

# COUNTERION CONDENSATION IN POLYELECTROLYTE SOLUTIONS

Slides:

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<https://polyelectrolyte.science>



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Okayama 700-8530, Japan

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**PennState**  
College of Earth  
and Mineral Sciences

# OUTLINE

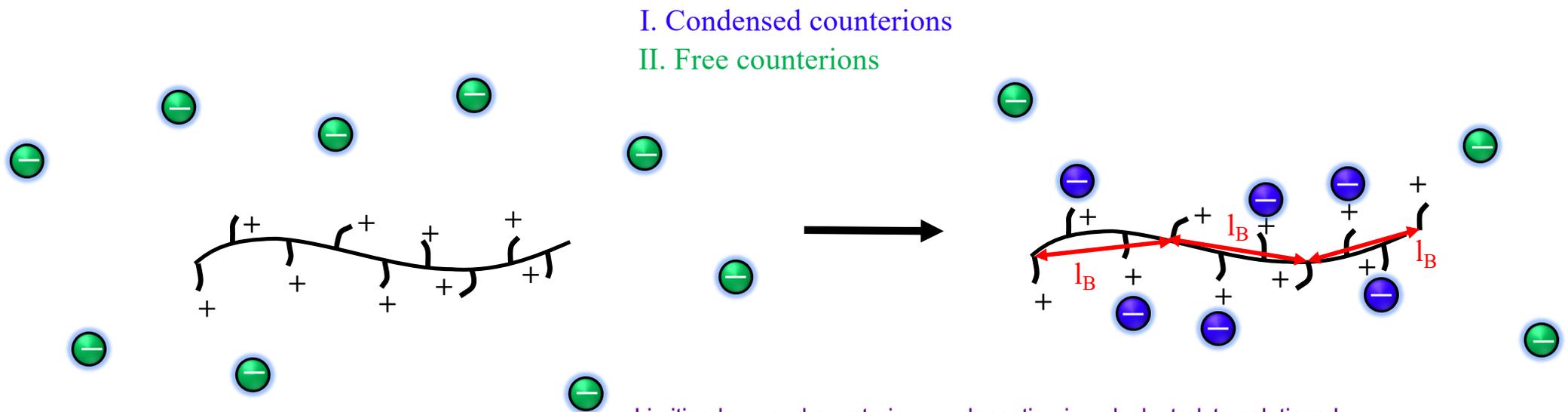
- Oosawa-Manning condensation
- Experimental tests
  - Influence of dielectric constant
  - Influence of charge density
  - Influence of counterion valence
- Ion-pairing



# COUNTERION CONDENSATION (I)

## Oosawa-Manning condensation theory

Counterions will condense onto the chain until the charge density decreases to a value of  $1/Zl_B$ .



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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[CITATION] Polyelectrolytes, Chap. 5

[F Oosawa](#) - (No Title), [1971](#) - cir.nii.ac.jp

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# COUNTERION CONDENSATION (II)



Biophysical Chemistry  
Volume 7, Issue 2, September 1977, Pages 95-102



Limiting laws and counterion condensation in polyelectrolyte solutions: IV. The approach to the limit and the extraordinary stability of the charge fraction

Gerald S. Manning

JOURNAL OF CHEMICAL PHYSICS

VOLUME 120, NUMBER 19

15 MAY 2004

Theory of counter-ion condensation on flexible polyelectrolytes: Adsorption mechanism

M. Muthukumar<sup>a)</sup>

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003



Soft Matter

PAPER

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Cite this: *Soft Matter*, 2022, 18, 1154

Where in the world are condensed counterions?

Qishun Tang <sup>a</sup> and Michael Rubinstein \*<sup>bc</sup>

Evaluation of the Counterion Condensation Theory of Polyelectrolytes

Dirk Stigter

Department of Pharmaceutical Chemistry, University of California, San Francisco, California 94143 USA

PRL **94**, 048302 (2005)

PHYSICAL REVIEW LETTERS

week ending  
4 FEBRUARY 2005

Manning-Oosawa Counterion Condensation

Ben O'Shaughnessy<sup>1,\*</sup> and Qingbo Yang<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Columbia University, New York, NY 10027, USA

<sup>2</sup>Department of Physics, Columbia University, New York, NY 10027, USA

(Received 15 April 2004; published 1 February 2005)

*Journal of Biomolecular Structure and Dynamics*, ISSN 0739-1102  
Volume 1 (1983), ©Adenine Press (1983).

Counter-Ion Condensation and System Dimensionality

**Bruno H. Zimm**  
Department of Chemistry, B-017  
University of California (San Diego)  
La Jolla, California 92093

and

**Marc Le Bret**  
Laboratoire de Physico-Chimie Macromoléculaire,  
Laboratoire associé au CNRS, 147  
Institut Gustave-Roussy  
94800 Villejuif, France

*Macromolecules* 1999, 32, 3481–3487

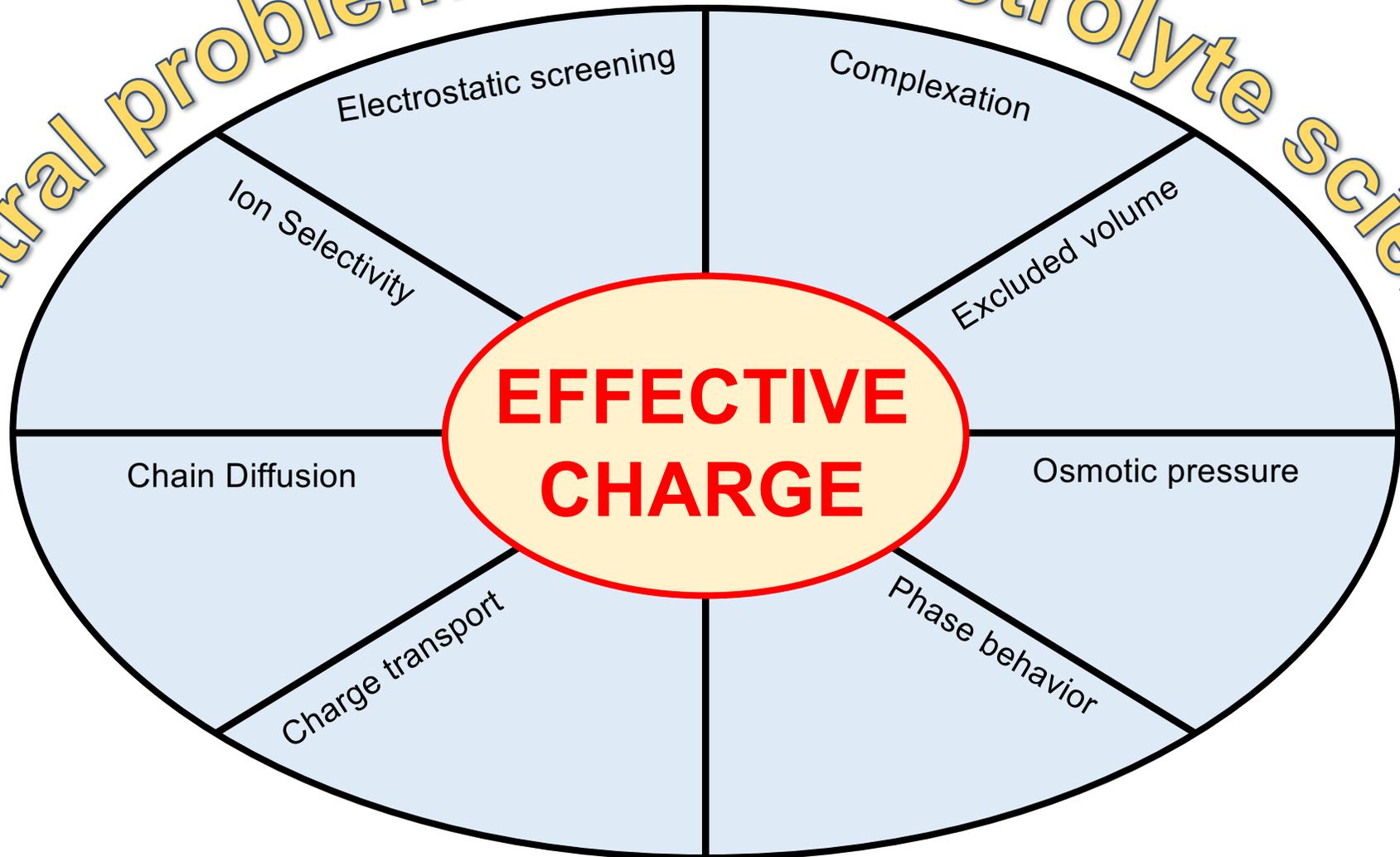
Counterion Condensation in Solutions of Rigid Polyelectrolytes

