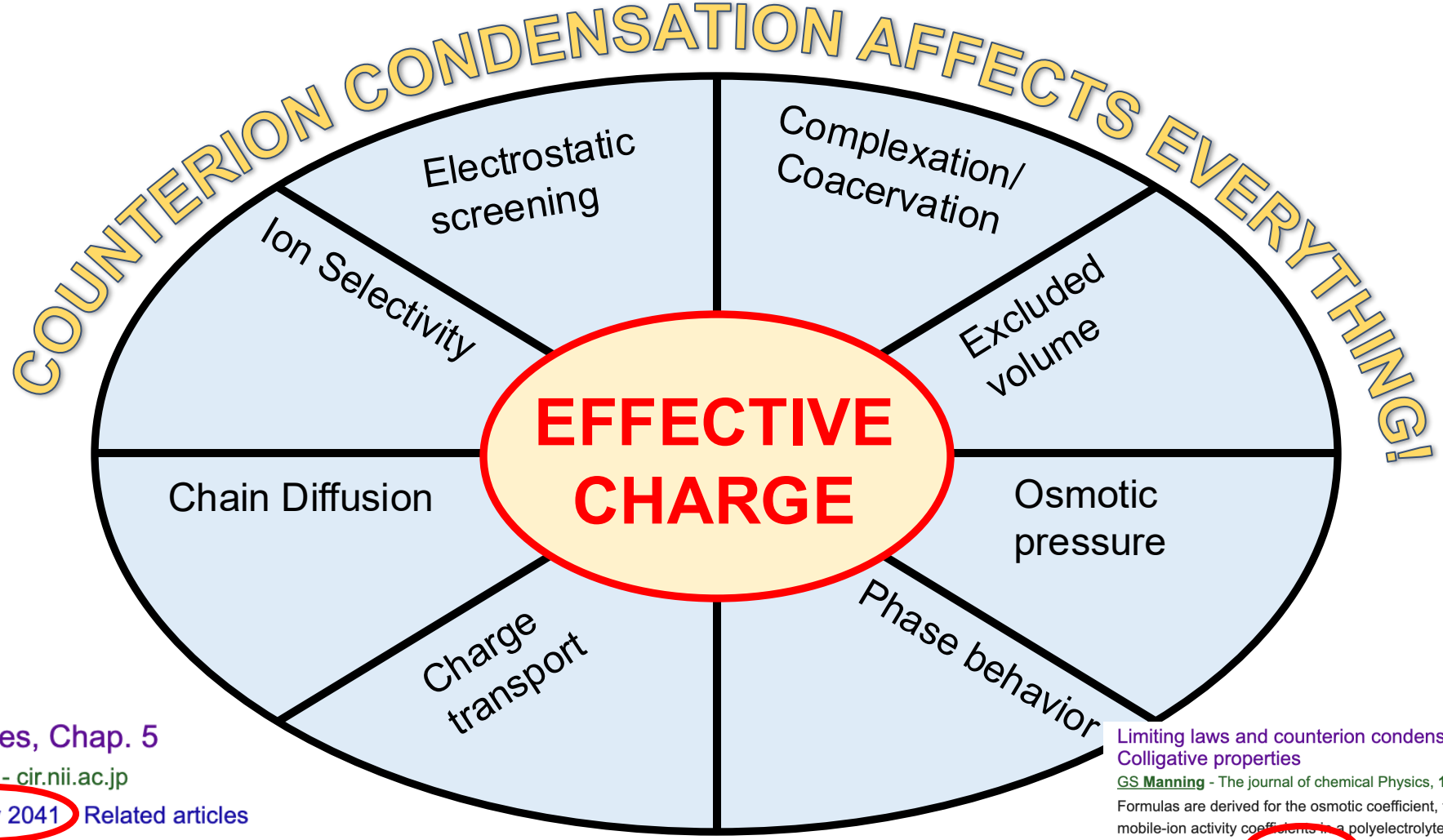



Fraction of charged monomers: $f \approx \frac{b}{zl_B}$

Bjerrum length: $l_B = \frac{e^2}{4\pi k_B T \epsilon}$

# COUNTERION CONDENSATION IS THE CENTRAL PROBLEM OF POLYELECTROLYTE SCIENCE




[CITATION] Polyelectrolytes, Chap. 5
F Oosawa - (No Title), 1971 - cir.nii.ac.jp
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Limiting laws and counterion condensation in polyelectrolyte solutions I. Colligative properties
GS Manning - The journal of chemical Physics, 1969 - pubs.aip.org
Formulas are derived for the osmotic coefficient, the Donnan salt-exclusion factor, and the mobile-ion activity coefficients in a polyelectrolyte solution with or without added sample salt. …
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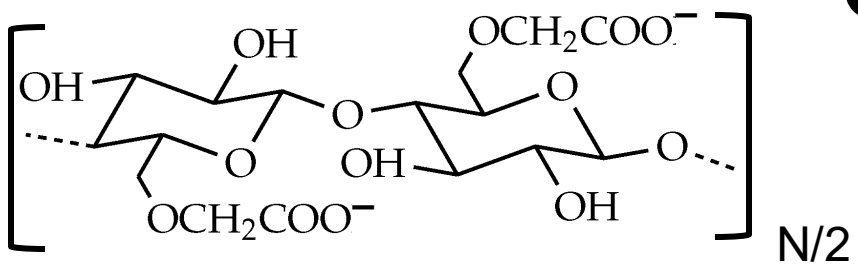
# METHODS FOR DETERMINING COUNTERION CONDENSATION




Theory-light

Theory-heavy

| Method | $f_{NaCMC}$ | $f_{MgCMC}$ |
|---|---|---|
| Ion selective potentiometry | 0.72 | 0.3 |
| Osmometry (Vapour pressure) | 0.67 | — |
| Osmometry (Membrane) | 0.69 | 0.37 |
| Conductivity | 0.5 | 0.22 |
| Dielectric spectroscopy | 0.35 | — |

- **Various methods yield different results for the fraction of free counterions.**
- **Osmotic pressure is one of the most direct (theory-light) methods to determine *f*:**

$$\Pi = k_B T f c$$

Each free counterion contributes $\approx k_B T$ to the osmotic pressure.

**DRAWBACK:** very difficult for non-aqueous systems.

# LIGHT SCATTERING FROM SALT-FREE POLYELECTROLYTES

$$S(0) = k_B T c \frac{dc}{d\Pi} \Longrightarrow \approx f^{-1}$$

In combination with $\boldsymbol{\Pi = k_B T f c}$, this provides a way to measure the fraction of free counterions

**SLS can be carried out in organic/volatile solvents**

Lifson, S. and Katchalsky, A., 1954. *Journal of Polymer Science*, 13(68), pp.43-55.
Alexandrowicz, Z., 1959. *Journal of Polymer Science*, *40*(136), pp.91-106.

This was recognized over 70 years ago!

# LIGHT SCATTERING FROM SALT-FREE POLYELECTROLYTES

Excess light scattering intensity

Structure factor

$$\Delta R(q) = K \rho_{pol}^2 N_A S(q)$$

Optical contrast factor

Polymer density

Static light scattering provides a way to measure the osmotic compresibility of a two-component solution

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In combination with $\Pi = k_B T f c$, this provides a way to measure the fraction of free counterions

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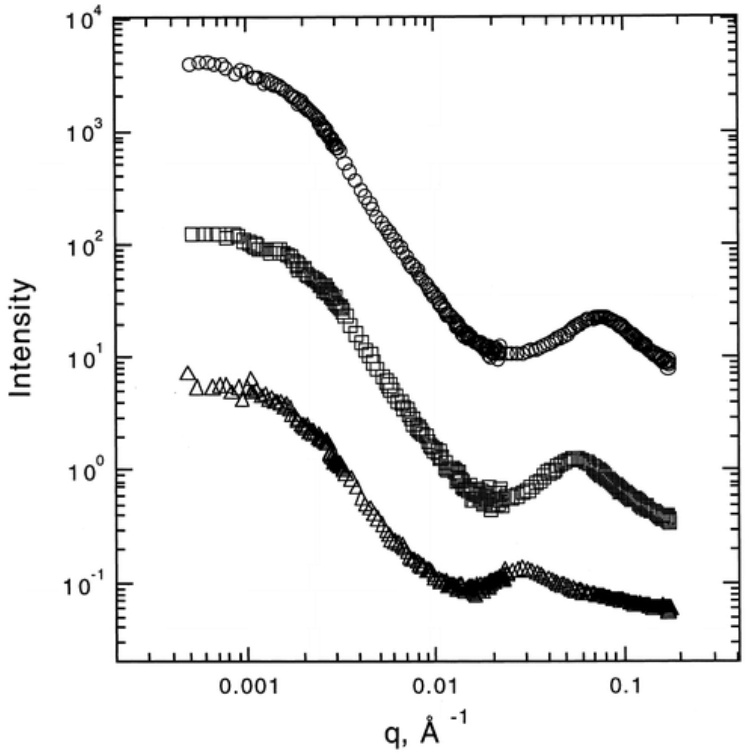
SANS/SLS




**Theory expects extremely weak scattering by polyelectrolytes at low $q$ but experiments show a huge low-$q$ upturn**



Ermi, B.D. and Amis, E.J., 1998. Domain structures in low ionic strength polyelectrolyte solutions. *Macromolecules*, *31*(21), pp.7378-7384.

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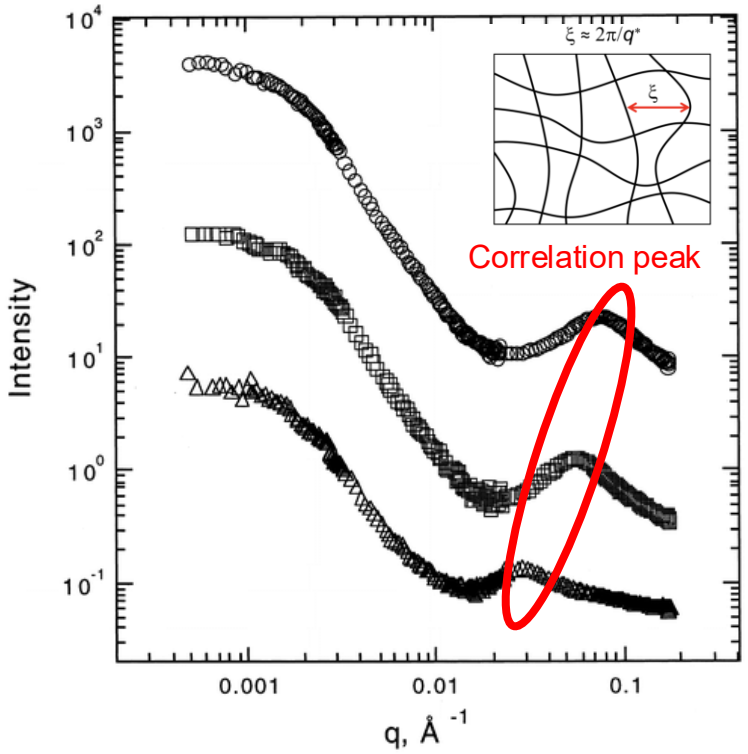


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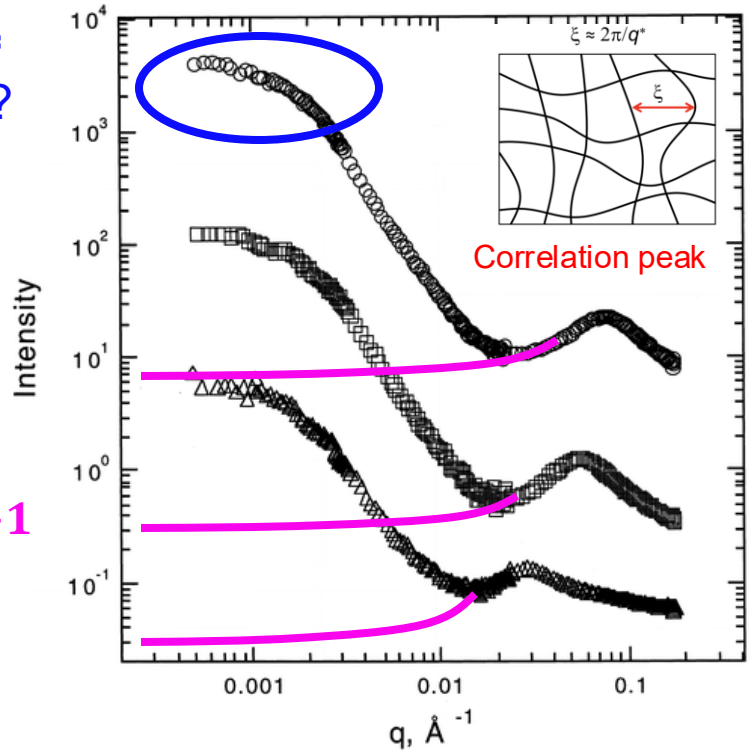
# SCATTERING FROM SALT-FREE POLYELECTROLYTES

SANS/SLS

Low $q$ upturn ≈ large domains?