Rebecca M. Nyquist, Bae-Yeun Ha, and Andrea J. Liu

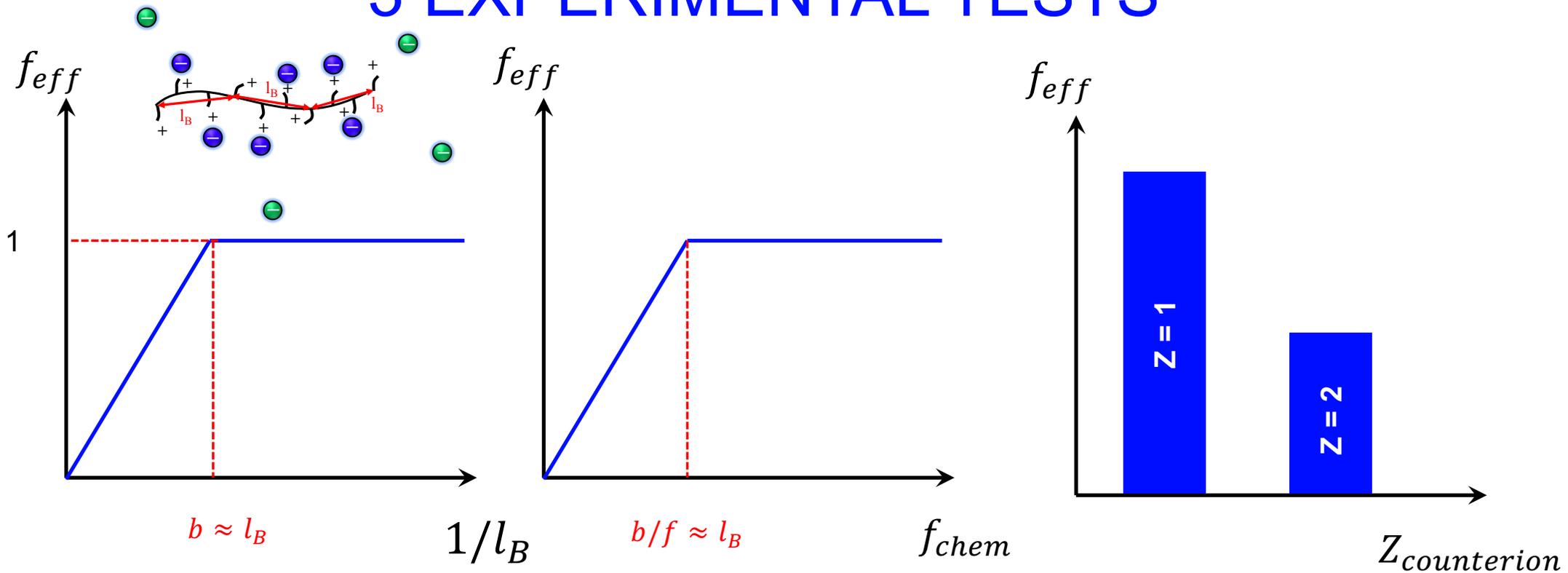
Department of Chemistry and Biochemistry, UCLA, Los Angeles, California 90095

Received July 14, 1998; Revised Manuscript Received November 13, 1998

# Central problem of polyelectrolyte sciences



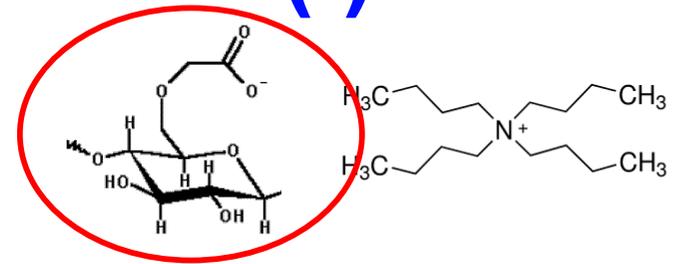
# 3 EXPERIMENTAL TESTS



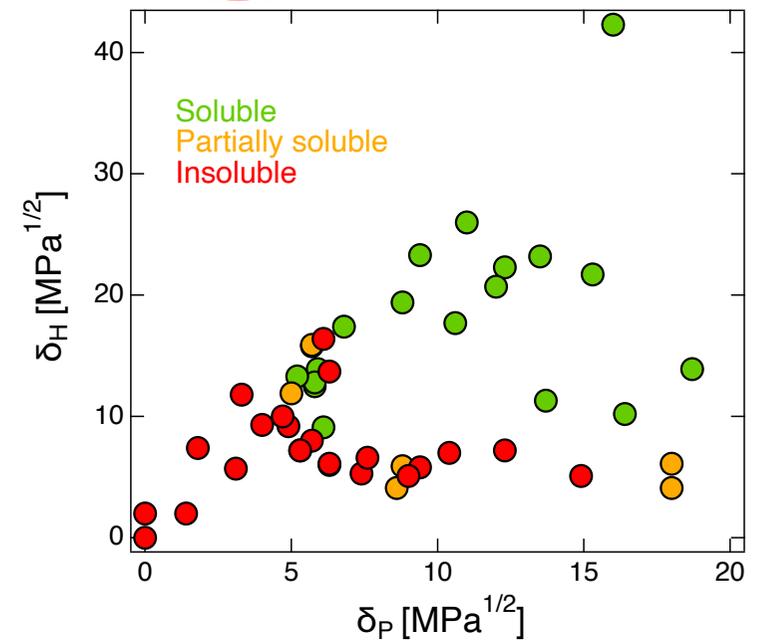
$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