$$S(0) = f^{-1}$$

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DLS

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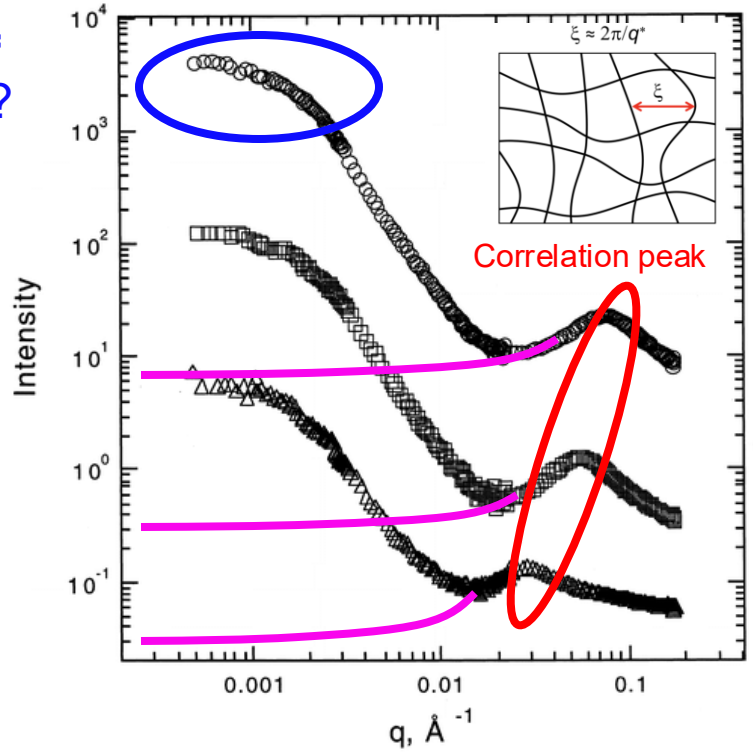


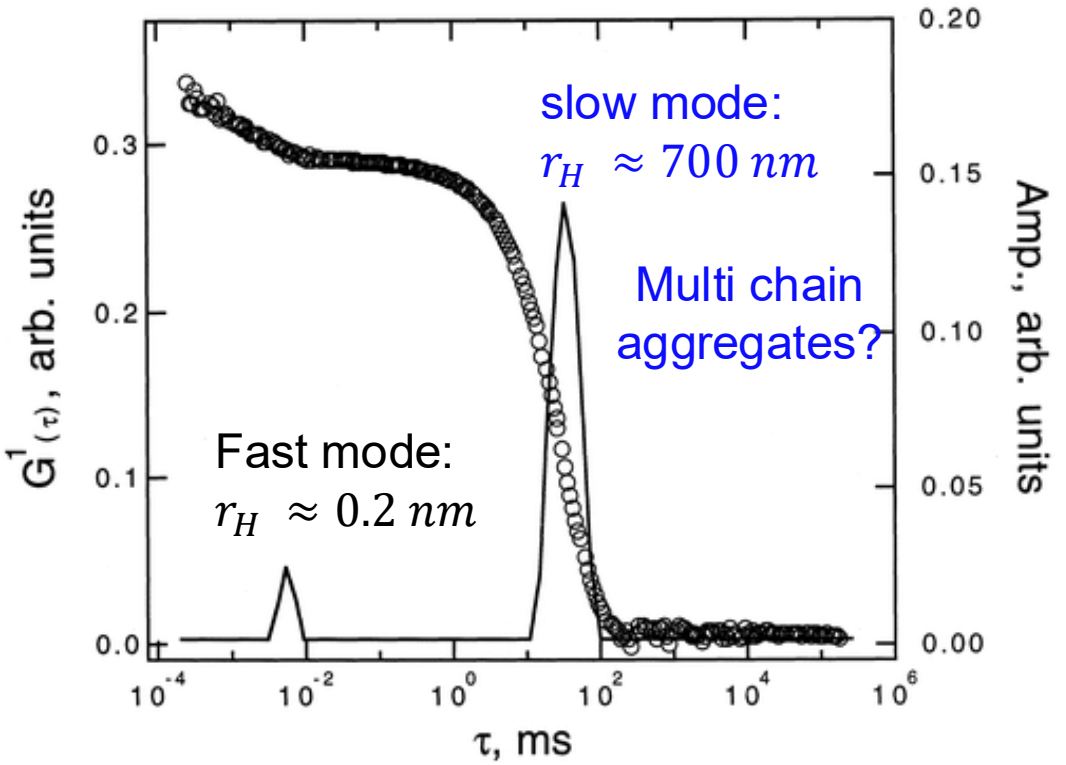


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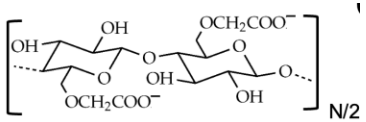
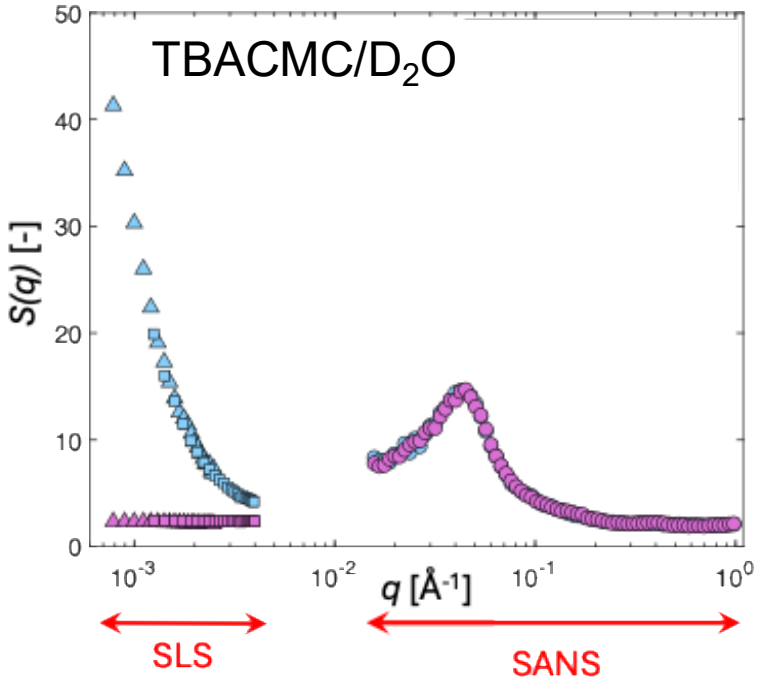
# FILTRATION (MOSTLY) REMOVES LOW-*Q* UPTURN




**SANS/SLS**




| Filter |
| --- |
| 0.1 μm pore size |
| 0.8 μm pore size |

- **Filtration through sufficiently small pores suppresses upturn & slow mode.**
- **Mesh size is not affected by filtration → no polymer removed (density measurements further support this)**
- **Solutions are stable for at least 1 month**

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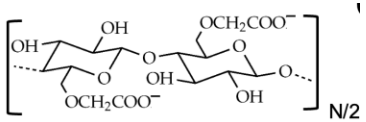


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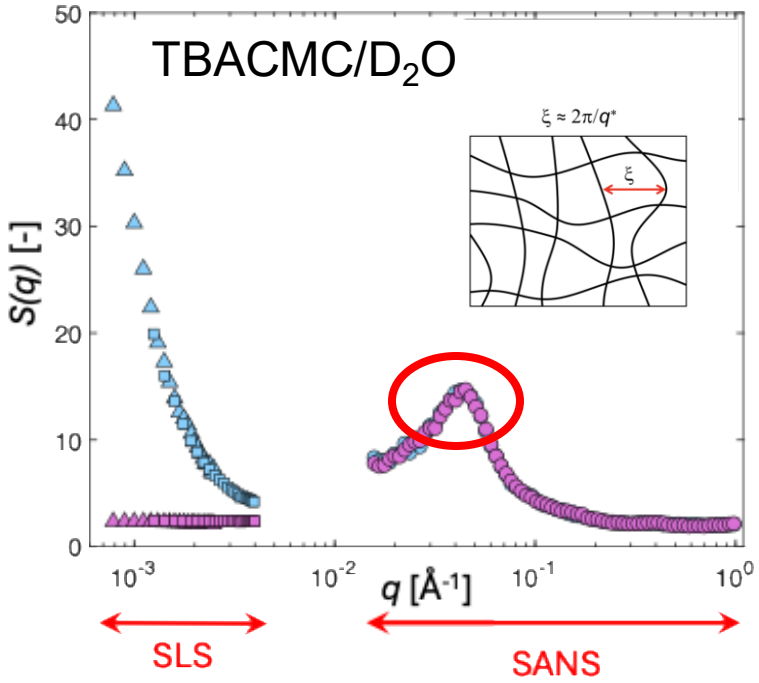


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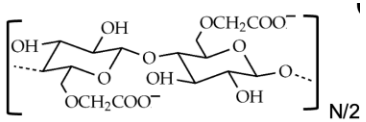


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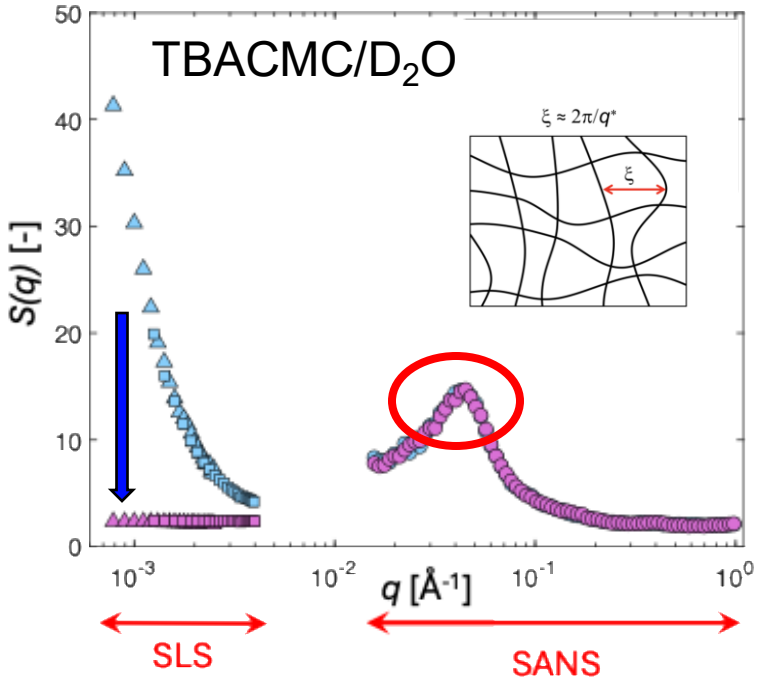


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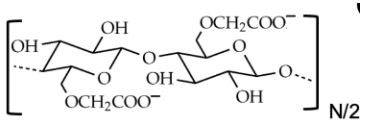


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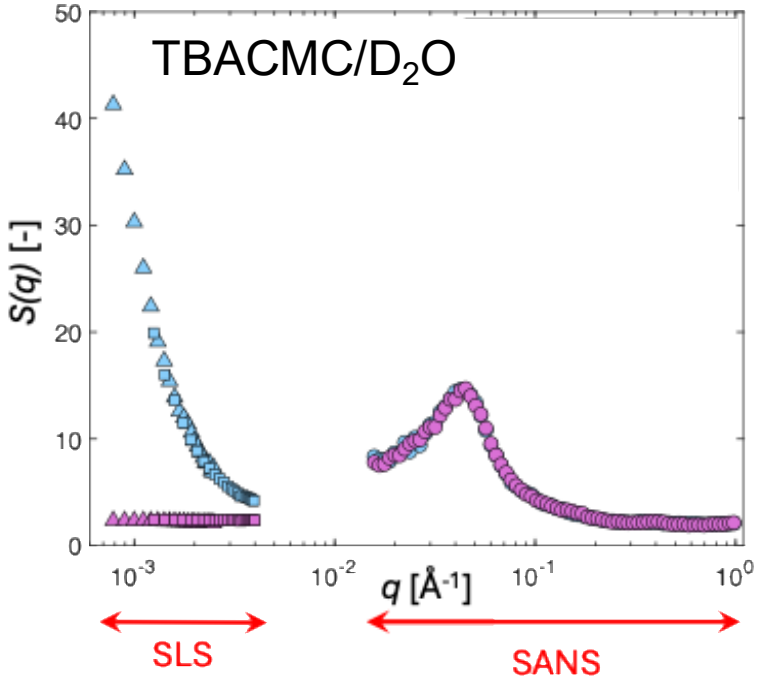


Filter
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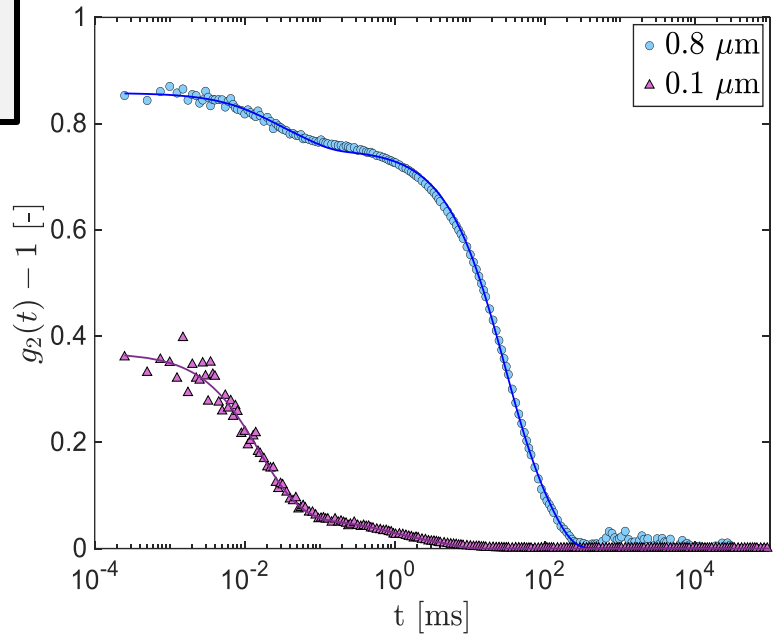
**DLS**

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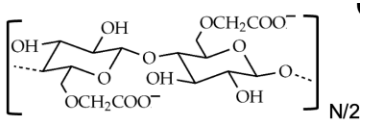


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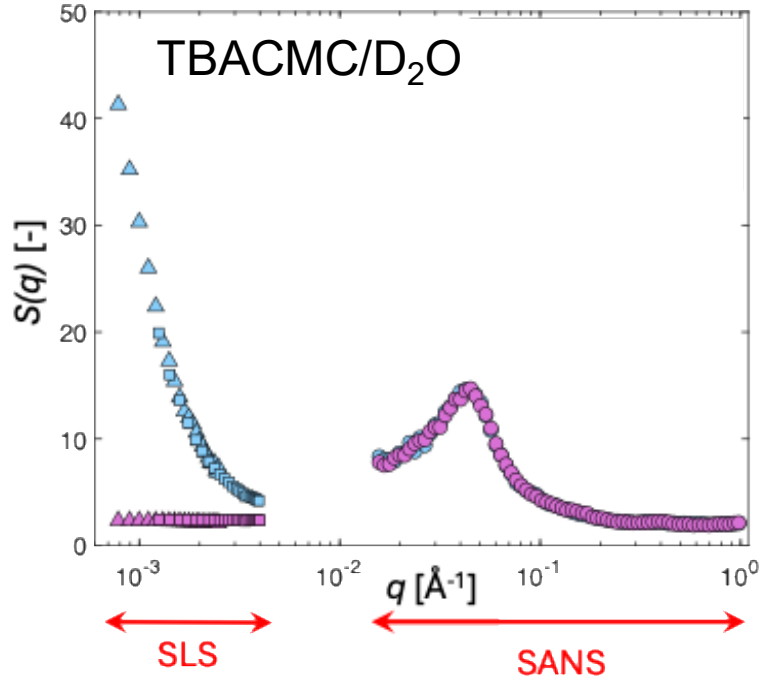


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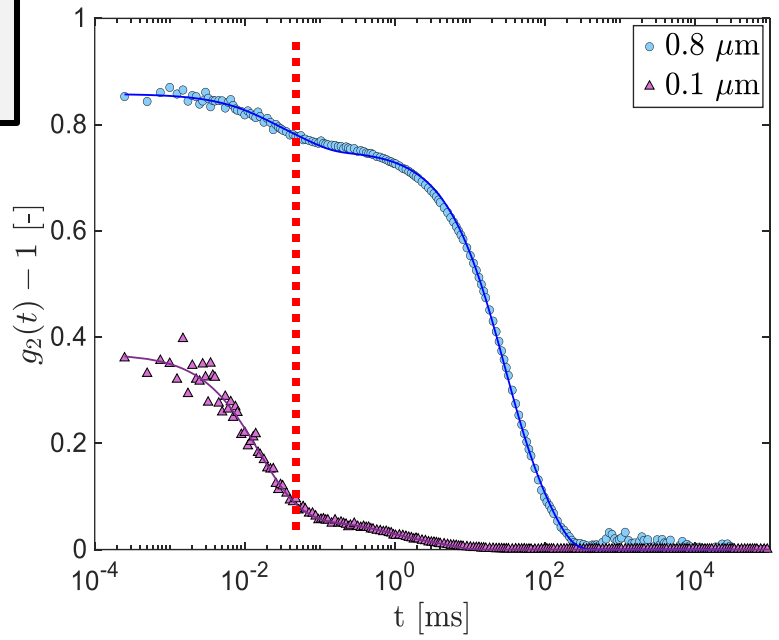


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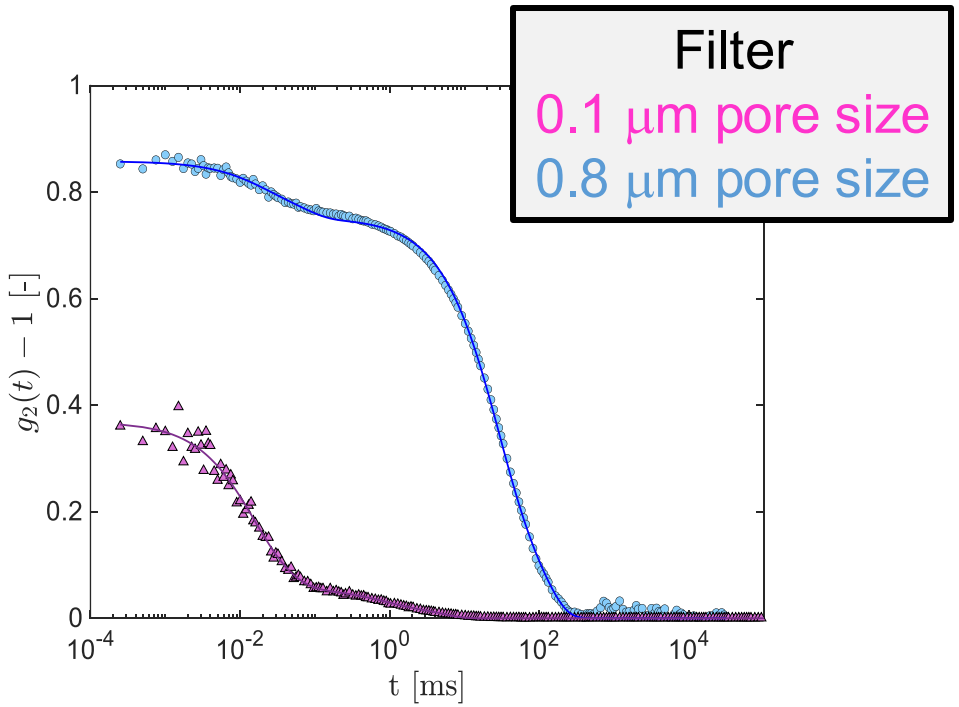
# CAN WE COMPLETELY REMOVE THE LOW-Q UPTURN?

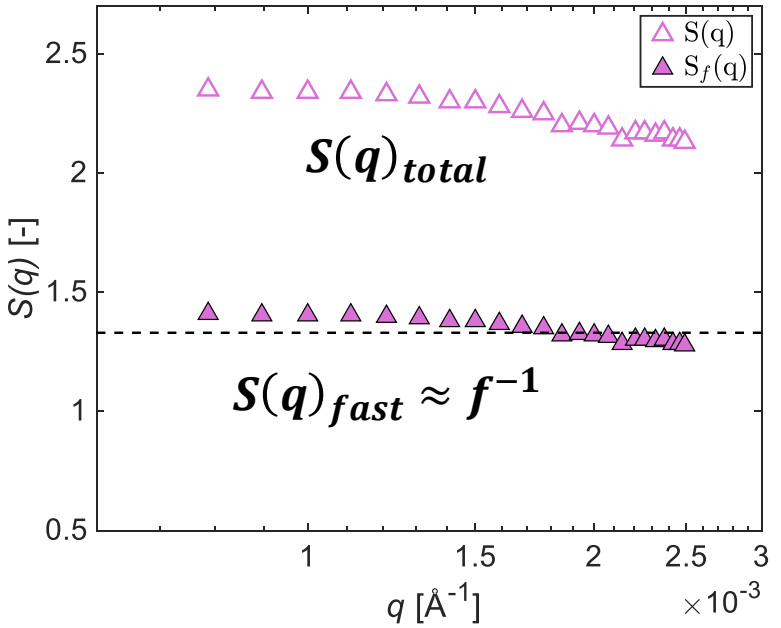
Fit autocorrelation function to bimodal decay:

$$g_1(\tau,q) = A_1(q)e^{-\Gamma_1(q)\tau}\left(1+\frac{\mu_{2,1}t^2}{2}\right) + A_2(q)e^{-\Gamma_2(q)\tau}\left(1+\frac{\mu_{2,2}t^2}{2}\right)$$




The relative amplitude of the fast decay in DLS is used to isolate the structure factor without the slow mode:

$$S(q)_{fast} = \frac{A_1(q)}{A_1(q)+A_2(q)}S(q)$$



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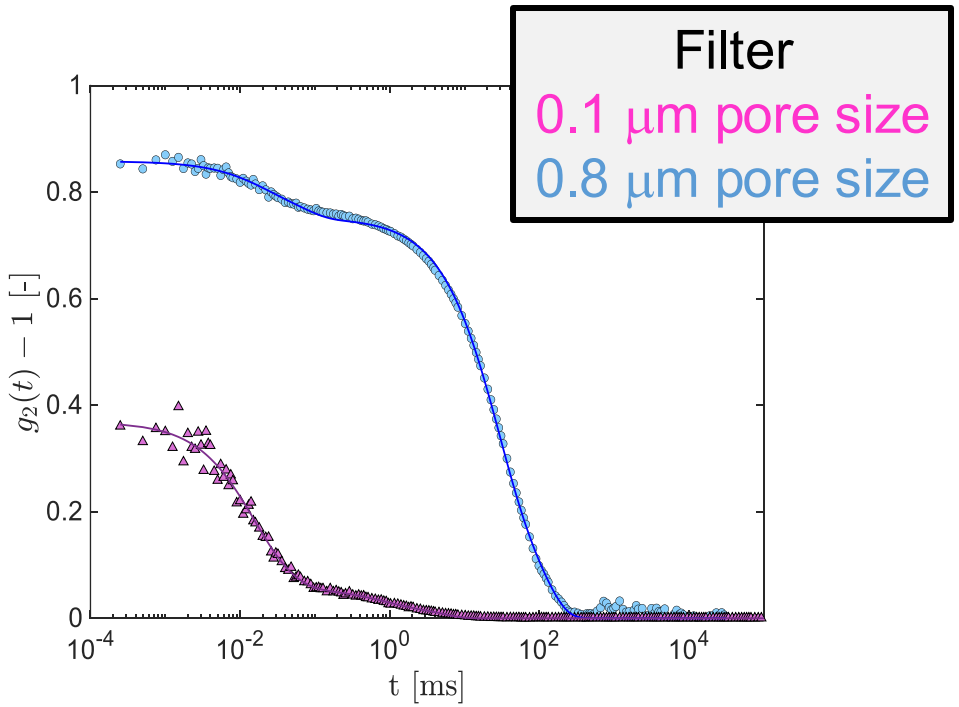


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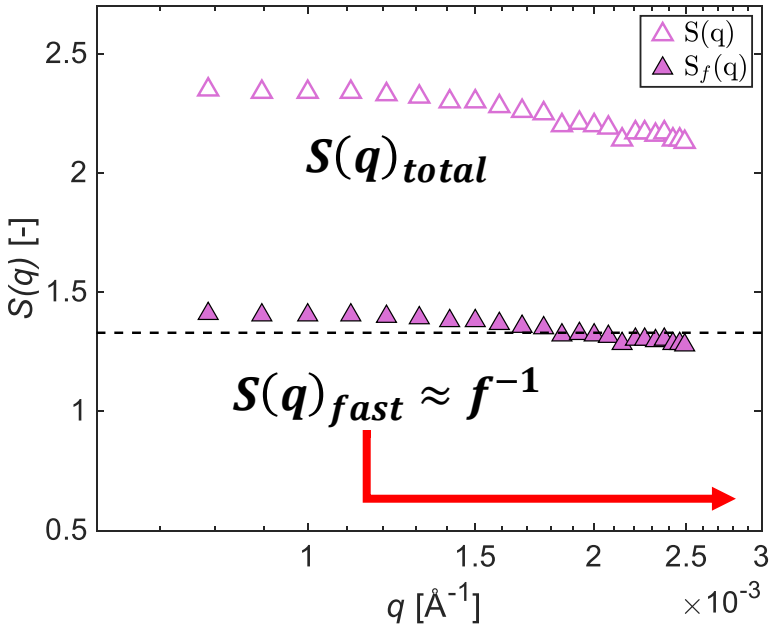