# EXPERIMENTAL SYSTEM (I)

## Carboxymethyl cellulose



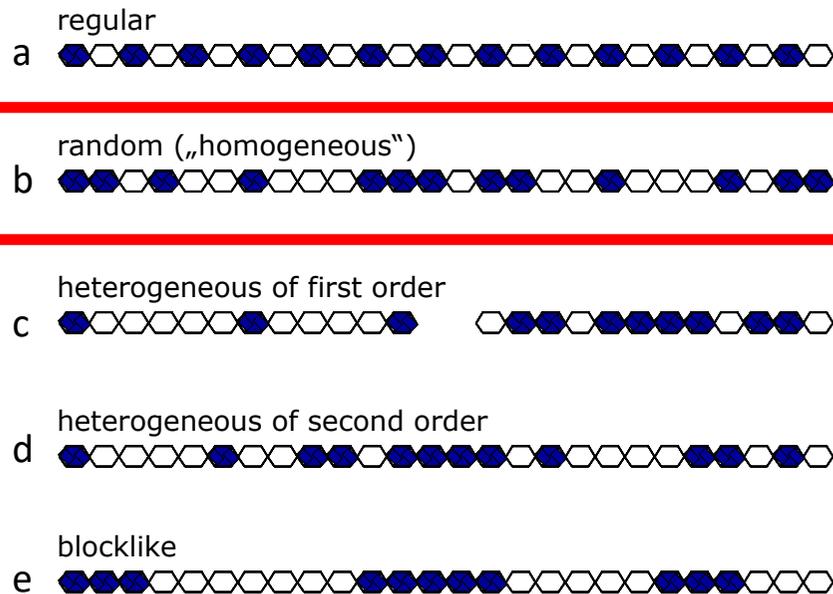
Solvent	$\epsilon$	Solution state for 1wt% TBACMC	Solution state for 1wt% NaCMC
Water	78	dissolved	dissolved
DMSO	48	dissolved	insoluble
DMF	38	dissolved	insoluble
Dipropylene glycol	24	dissolved	insoluble
Acetone	22	swollen	insoluble
propan-1-ol	18	dissolved	insoluble
propan-2-ol	18	swollen	insoluble
1-Octanol	10	swollen	insoluble
Pyridine	12.4	dissolved	insoluble
THF	7.8	insoluble	insoluble
1-Decanol	6.5	swollen	insoluble
Xylene	2.6	insoluble	insoluble
Toluene	2.4	insoluble	insoluble
Benzene	2.3	insoluble	insoluble
Hexane	2.0	insoluble	insoluble



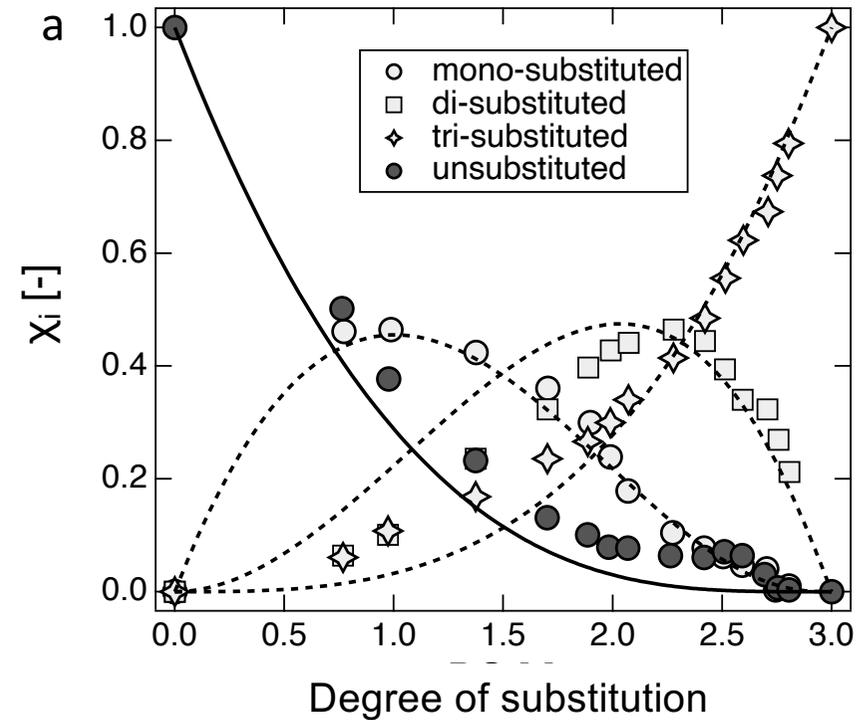
*Hansen solubility parameters*

# EXPERIMENTAL SYSTEM (II)

## Substitution patterns



A. Adden, "Thesis, technischen universitat carolo-wilhelmina, 2009,".



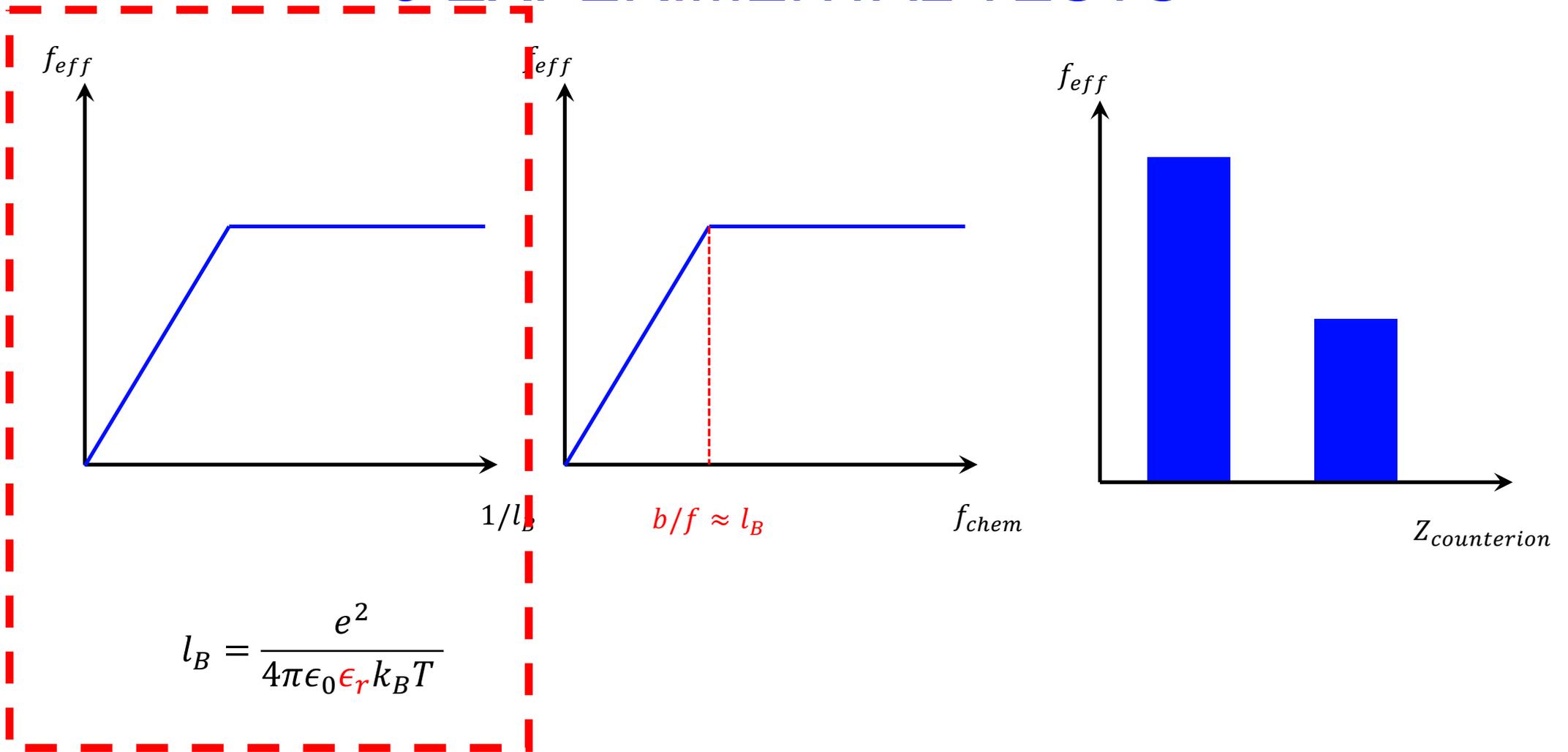
H. Kono, K. Oshima, H. Hashimoto, Y. Shimizu, and K. Tajima, Carbohydrate polymers 146, 1–9 (2016).