$f \approx 0.7$

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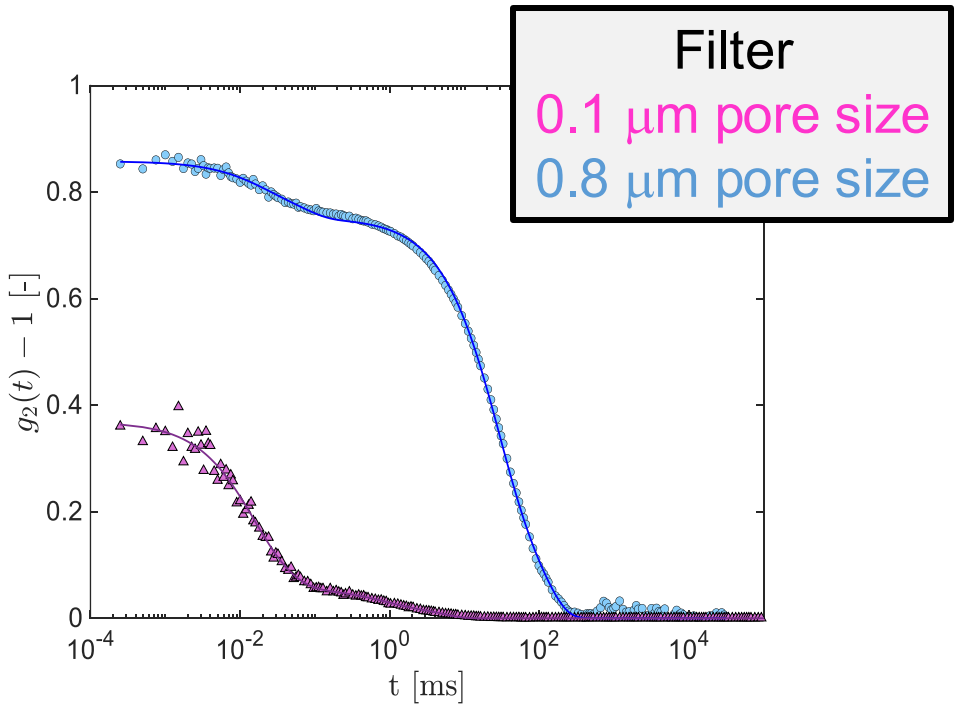


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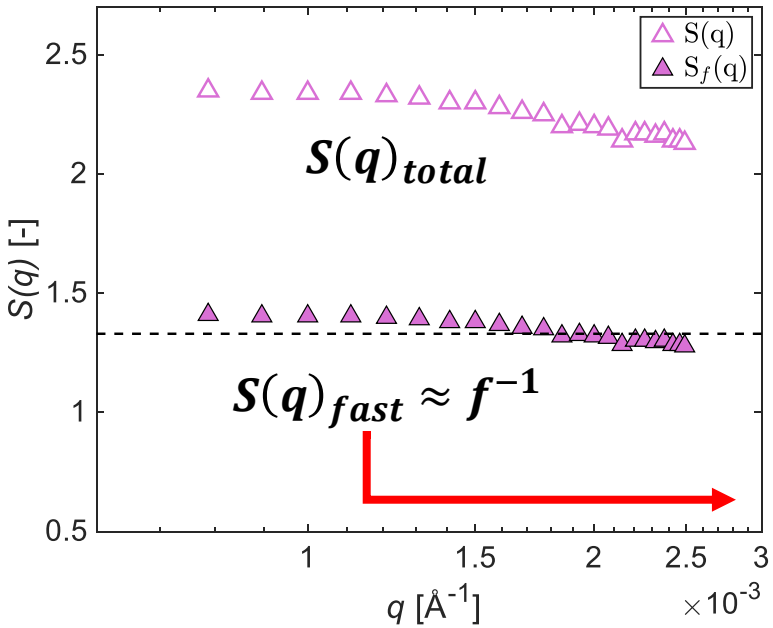
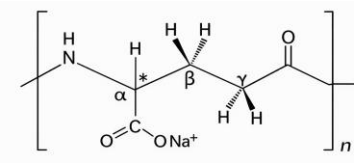
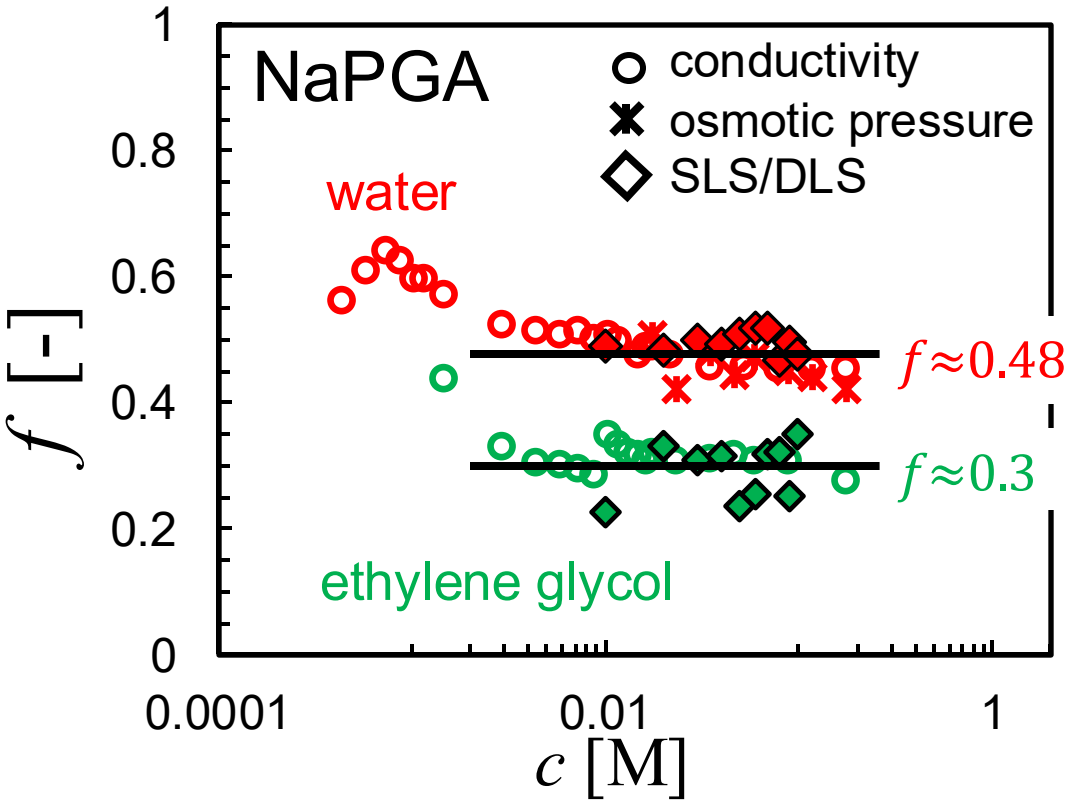


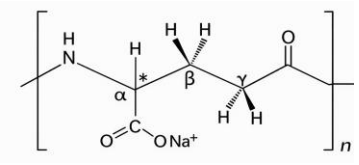

$f \approx 0.7$
$f_{cond} \approx 0.6$
***not bad!***



# SLS/DLS METHOD: POLYGLUTAMIC ACID




**Osmotic pressure measured by SLS after removing the slow mode contribution with DLS splitting gives the correct osmotic pressure**



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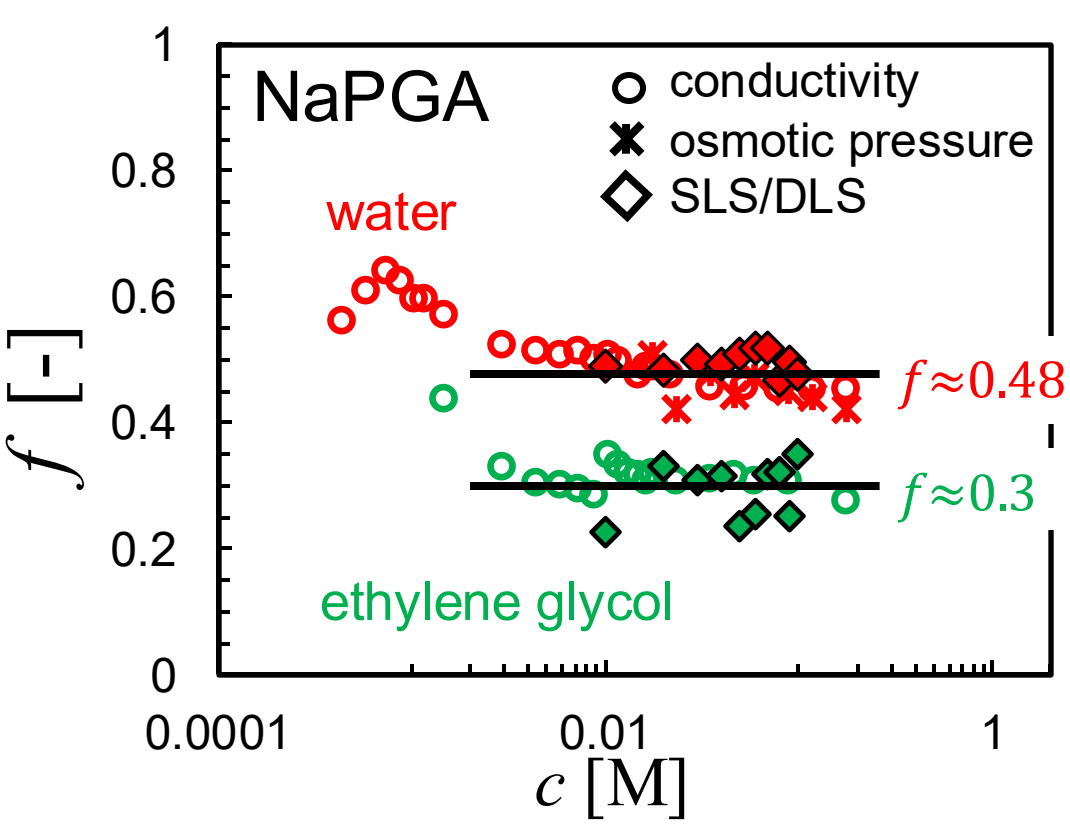


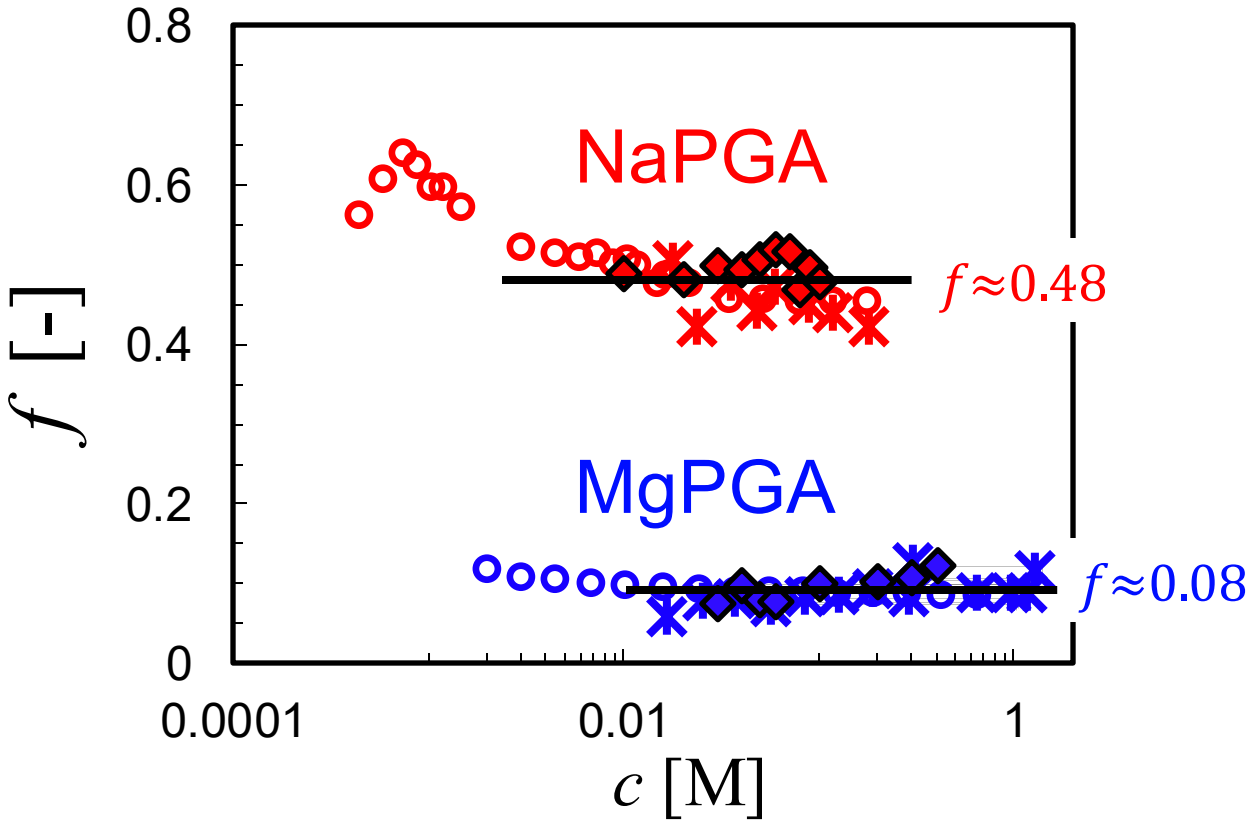


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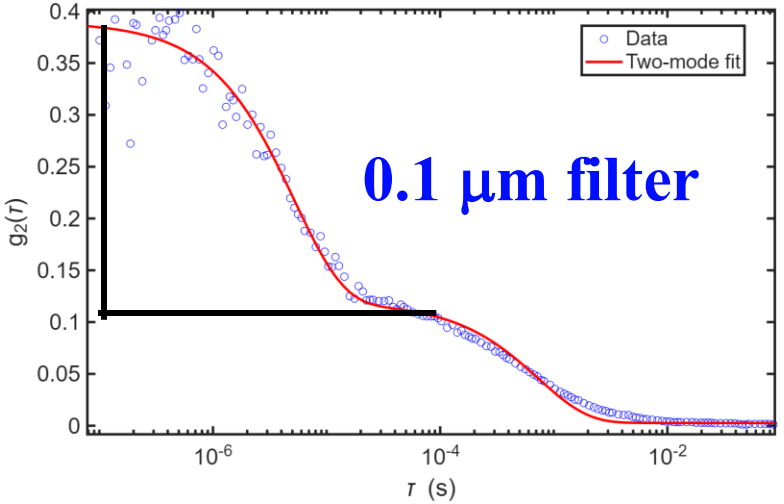
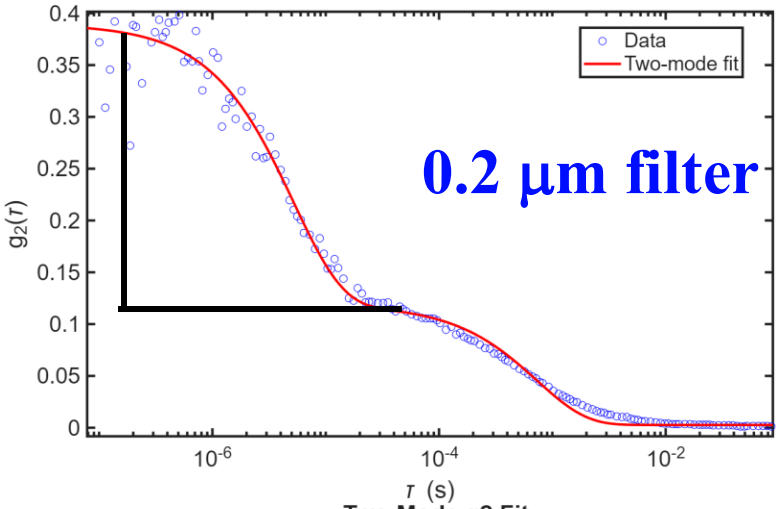
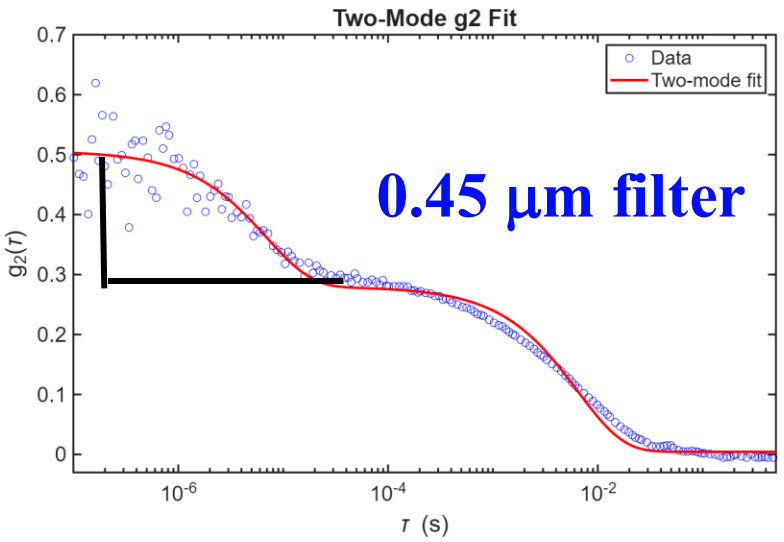
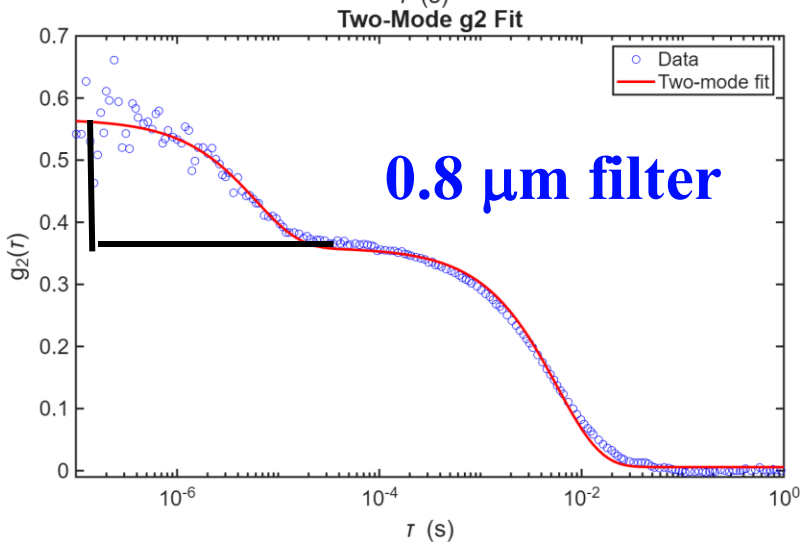
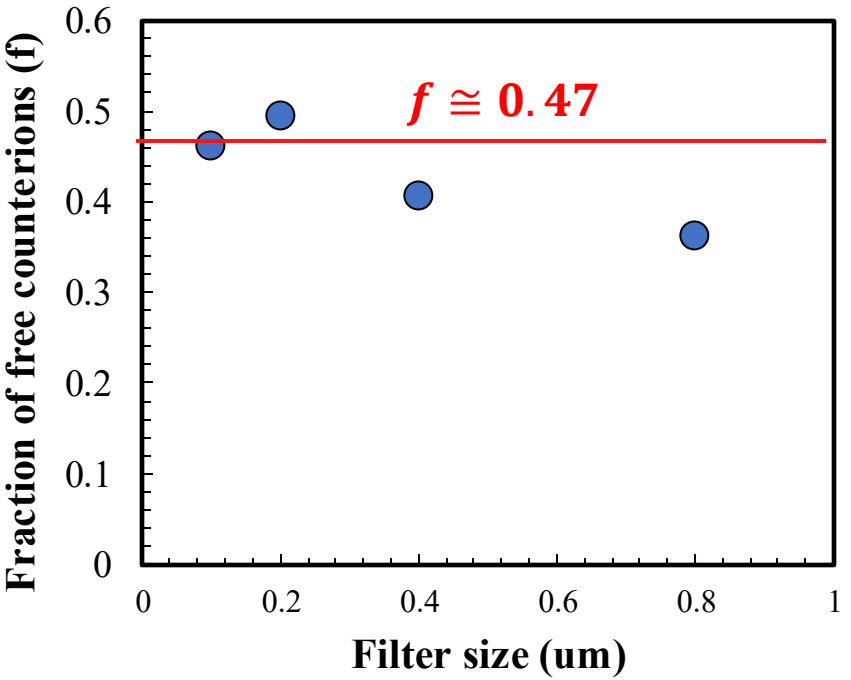
# VARYING FILTER SIZE



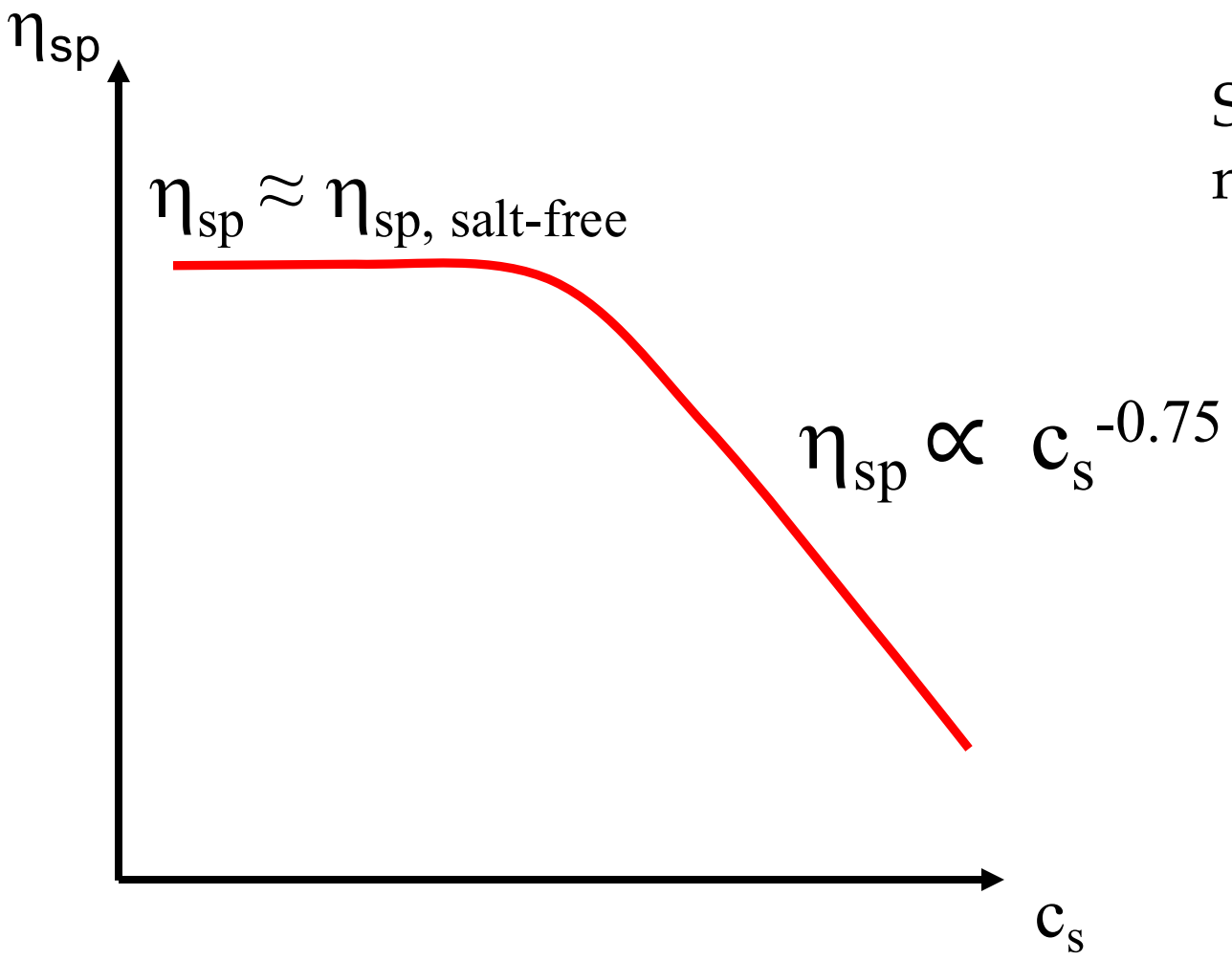




**While the slow mode becomes more prominent as the filter size increase, *f* remains constant, as it should**

# VISCOSITY METHOD




Scaling theory predicts for semidilute non-entangled solutions:

$$\eta_{sp}(c_S) = \frac{\eta(0)}{\left[1 + \frac{2c_S}{f c_p}\right]^{0.75}}$$



Matsumoto, A., Ikeda, M., Sugihara, S. and Maeda, Y., 2025. Nihon Reoroji Gakkaishi, 53(1), pp.1-10.
Dobrynin, A.V., Colby, R.H. and Rubinstein, M., 1995. Macromolecules, 28(6), pp.1859-1871.

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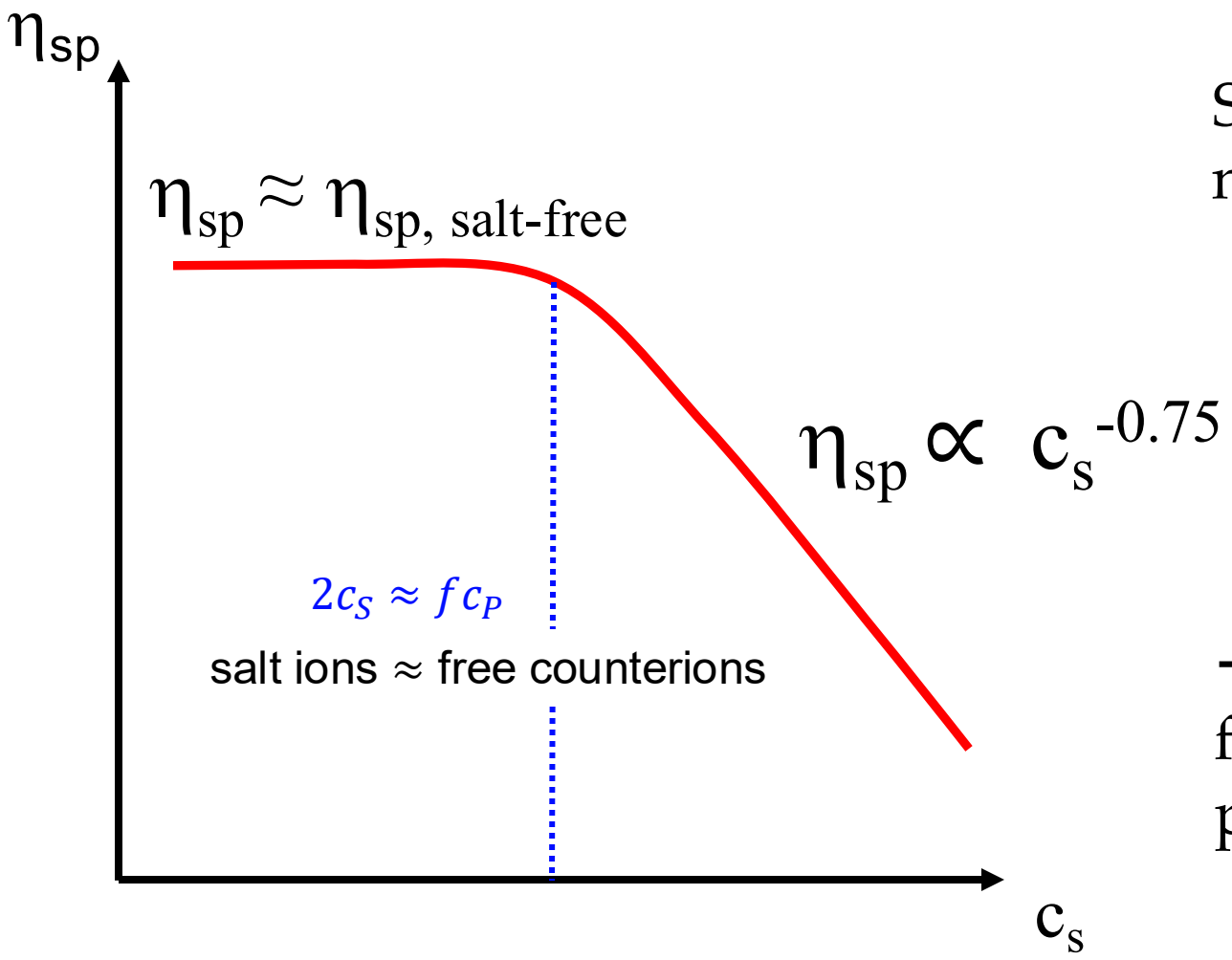