# OUTLINE

- Oosawa-Manning condensation
- Experimental tests
  - Influence of dielectric constant
  - Influence of charge density
  - Influence of counterion valence
- Ion-pairing



# 3 EXPERIMENTAL TESTS

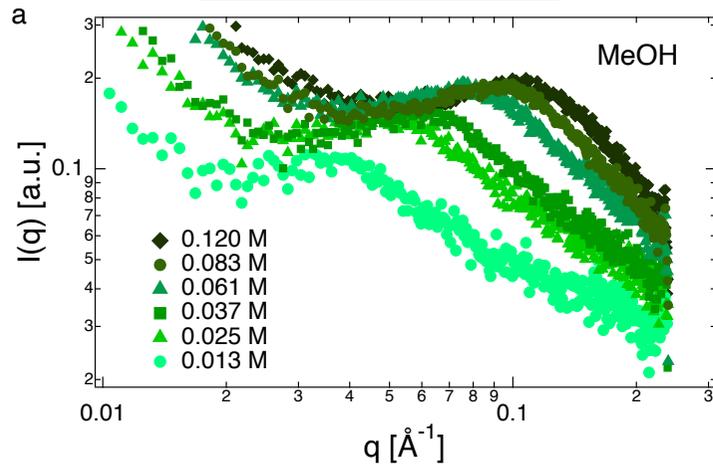


# DETERMINING THE FRACTION OF FREE COUNTERIONS

Colby et al 1997:

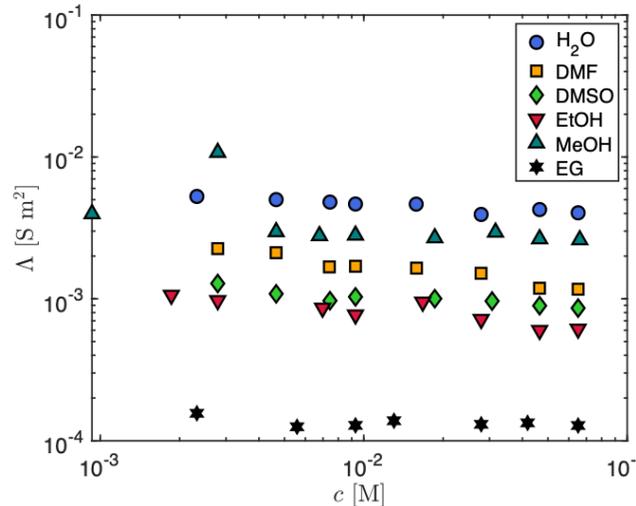
$$\Lambda = fc \left[ \lambda_0 + \frac{ce^2\xi^2 \ln\left(\frac{\xi}{D}\right)}{3\pi\eta_s} \right]$$

**SAXS/SANS**

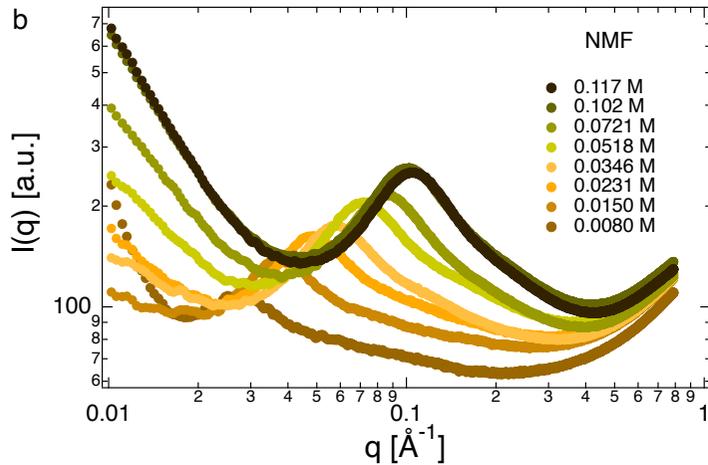
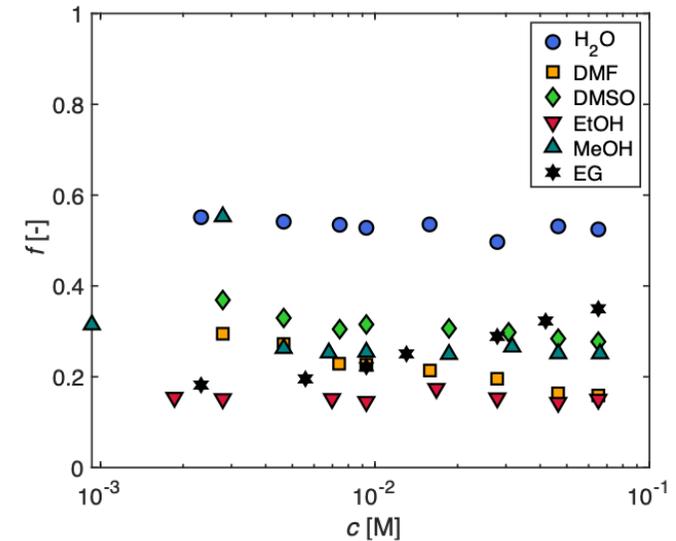


$$\xi = 2\pi/q^*$$

**CONDUCTIVITY**

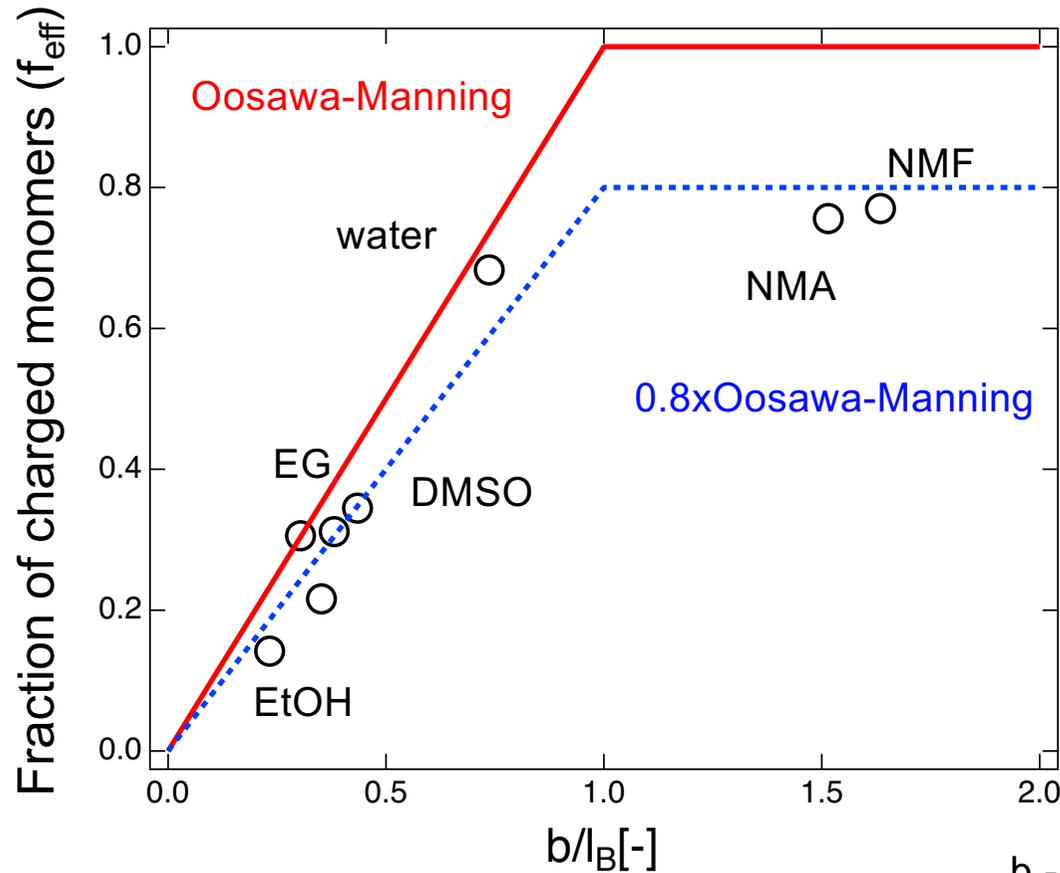


**FRACTION OF CHARGED MONOMERS**



Colby, R.H., Boris, D.C., Krause, W.E. and Tan, J.S., 1997. Polyelectrolyte conductivity. *Journal of Polymer Science Part B: Polymer Physics*, 35(17), pp.2951-2960.

# FRACTION OF FREE COUNTERIONS VS. DIELECTRIC CONSTANT (II)



Oosawa-Manning prediction:

$$\frac{f_{eff}}{f_{chem}} = 1 \text{ if } \frac{b}{l_B} > 1$$

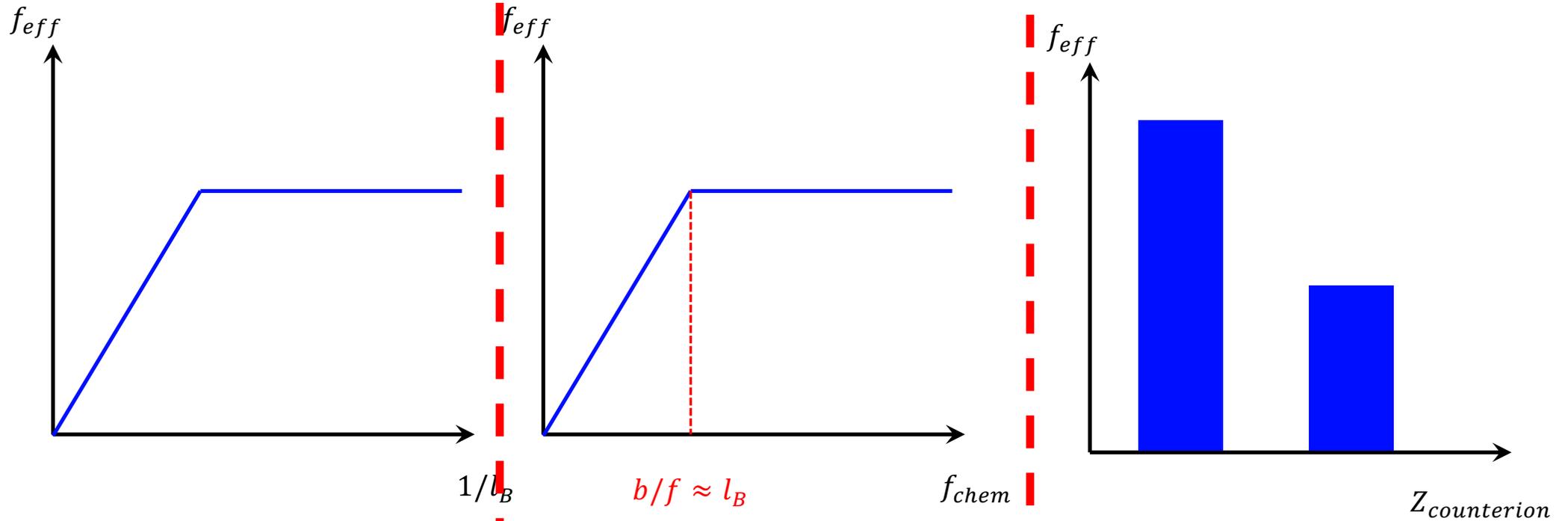
$$f_{eff} = \frac{b}{l_B} \text{ if } \frac{b}{l_B} < 1$$

Experiments:  $\approx 20\%$  lower charge than predicted

$b$  - distance between charged groups

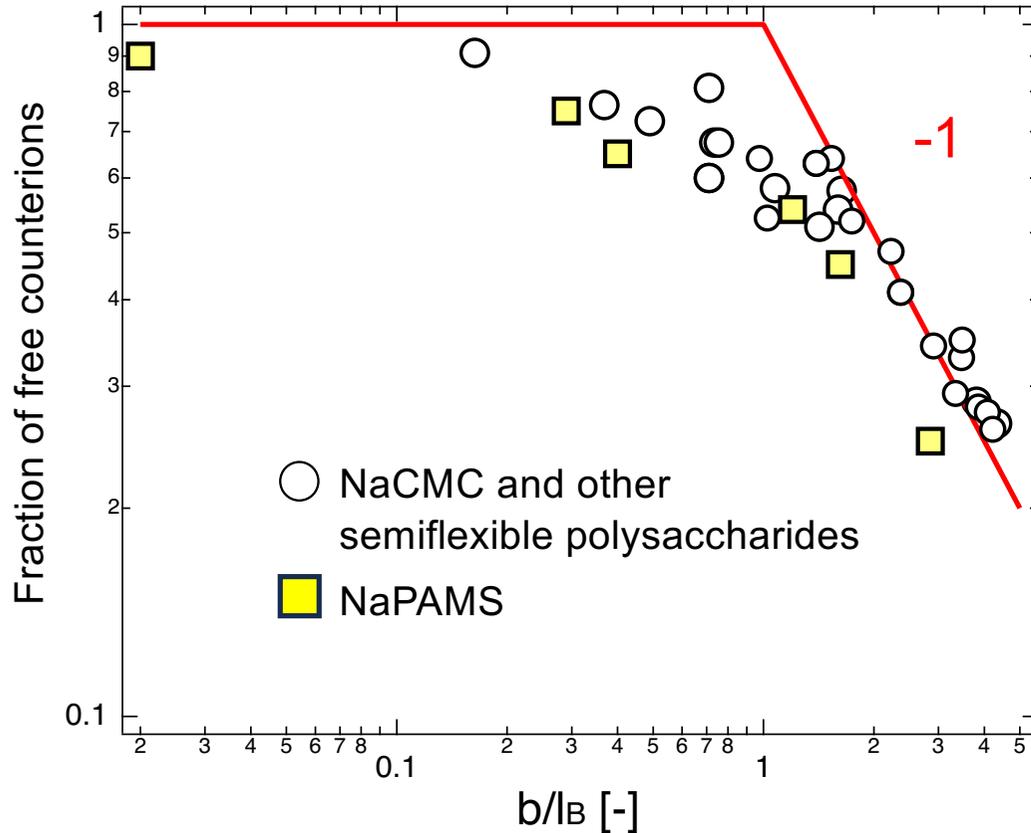


# 3 EXPERIMENTAL TESTS



$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

# FRACTION OF FREE COUNTERIONS VS. CHEMICAL CHARGE DENSITY



Oosawa-Manning prediction:

$$f = 1 \text{ if } \frac{b}{l_B} < 1$$

$$f \sim \frac{1}{b} \text{ if } \frac{b}{l_B} > 1$$

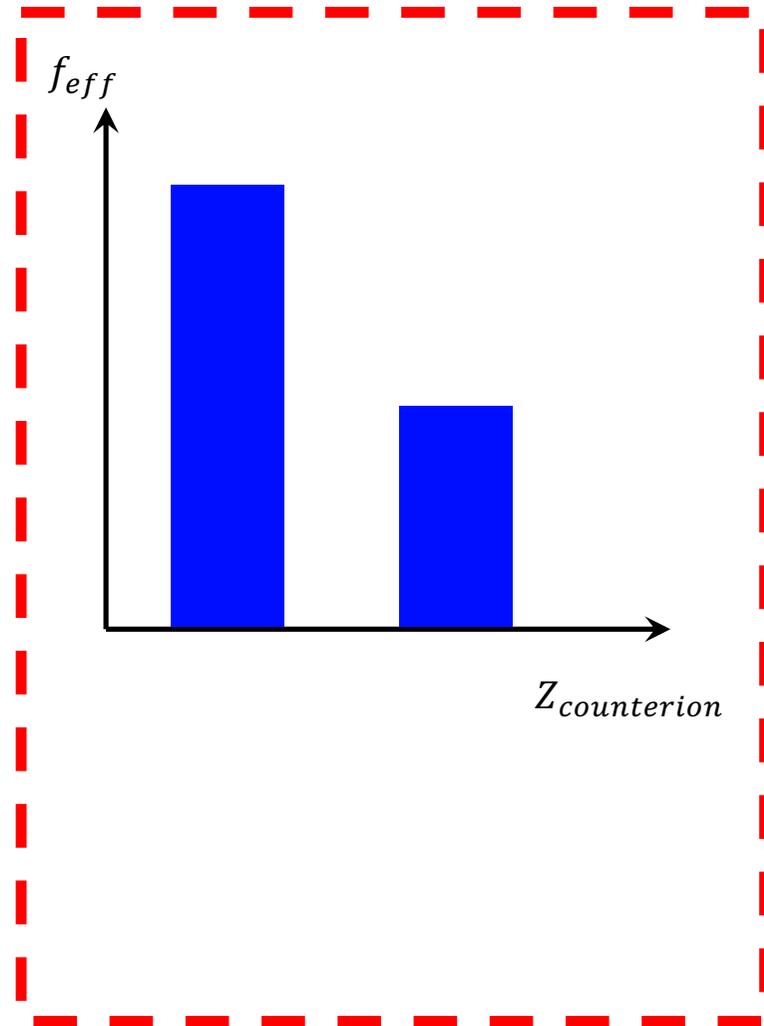
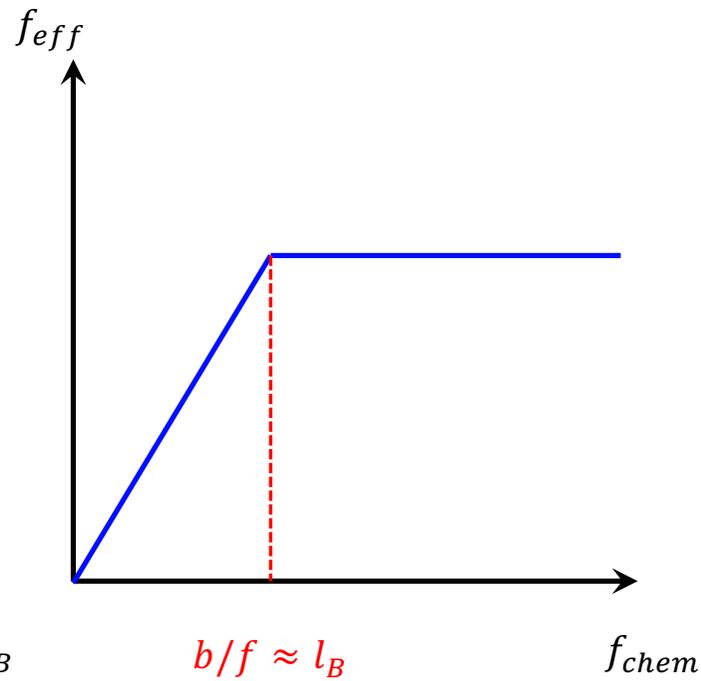
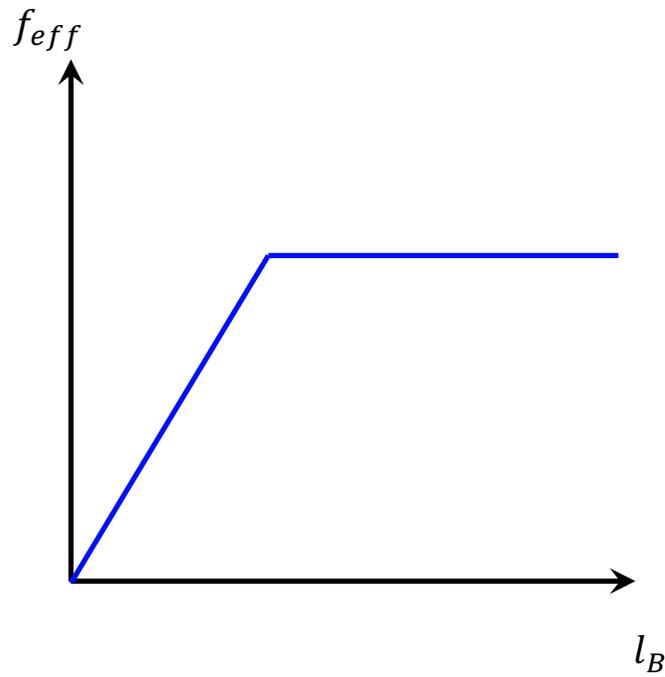
Experiments show a somewhat less sharp transition

$b$  – distance between charges  
 $l_B$  – Bjerrum length

Kowblansky, M. and Zema, P., 1981. *Macromolecules*, 14(1), 170.

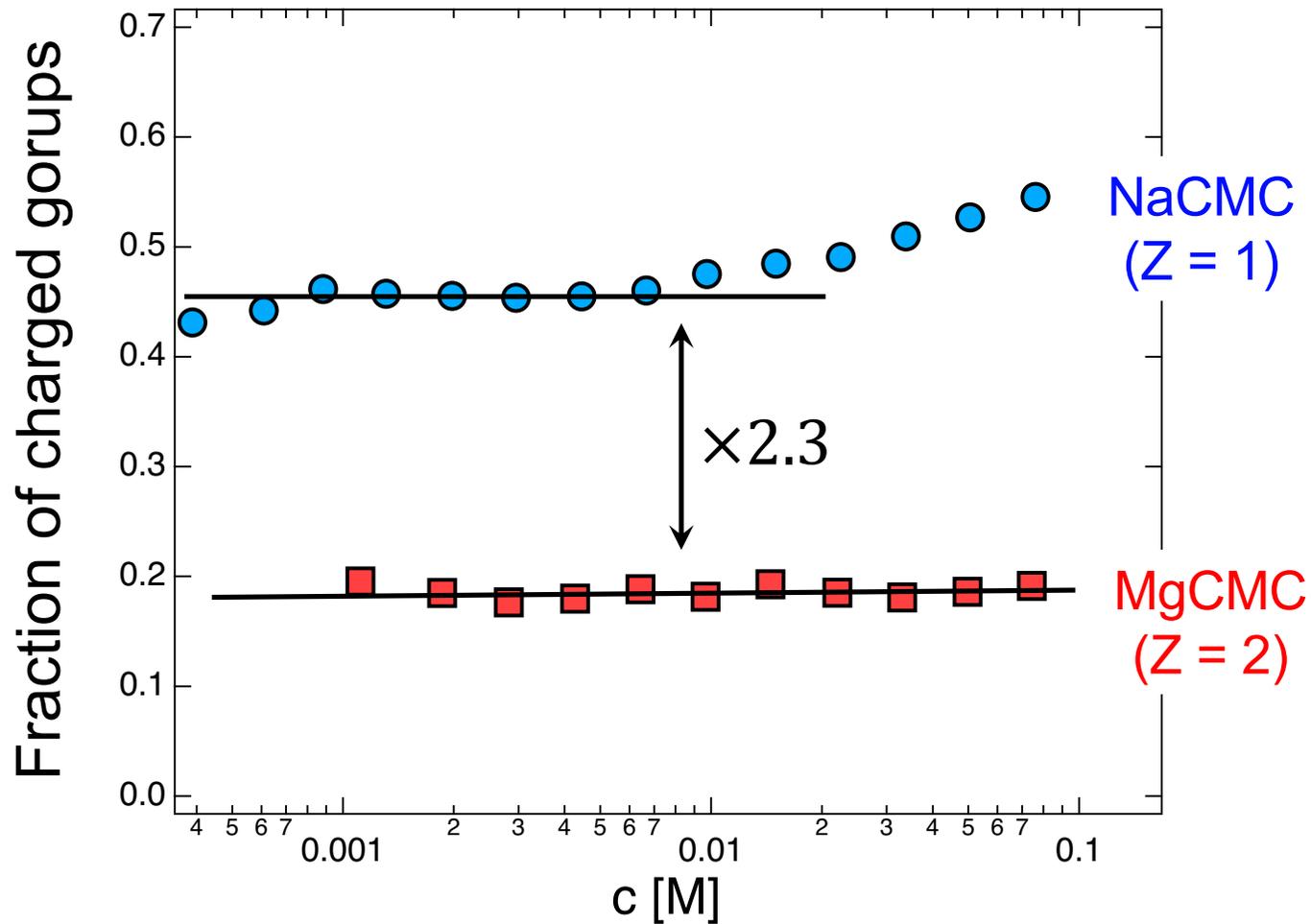


# 3 EXPERIMENTAL TESTS



$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

# INFLUENCE OF COUNTERION VALENCE



Oosawa-Manning  
prediction:

$$f_{eff} = \frac{b}{l_B Z_{counterion}}$$

Experimental result:

$$\frac{f_{eff}^{Na}}{f_{eff}^{Mg}} \approx 2.3$$

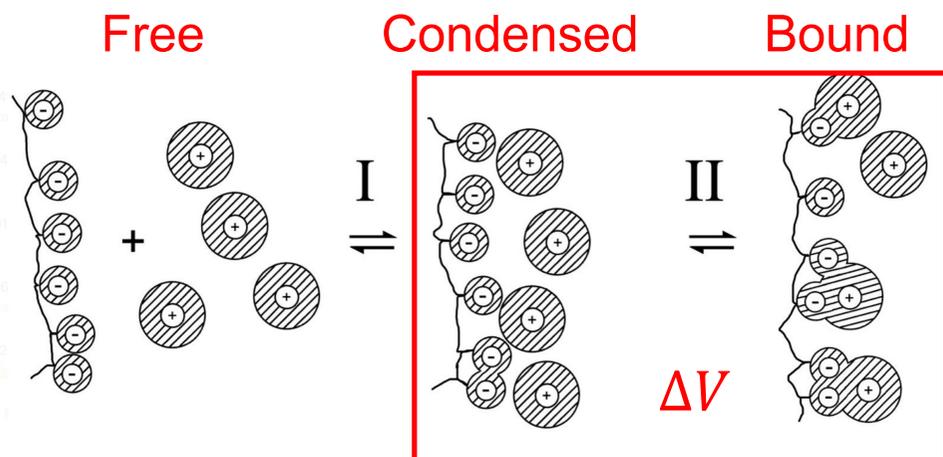


# OUTLINE

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# ION PAIR FORMATION



Electrostricted water ( $\rho \approx 1.1 \text{ g/mL}$ )

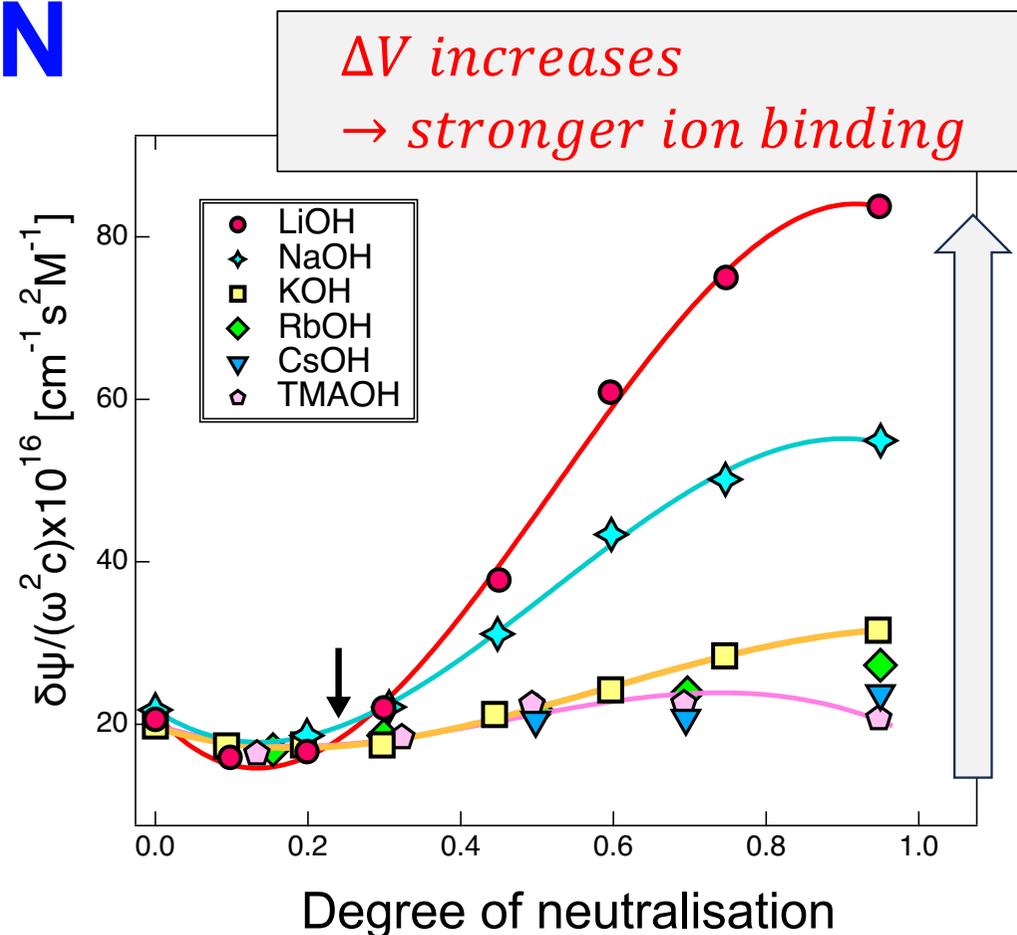


Bulk water ( $\rho \approx 1 \text{ g/mL}$ )

Ultrasound absorption

$$\delta\omega \sim \frac{\Delta V^2}{1 + \left(\frac{\omega}{\omega_c}\right)^2}$$

Atkinson, G., Baumgartner, E. and Fernandez-Prini, R., 1971. *Journal of the American Chemical Society*, 93(24), pp.6436-6443.

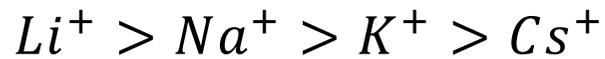


$\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$

Zana, R., Tondre, C., Rinaudo, M. and Milas, M., 1971. *Journal de Chimie Physique*, 68, pp.1258-1266.

# INFLUENCE OF COUNTERION TYPE ON CHARGE FRACTION

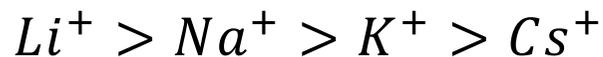
Ion pair formation strength:



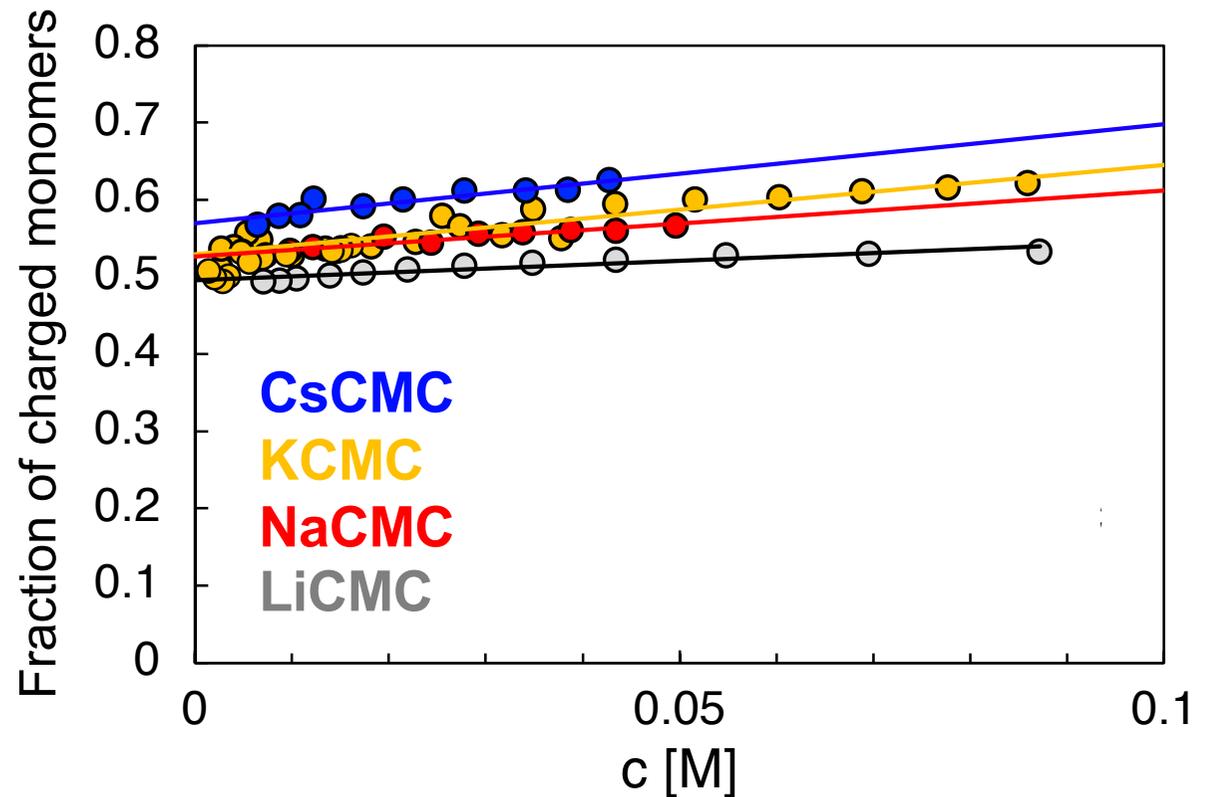
~ 40% ion-pairs

No ion pairs

Ion bound counterions



≈ 10% difference



# SUMMARY & OPEN QUESTIONS

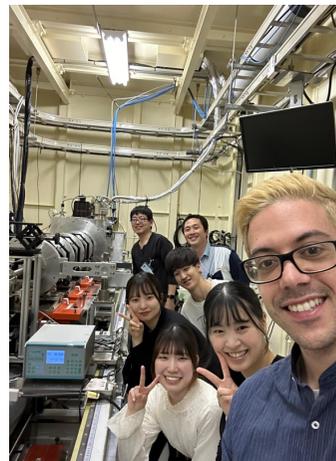
- **Oosawa-Manning** condensation correctly predicts the dependence of polyelectrolyte effective charge on dielectric constant, bare charge density and counterion valence.
- Condensation threshold is **broader** than predicted by theory
- **Ion-pairing** due to solvation shell sharing takes place but has a minor effect on the effective charge of the polyelectrolytes.

# ACKNOWLEDGEMENTS

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