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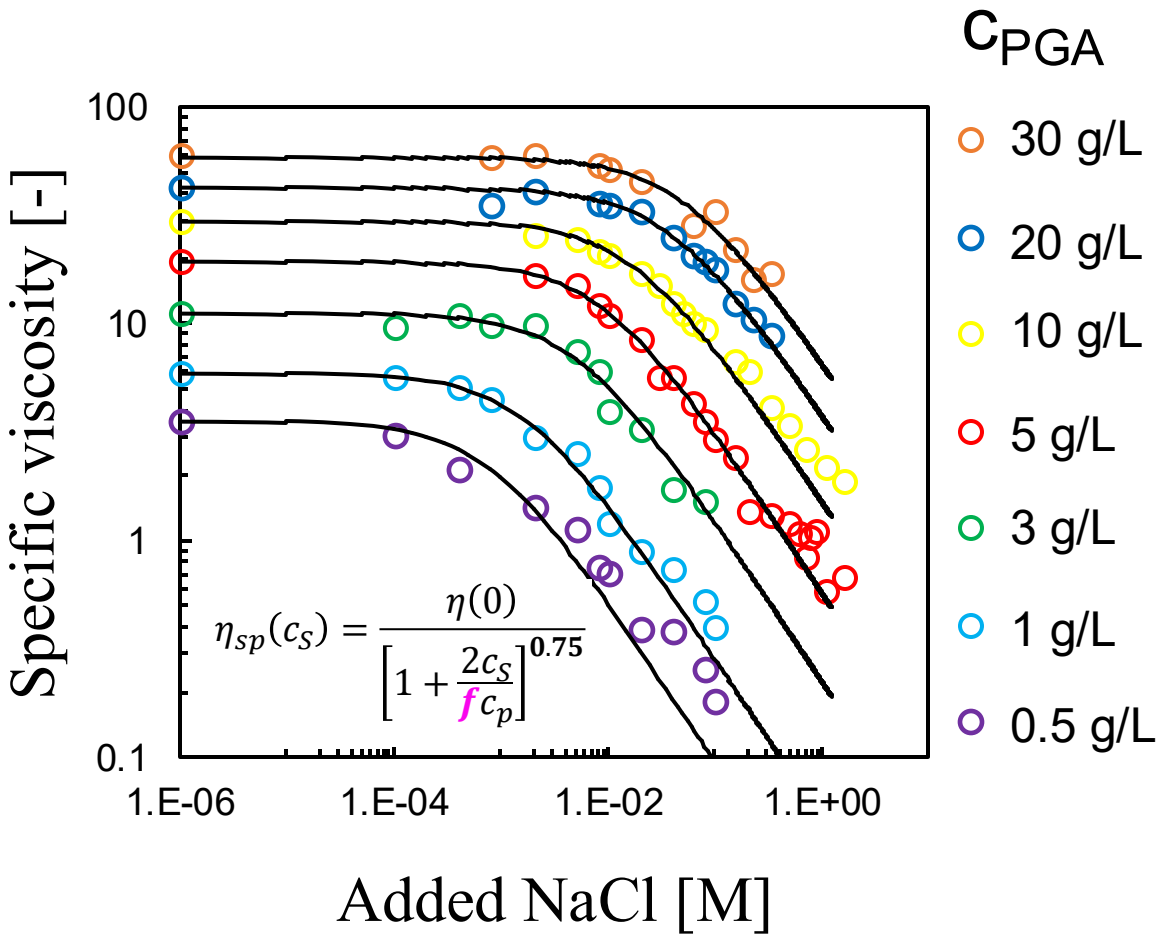
$$\eta_{sp}(c_S) = \frac{\eta(0)}{\left[1 + \frac{2c_S}{f c_p}\right]^{0.75}}$$

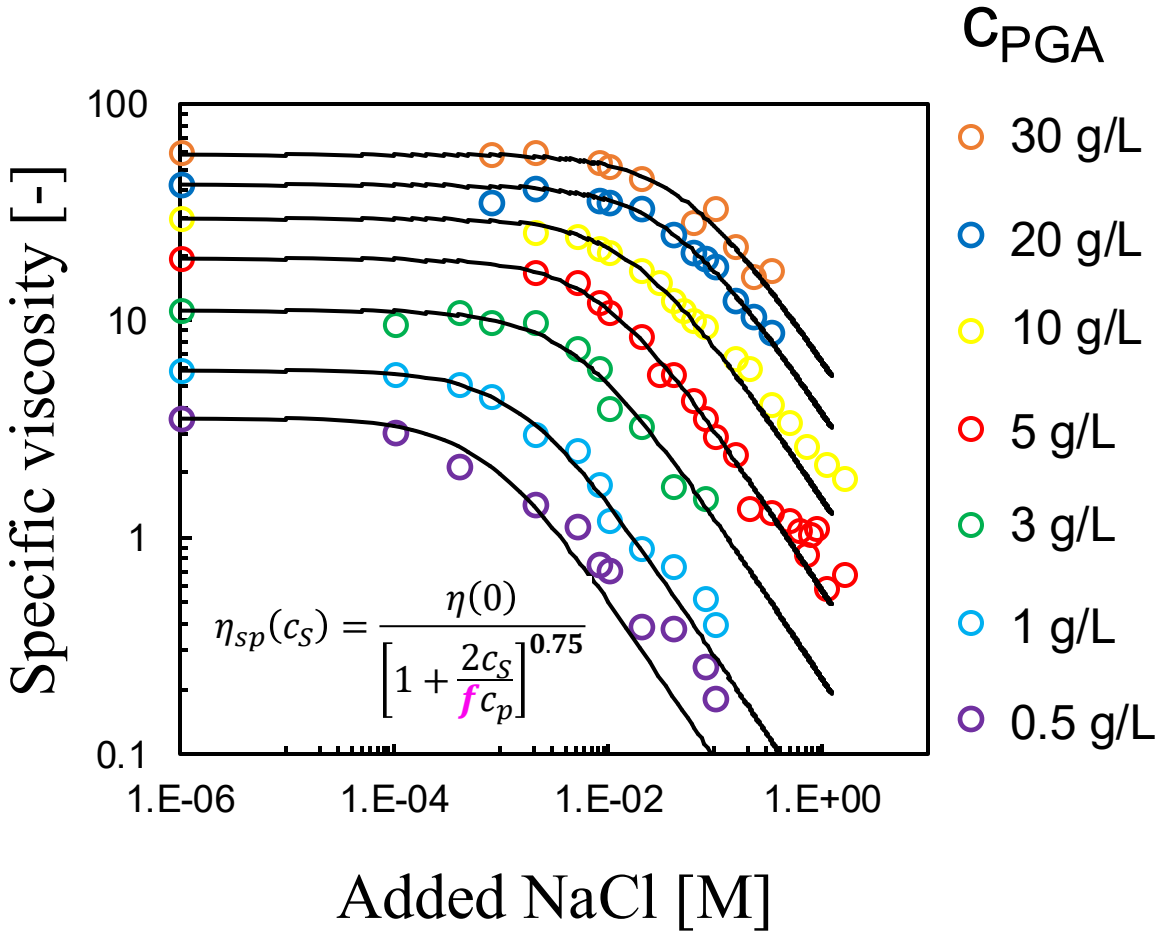
→ Measuring the viscosity as a function of added salt concentration provides a way of estimating $f$

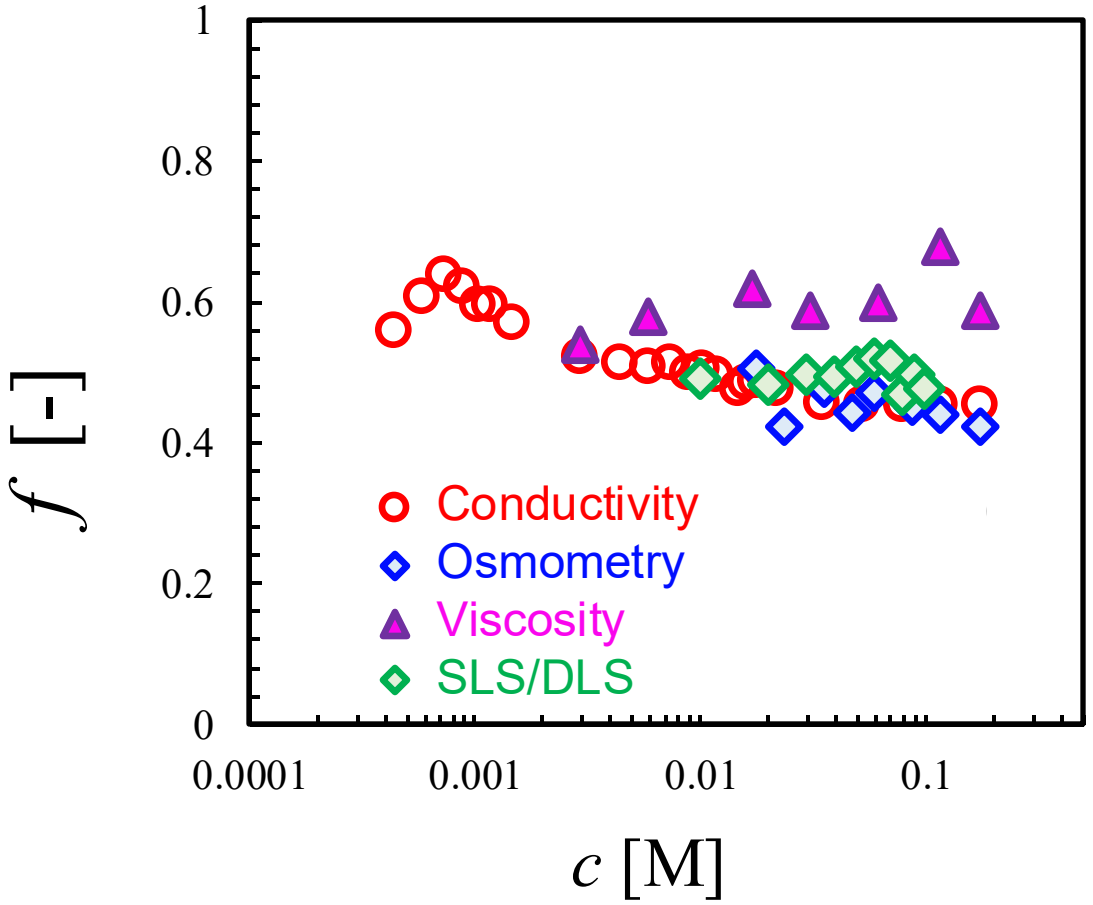

Matsumoto, A., Ikeda, M., Sugihara, S. and Maeda, Y., 2025. Nihon Reoroji Gakkaishi, 53(1), pp.1-10.
Dobrynin, A.V., Colby, R.H. and Rubinstein, M., 1995. Macromolecules, 28(6), pp.1859-1871.

# VISCOSITY METHOD: NaPGA/water

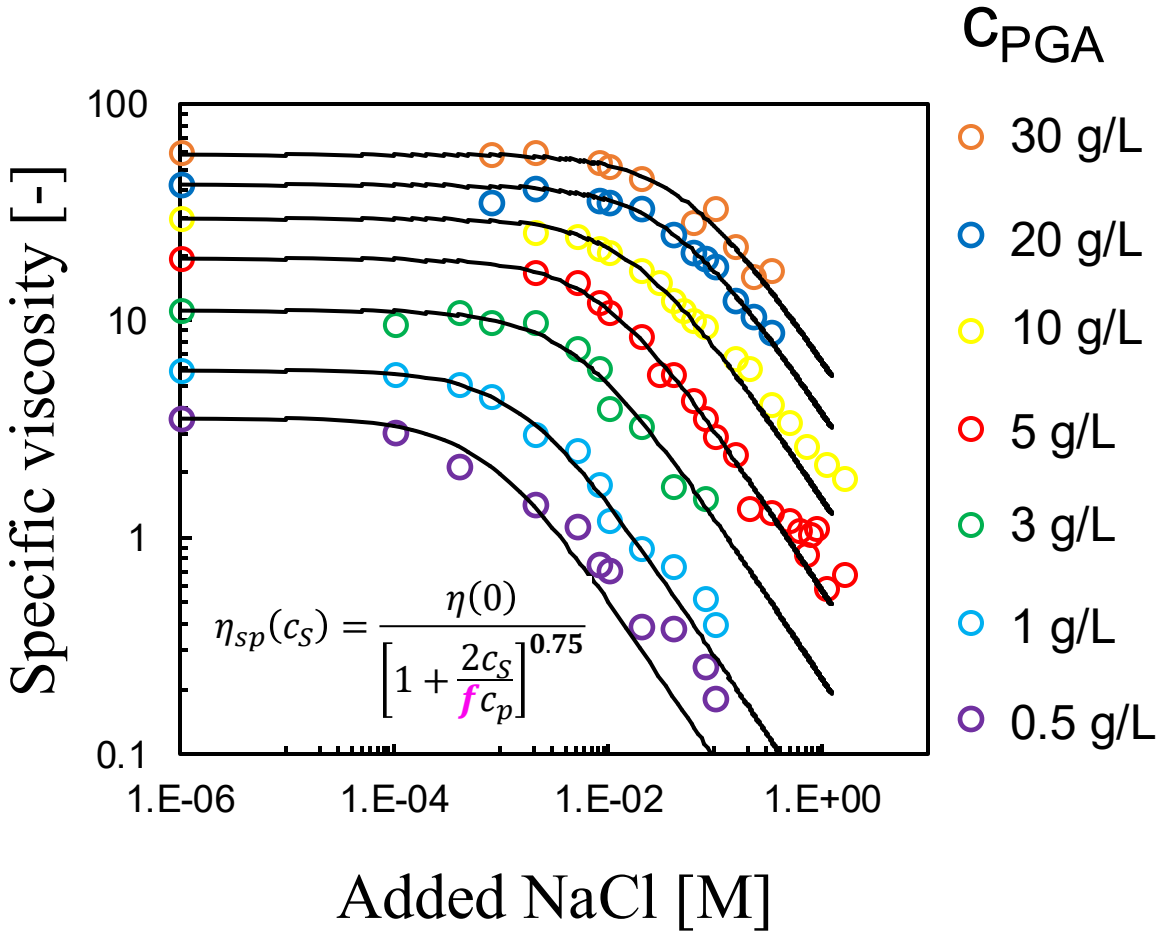


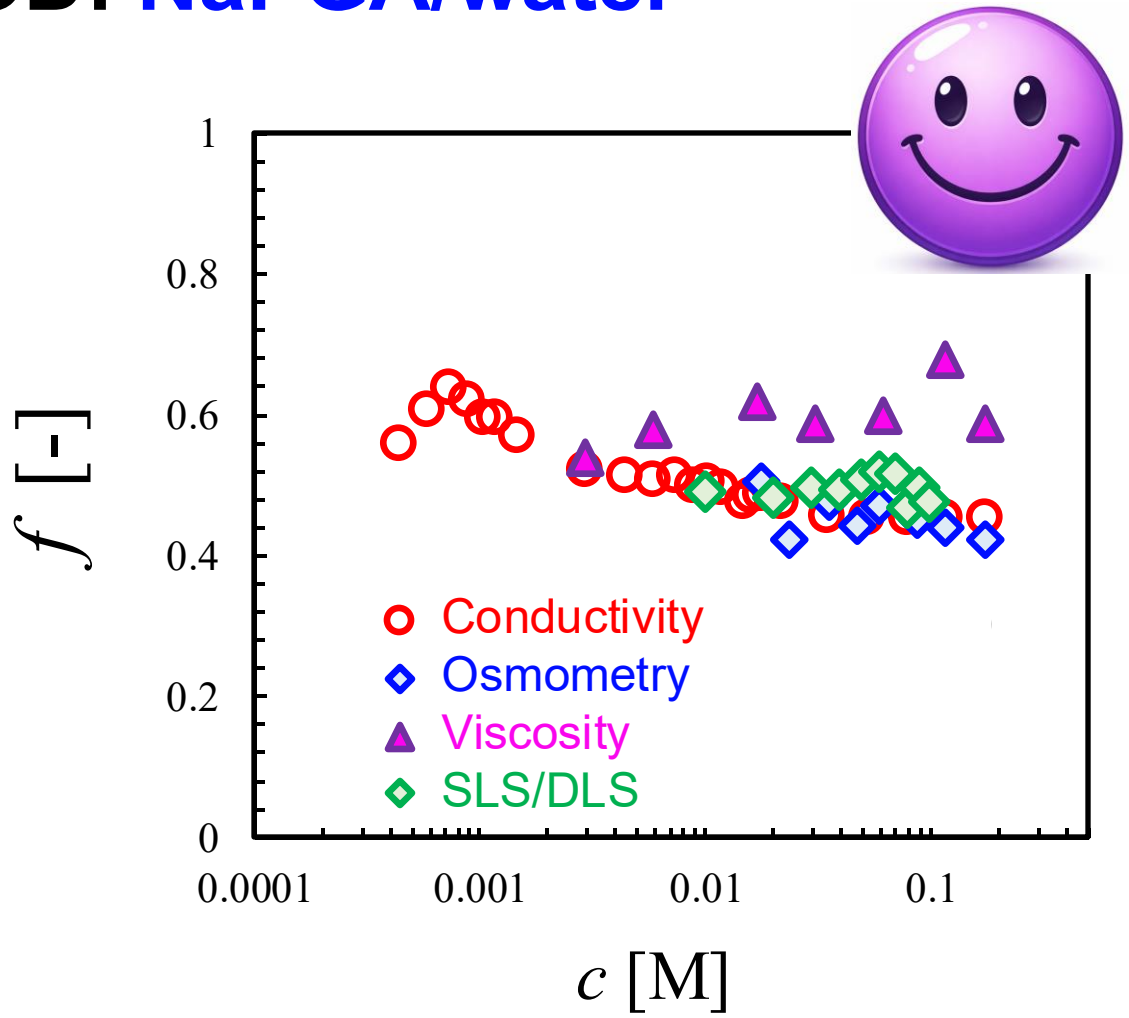
# VISCOSITY METHOD: NaPGA/water



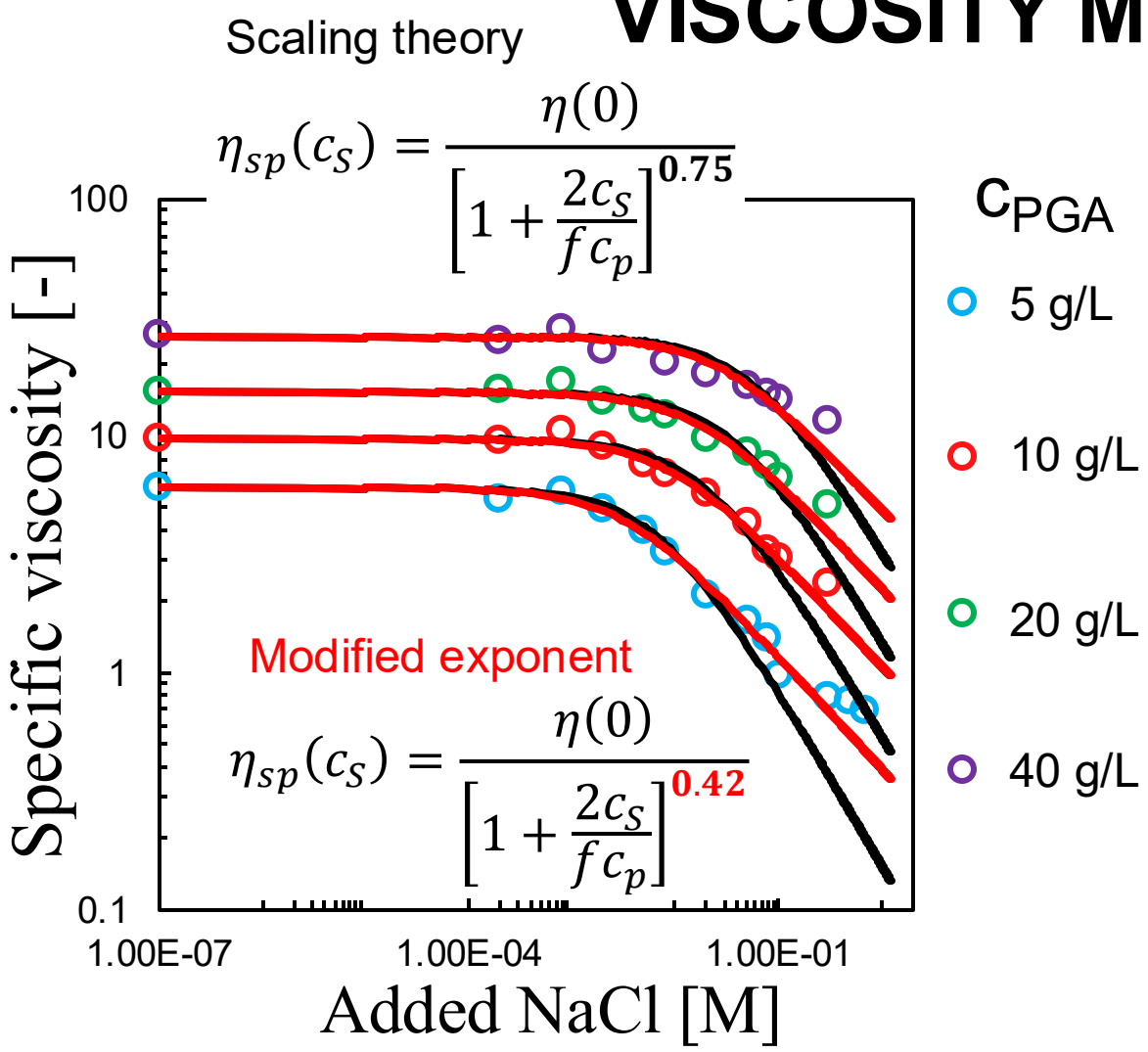
# VISCOSITY METHOD: NaPGA/water




**Reasonable agreement between viscosity and other methods**

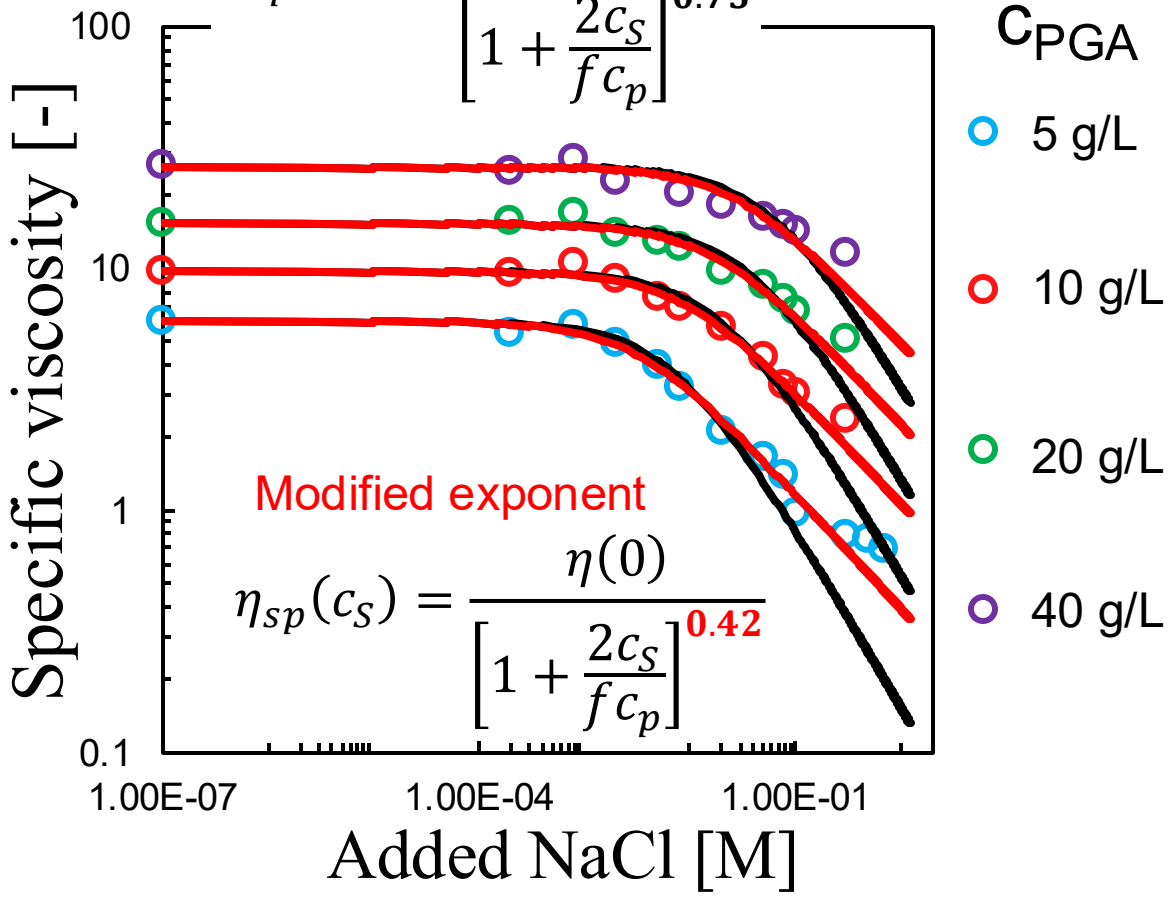
# VISCOSITY METHOD: NaPGA/ethylene glycol

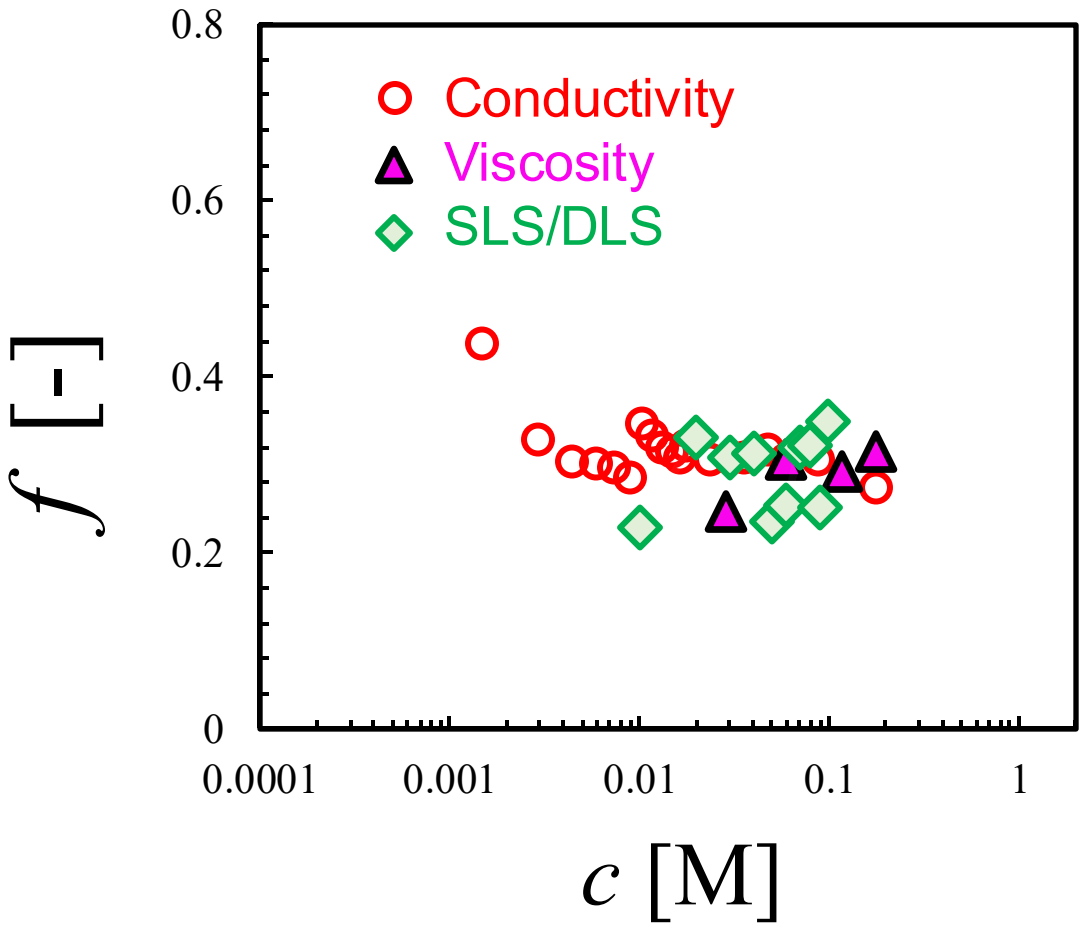


# VISCOSITY METHOD: NaPGA/ethylene glycol

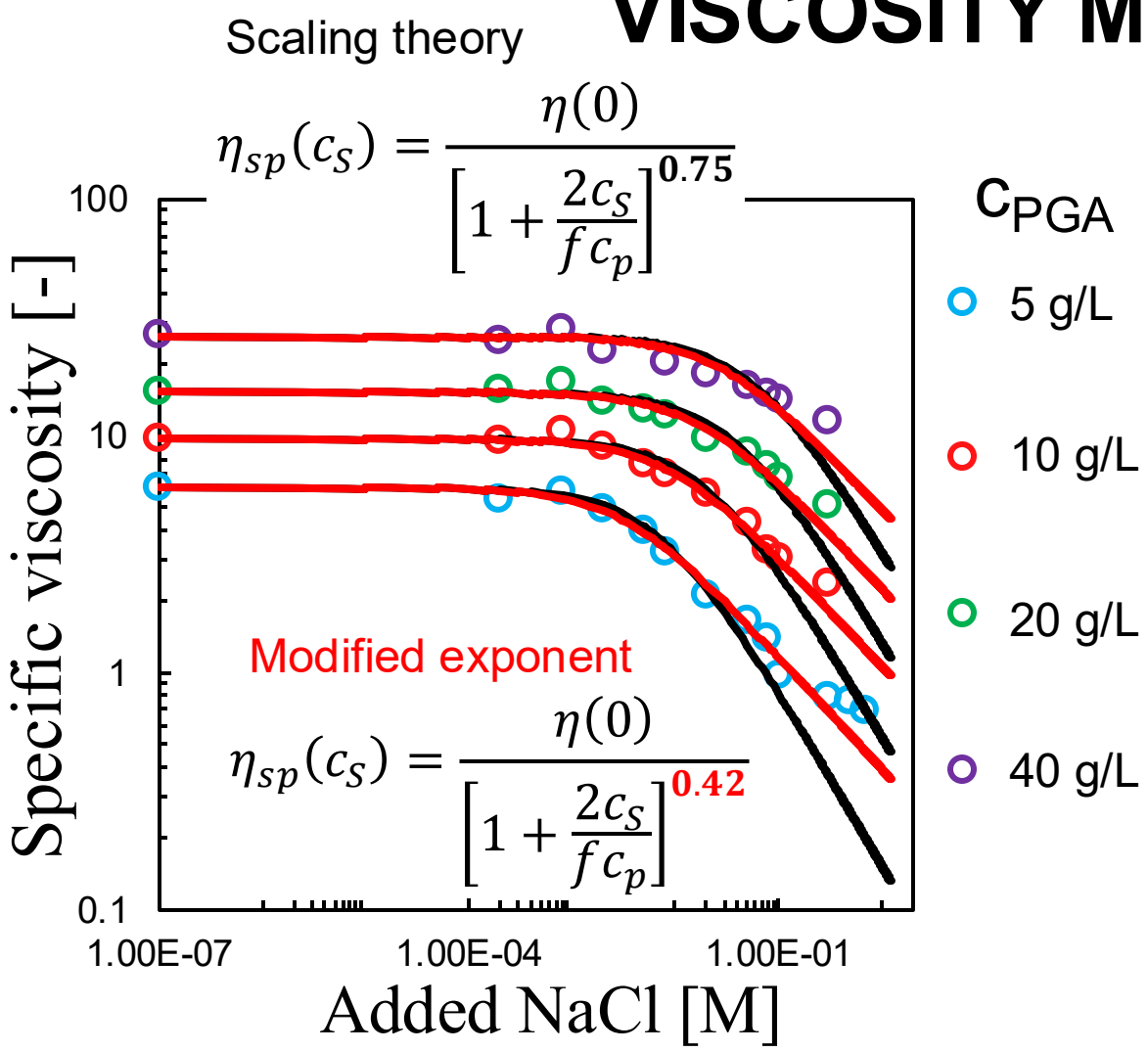
Scaling theory

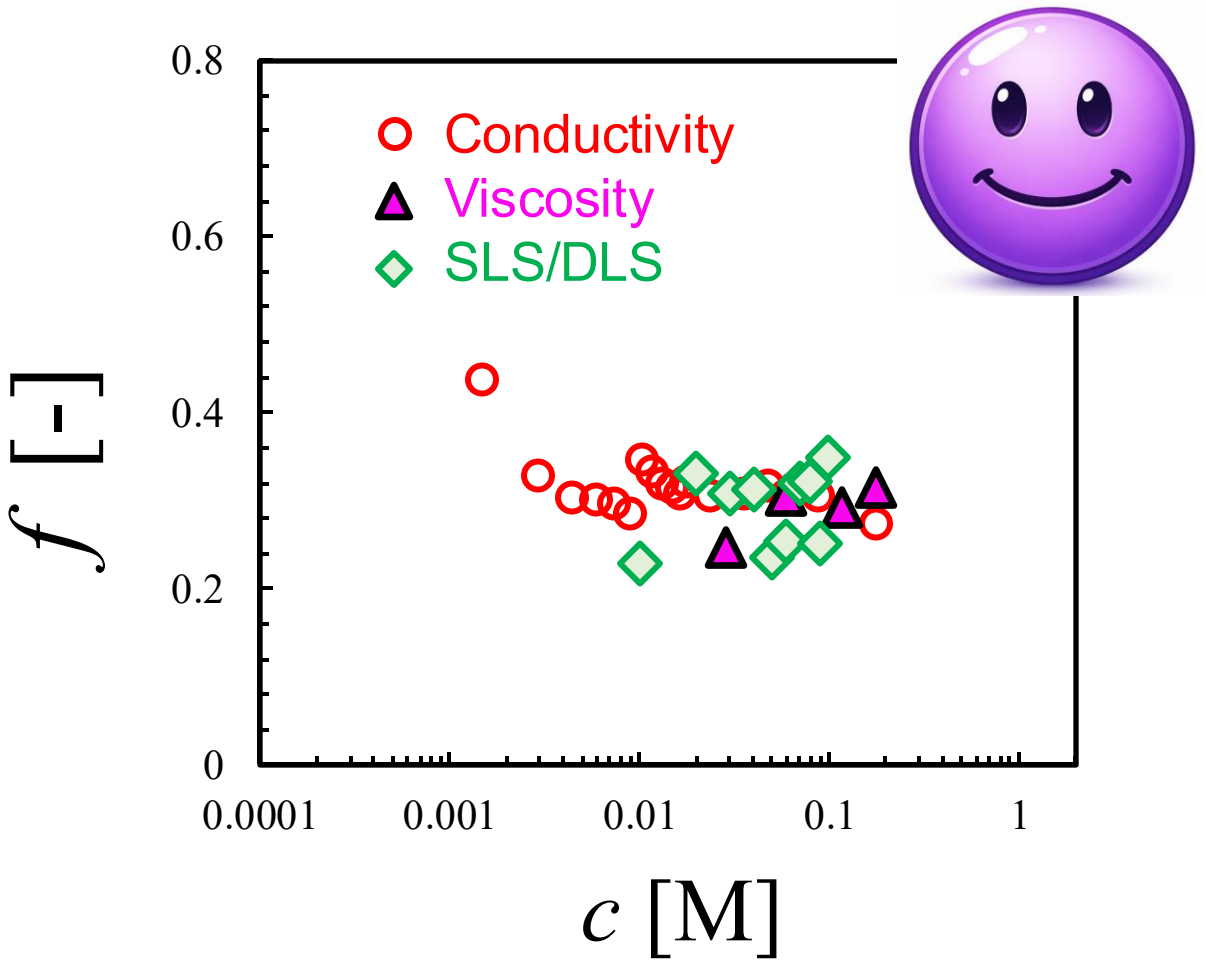
$$\eta_{sp}(c_S) = \frac{\eta(0)}{\left[1 + \frac{2c_S}{f c_p}\right]^{0.75}}$$



# VISCOSITY METHOD: NaPGA/ethylene glycol






**Reasonable agreement between viscosity and other methods, but we need to use a modified exponent, not predicted by theory**

# CONCLUSIONS

- Combined static and dynamic **light scattering offers a way to measure the osmotic pressure of polyelectrolytes**.
- The fraction of free counterions can be derived from such measurements.
- Main advantages of SLS/DLS over membrane osmometry or freezing point depression: 1) it can be easily applied to organic solvents, 2) it becomes *more* sensitive as the fraction of free counterions decreases.
- **Viscosity vs. added** salt measurements can also be used to estimate the fraction of free counterions. Experimental results deviate from the theoretical prediction, therefore the method is semi-empirical at this point.

# ACKNOWLEDGEMENTS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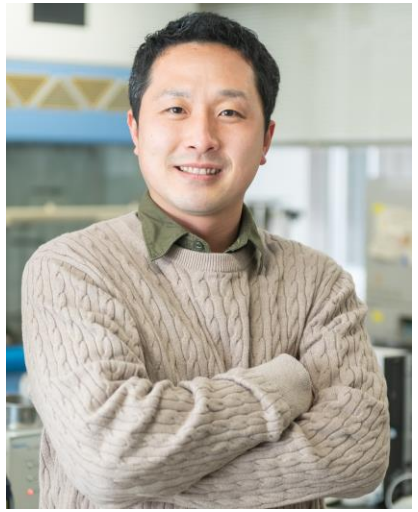

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Japan Atomic Energy Agency JRR-3

Japan Research Reactor-3


Slides:

Pre-print: