POLYELECTROLYTES IN ORGANIC SOLVENTS: SCATTERING BEHAVIOUR AND COUNTERION CONDENSATION

Slides:

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International Polyelectrolyte Symposium 2025

PennState
College of Earth
and Mineral Sciences

OUTLINE

- Oosawa-Manning condensation

- Counterion condensation: Experimental tests

  - Influence of dielectric constant

  - Influence of charge density

  - Influence of counterion valence

- Ion pair formation
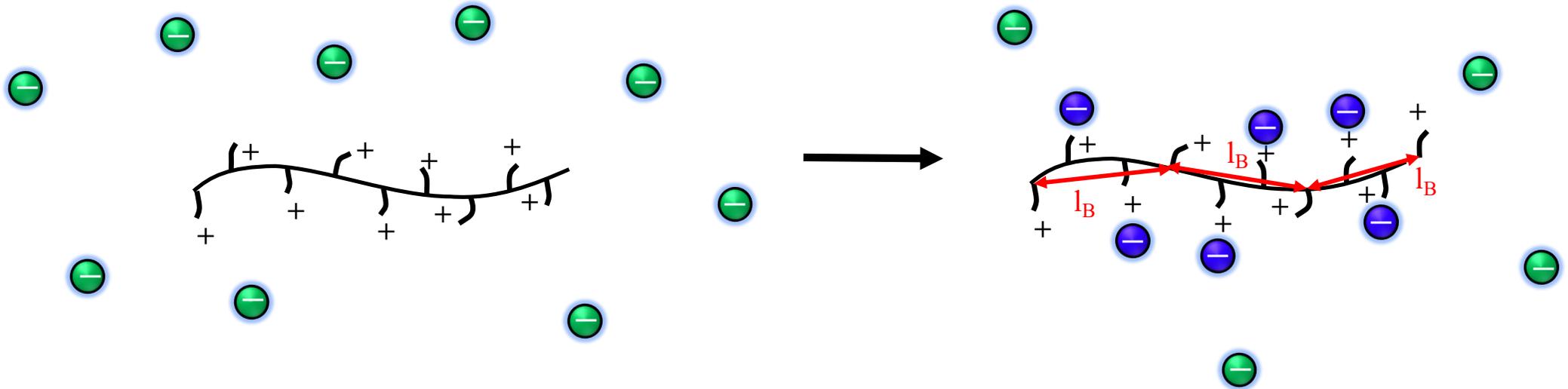
- Scattering properties: condensation & delocalisation

COUNTERION CONDENSATION (I)

Oosawa-Manning condensation theory

Counterions will condense onto the chain until the charge density decreases to a value of $1/Zl_B$.
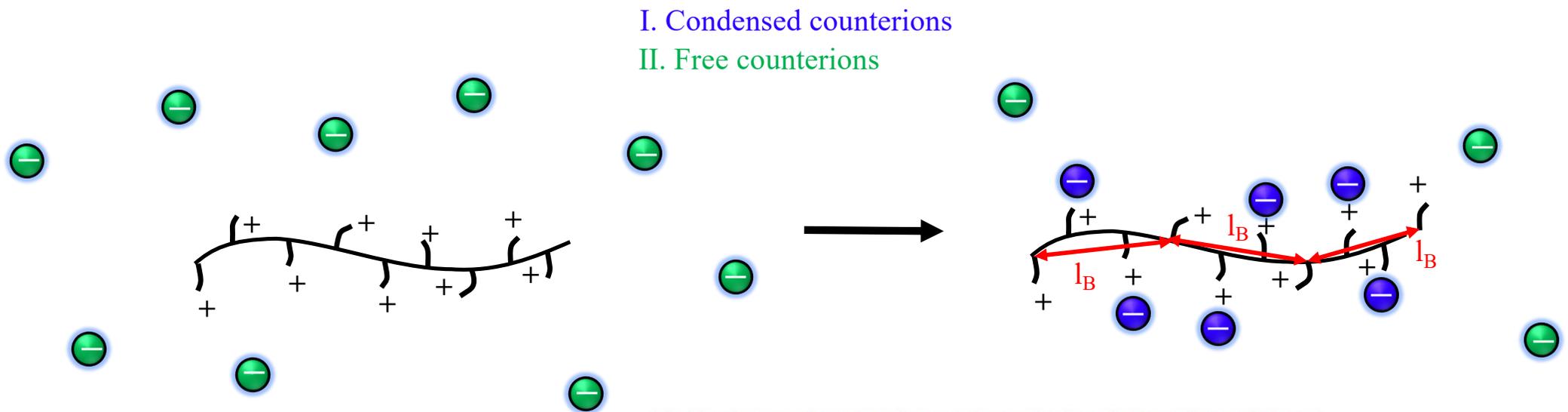
I. Condensed counterions
II. Free counterions

COUNTERION CONDENSATION (I)

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I. Condensed counterions
II. Free counterions

1

COUNTERION CONDENSATION (II)

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

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

M. Muthukumar[a]
Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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OF CHEMISTRY

Soft Matter

PAPER

Check for updates

Where in the world are condensed counterions?

Qishun Tang [iD] [a] and Michael Rubinstein [iD] *[bc]

Evaluation of the Counterion Condensation Theory of Polyelectrolytes

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

Manning-Oosawa Counterion Condensation

Ben O'Shaughnessy[1,*] and Qingbo Yang[2]
[1]*Department of Chemical Engineering, Columbia University, New York, NY 10027, USA*
[2]*Department of Physics, Columbia University, New York, NY 10027, USA*
(Received 15 April 2004; published 1 February 2005)

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
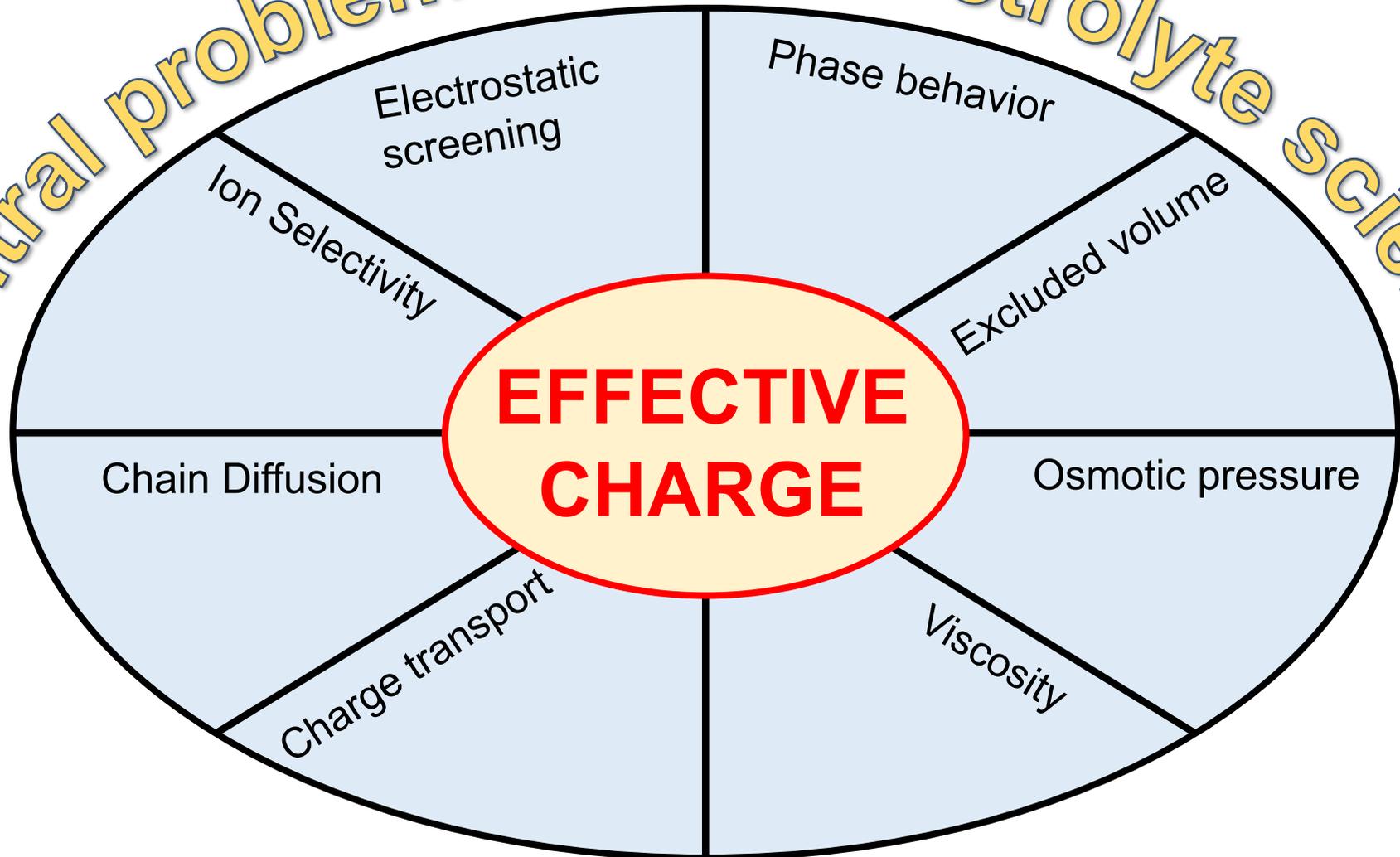94800 Villejuif, France

Counterion Condensation in Solutions of Rigid Polyelectrolytes
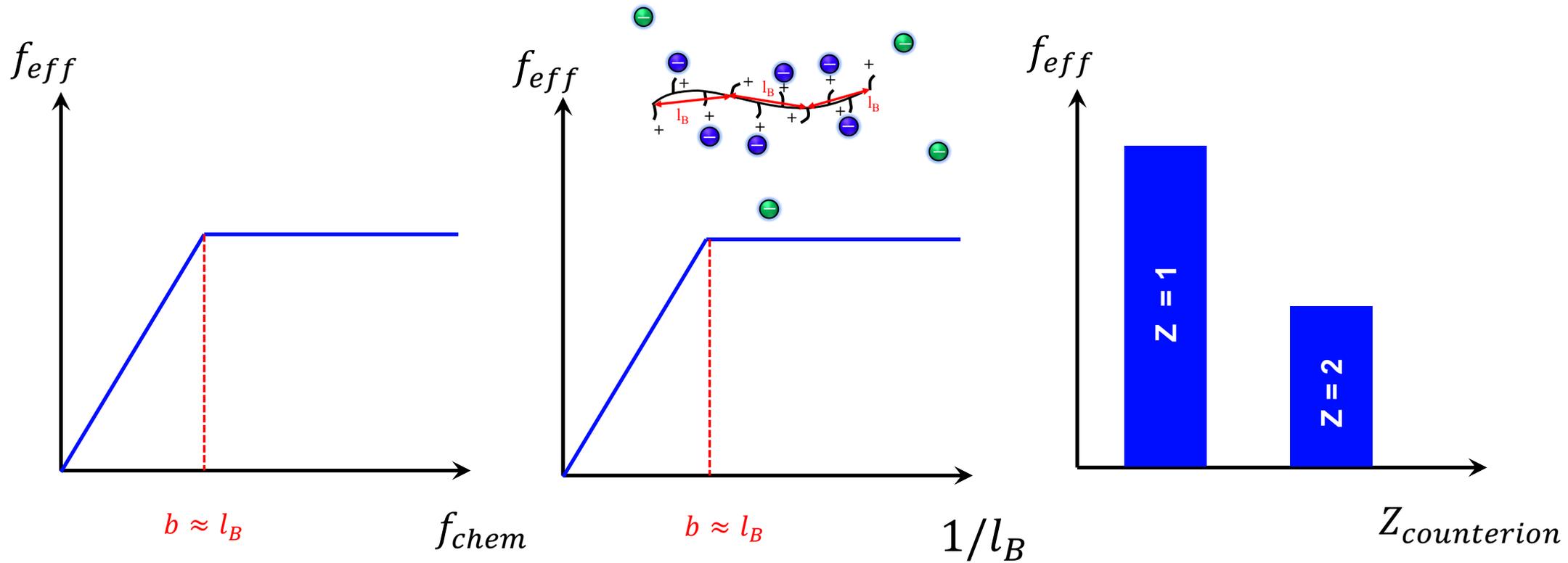
Rebecca M. Nyquist, Bae-Yeun Ha, and Andrea J. Liu

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

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

2

Central problem of polyelectrolyte science

EFFECTIVE CHARGE

Electrostatic screening

Phase behavior

Ion Selectivity

Excluded volume

Chain Diffusion

Osmotic pressure

Charge transport

Viscosity
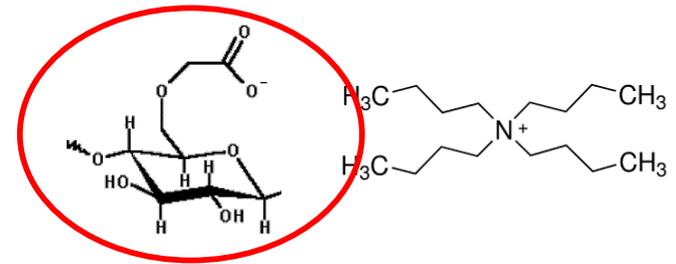
3

3 EXPERIMENTAL TESTS

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

b — distance between charges
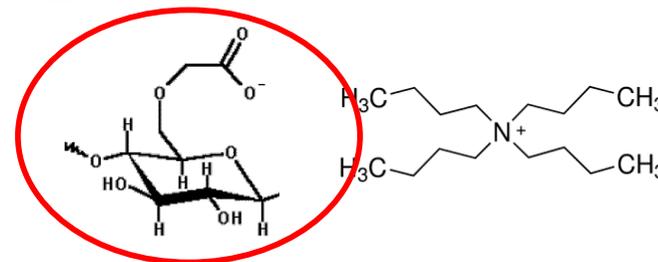
4

EXPERIMENTAL SYSTEM

Carboxymethyl cellulose

Hou et al Solutions of Carboxymethylcellulose with Organic Counterions (I): The Influence of Counterion Properties on the Polymer Structure and Solubility. *Macromolecules, ASAP* (2025).
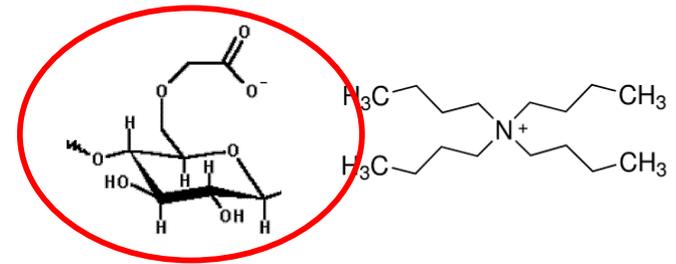
EXPERIMENTAL SYSTEM

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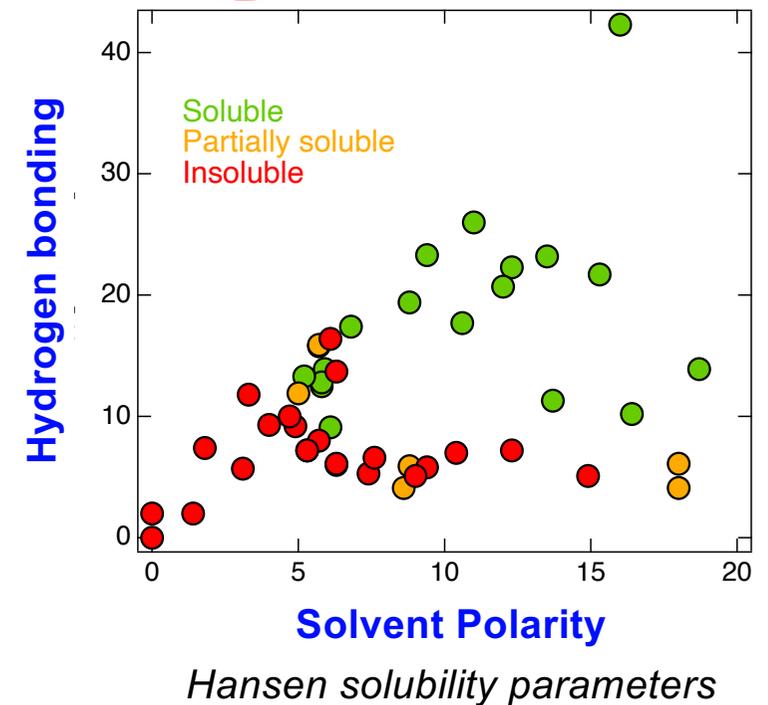| Solvent	ε	Solution state for 1wt% TBACMC	Solution state for 1wt% NaCMC
Water	78	dissolved	dissolved
DMSO	48	dissolved	insoluble
DMF	38	dissolved	insoluble
Dipropylene glycol	24	dissolved	insoluble
Acetone	22	swollen	insoluble
propan-1-ol	18	dissolved	insoluble
propan-2-ol	18	swollen	insoluble
1-Octanol	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

Hou et al Solutions of Carboxymethylcellulose with Organic Counterions (I): The Influence of Counterion Properties on the Polymer Structure and Solubility. *Macromolecules, ASAP* (2025).

Figure 1: Left: Solubility of tetrabutylammonium and sodium salts of CMC. Replacing TBA+ counterions leads to a large increase in the solubility of CMC in organic med Solubility diagram for TBACMC as 1 wt% as a function of solvent permittivity (e) for

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    - Influence of dielectric constant

    - Influence of charge density

    - Influence of counterion valence

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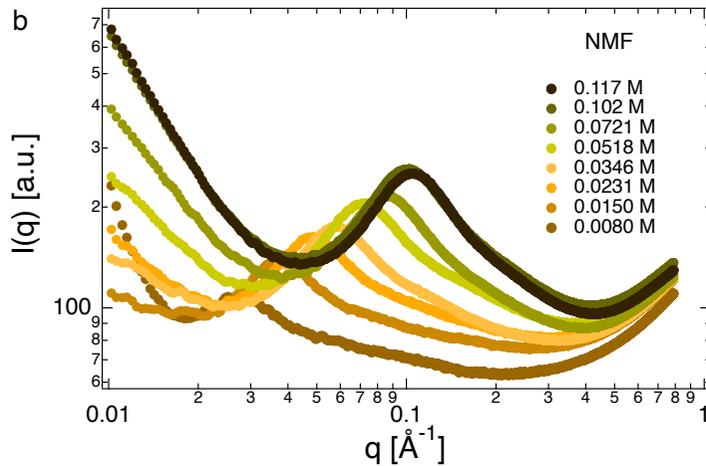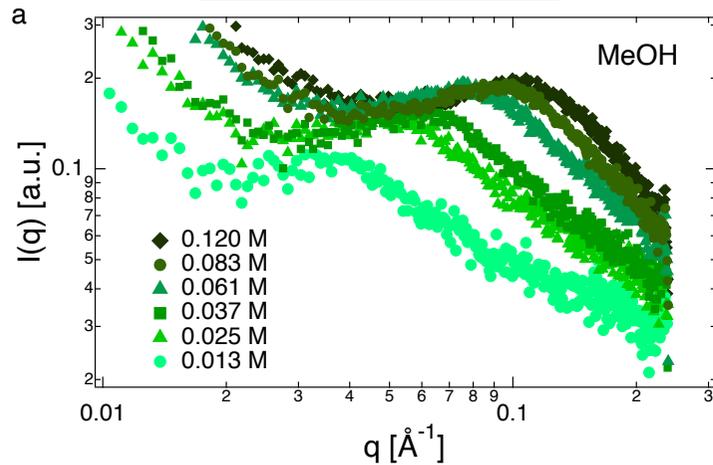
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DETERMINING THE FRACTION OF FREE COUNTERIONS

Colby et al 1997:

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

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.

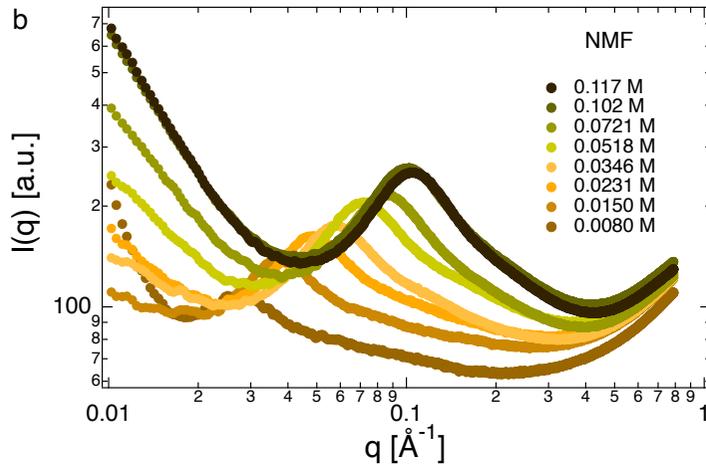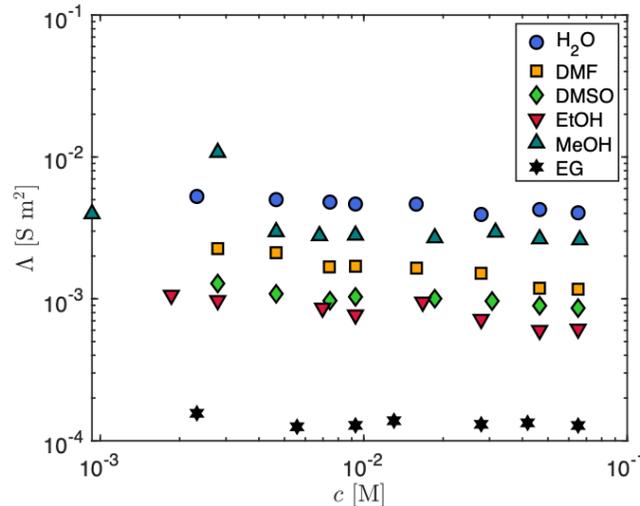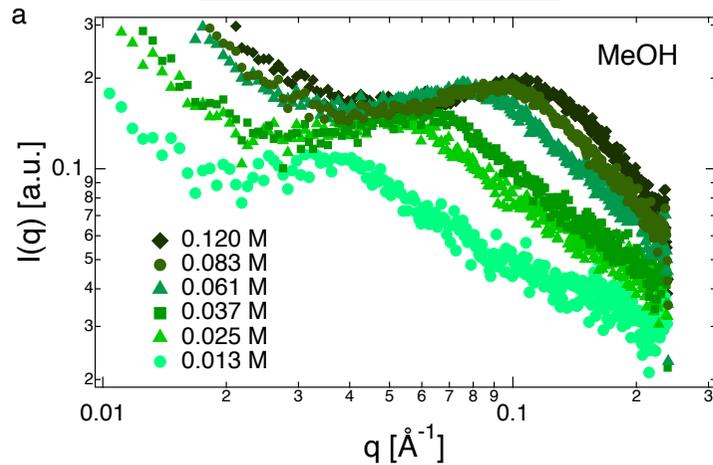# DETERMINING THE FRACTION OF FREE COUNTERIONS

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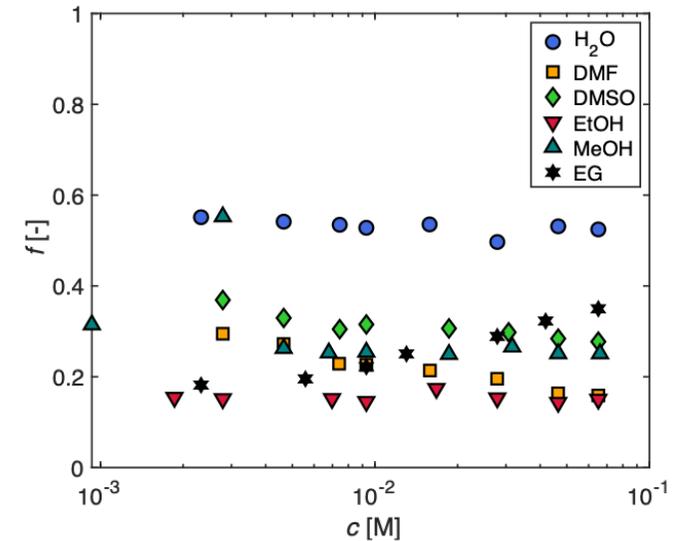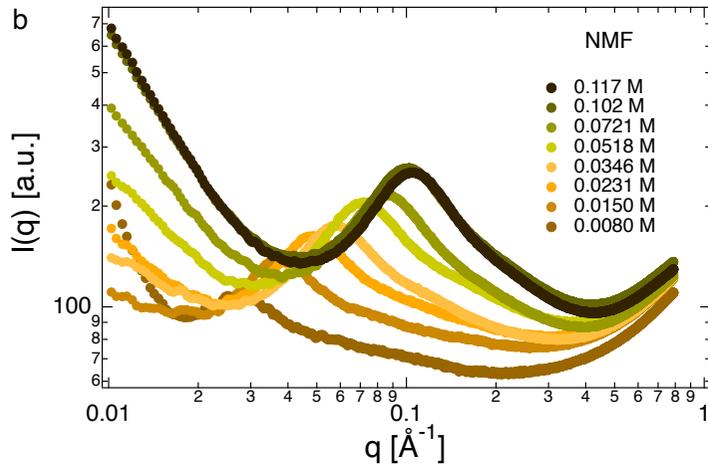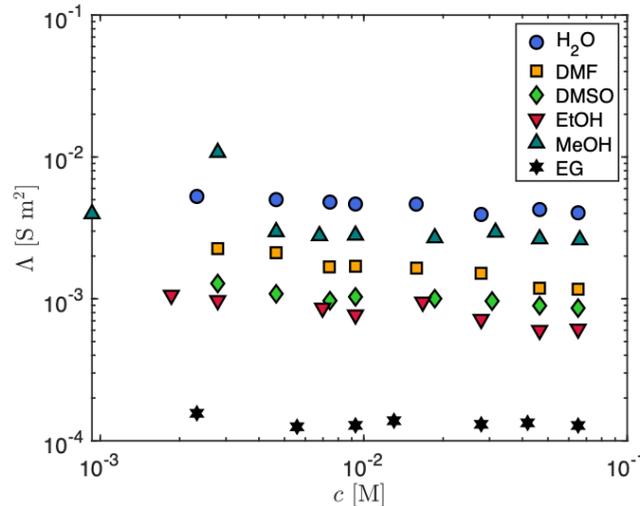$$\Lambda = fc\left[\lambda_0 + \frac{ce^2\xi^2 \ln\left(\frac{\xi}{D}\right)}{3\pi\eta_s}\right]$$

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

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SAXS/SANS

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

CONDUCTIVITY

a

b

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.

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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.

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3 EXPERIMENTAL TESTS

$$l_B = \frac{e^2}{4\pi\epsilon_0 \epsilon_r k_B T}$$
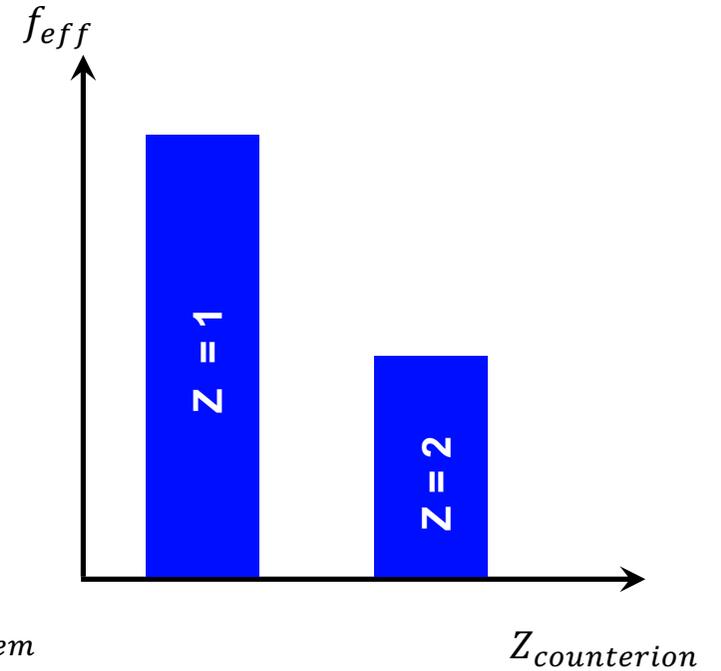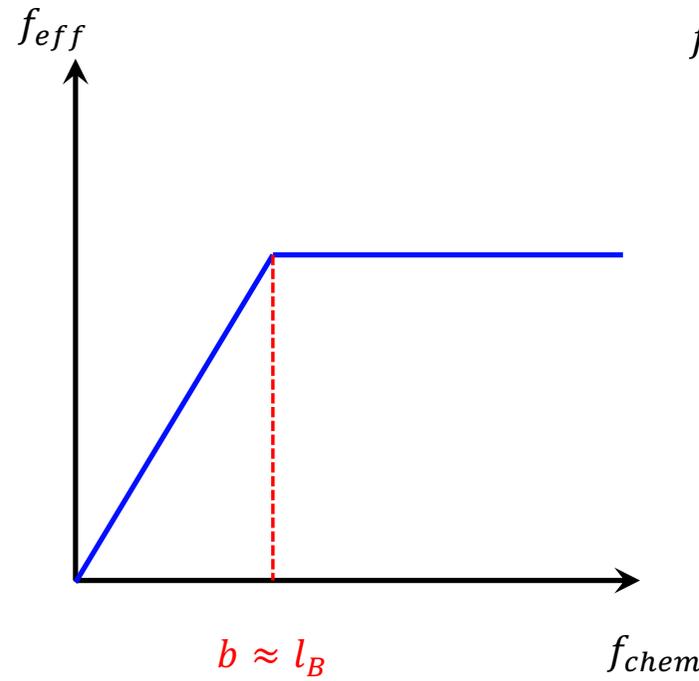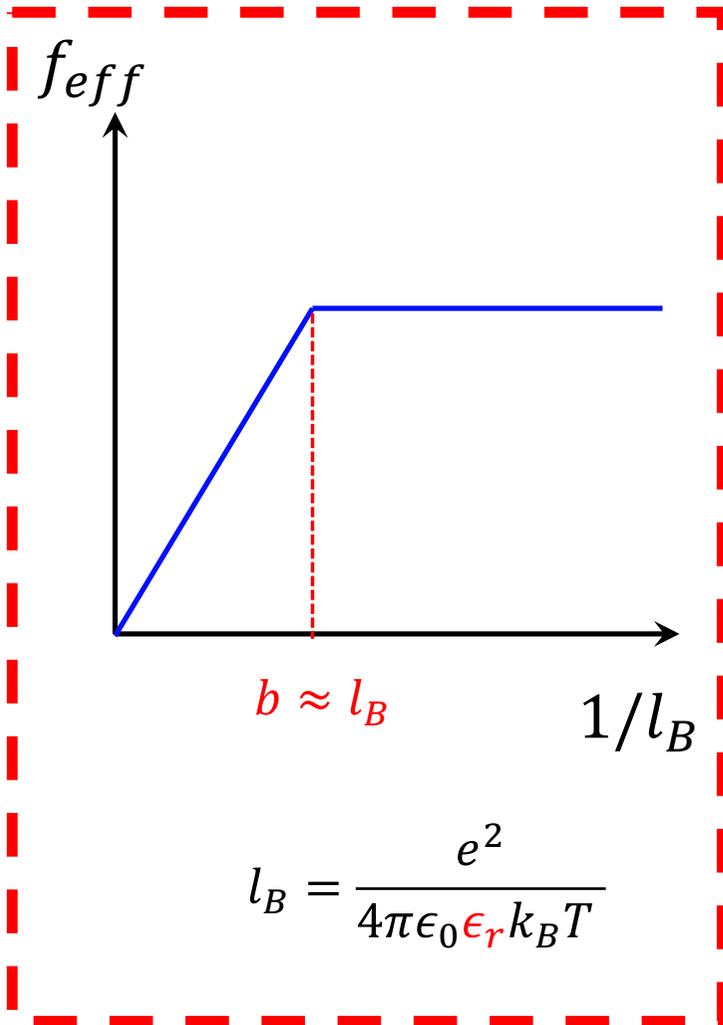
b − distance between charges

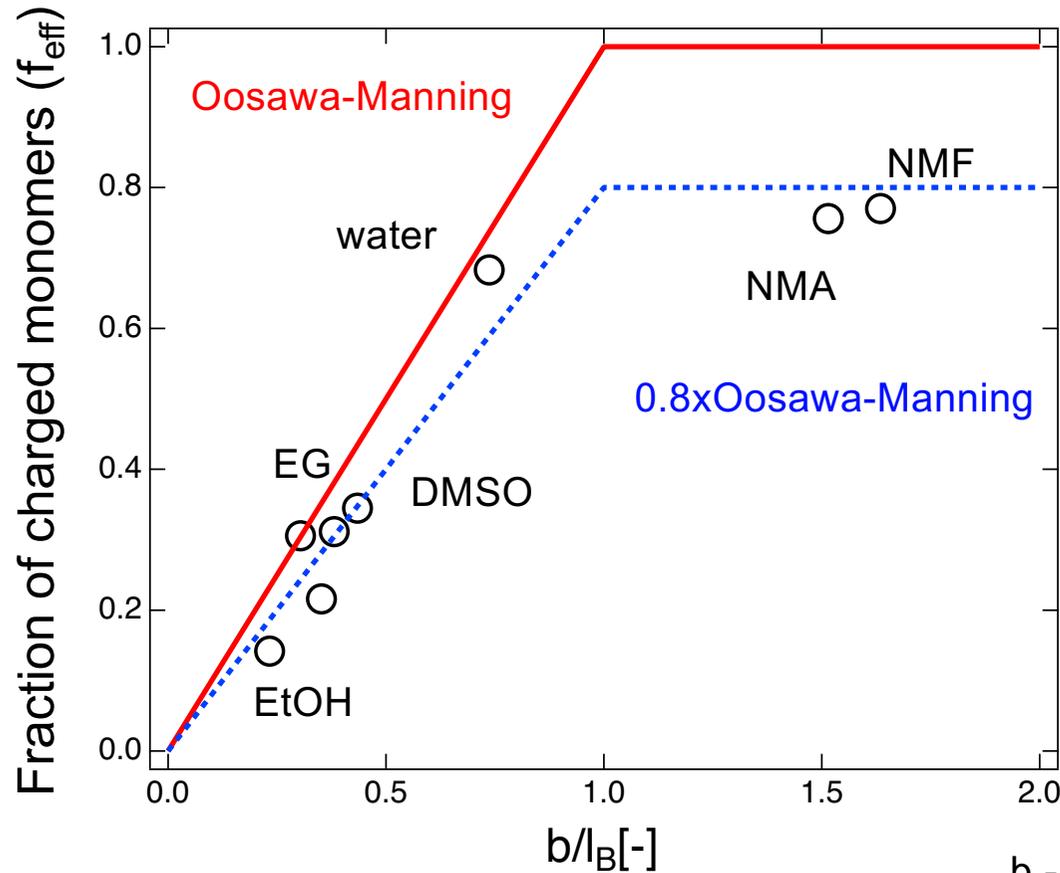# FRACTION OF FREE COUNTERIONS VS. DIELECTRIC CONSTANT (II)
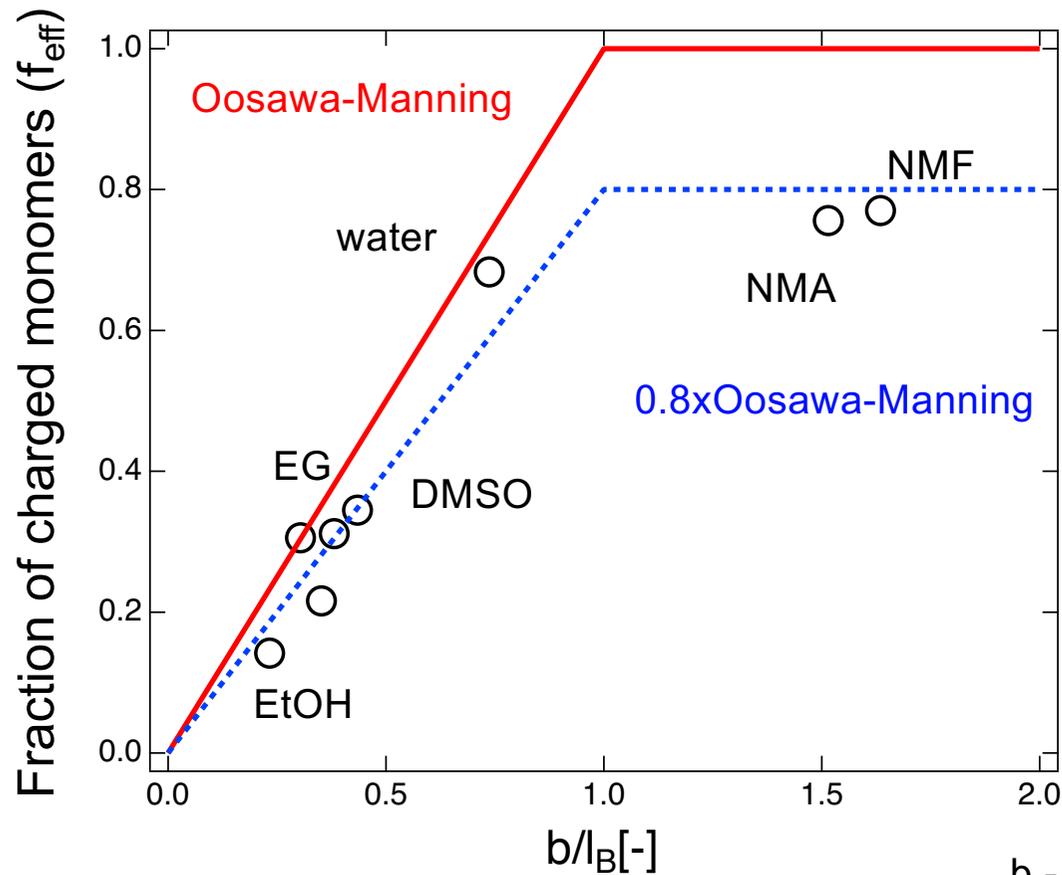
Oosawa-Manning prediction:

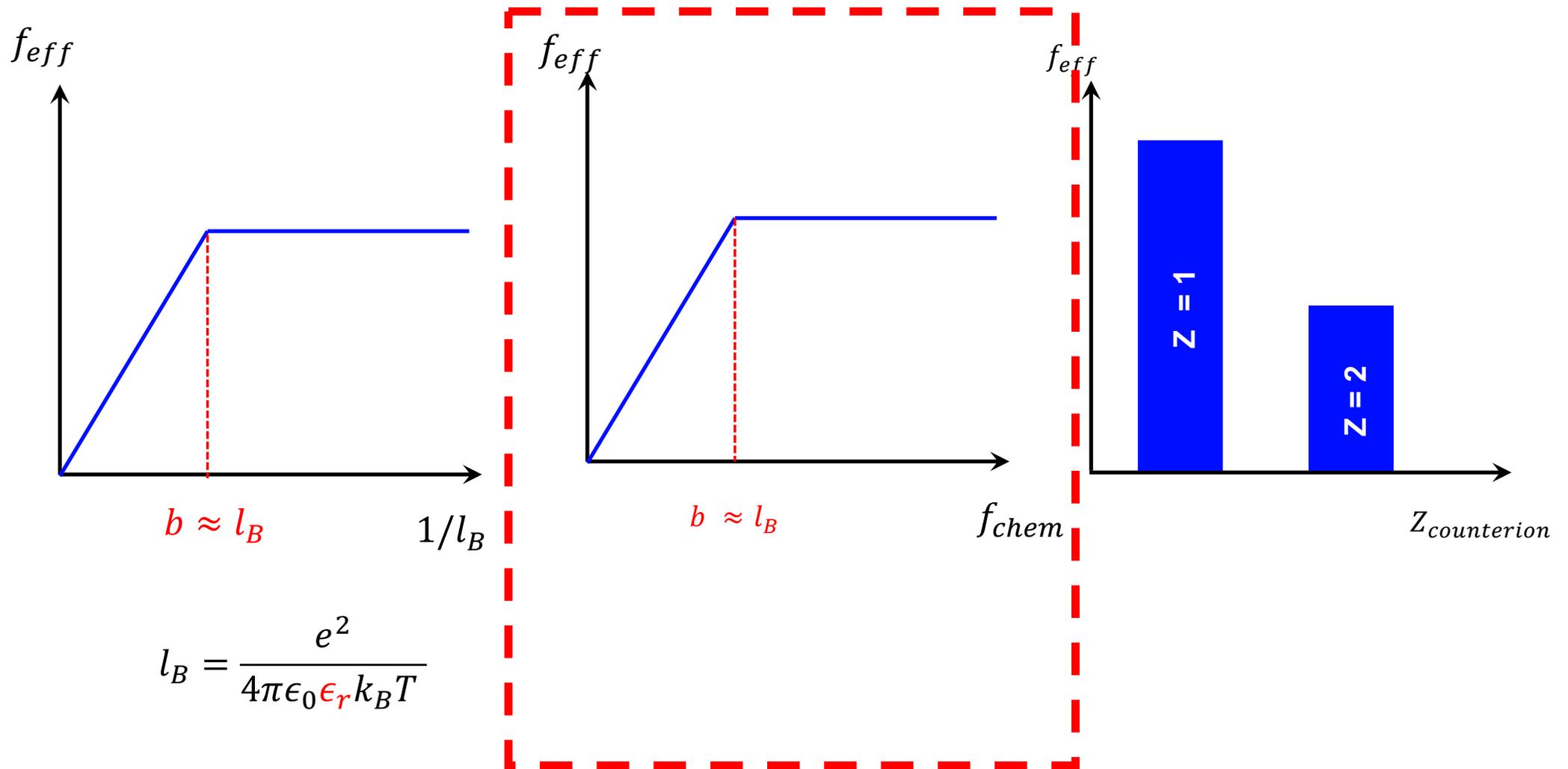$$\frac{f_{eff}}{f_{chem}} = 1 \; if \; \frac{b}{l_B} > 1$$

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

Experiments: ≈ 20% lower charge than predicted

b - distance between charged groups

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FRACTION OF FREE COUNTERIONS VS. CHEMICAL CHARGE DENSITY

Oosawa-Manning prediction:

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

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

b – distance between charges
l_B – Bjerrum length

Kowblansky, M. and Zema, P., 1981. *Macromolecules, 14*(1), pp.166-170.

9

FRACTION OF FREE COUNTERIONS VS. CHEMICAL CHARGE DENSITY

Oosawa-Manning prediction:
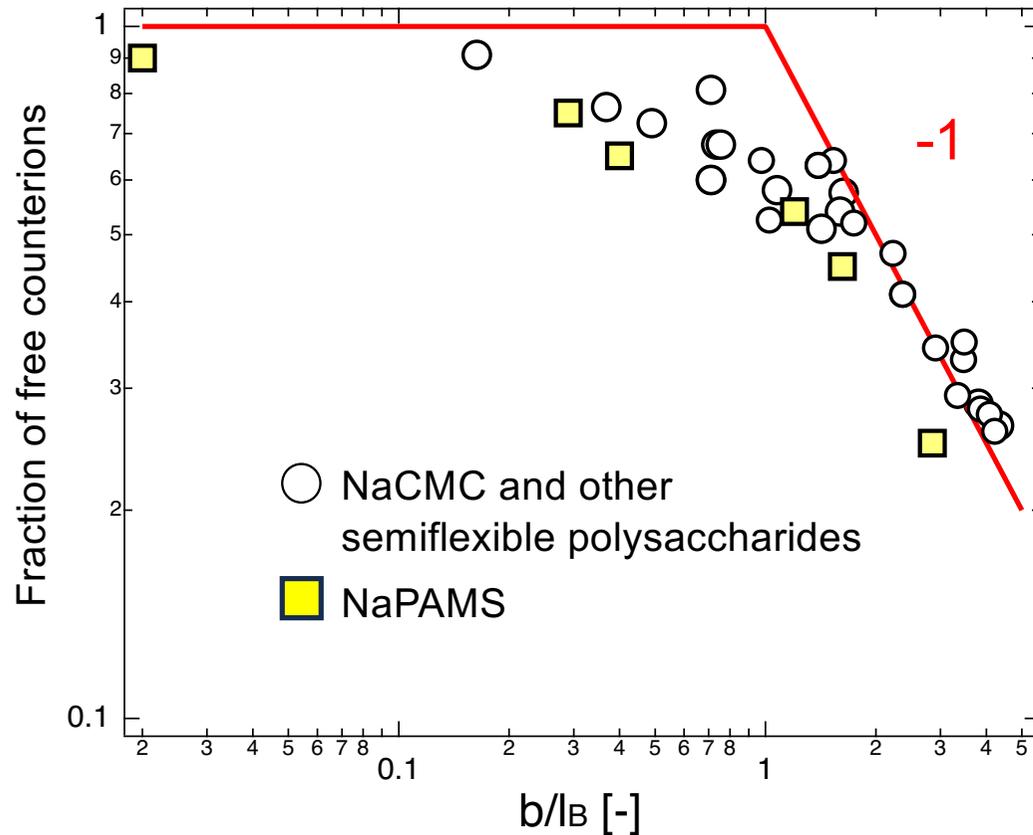
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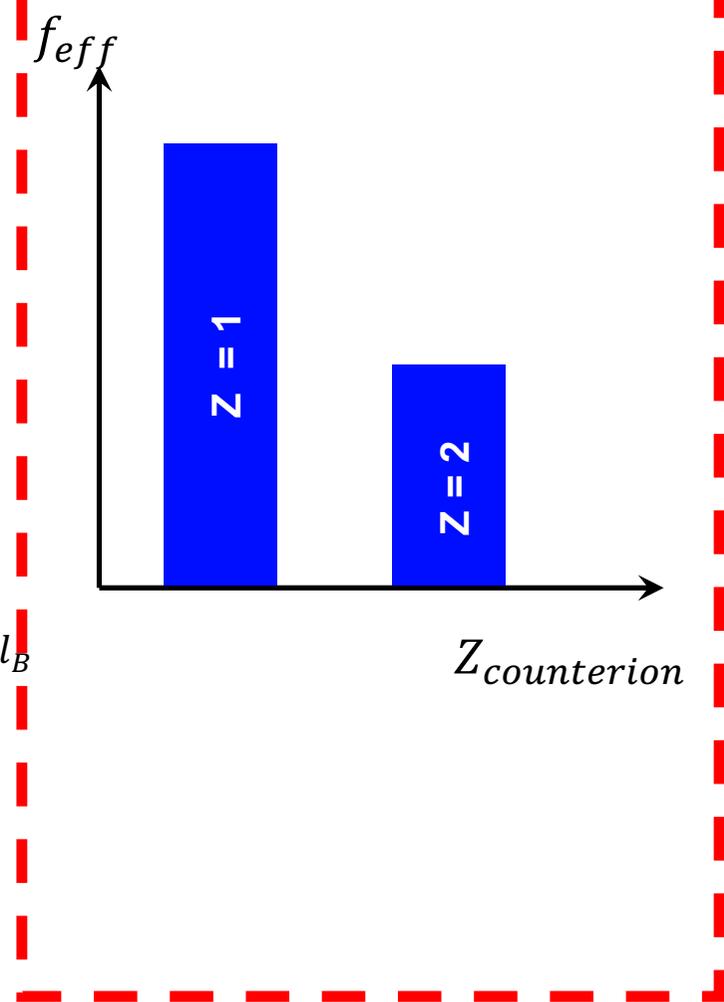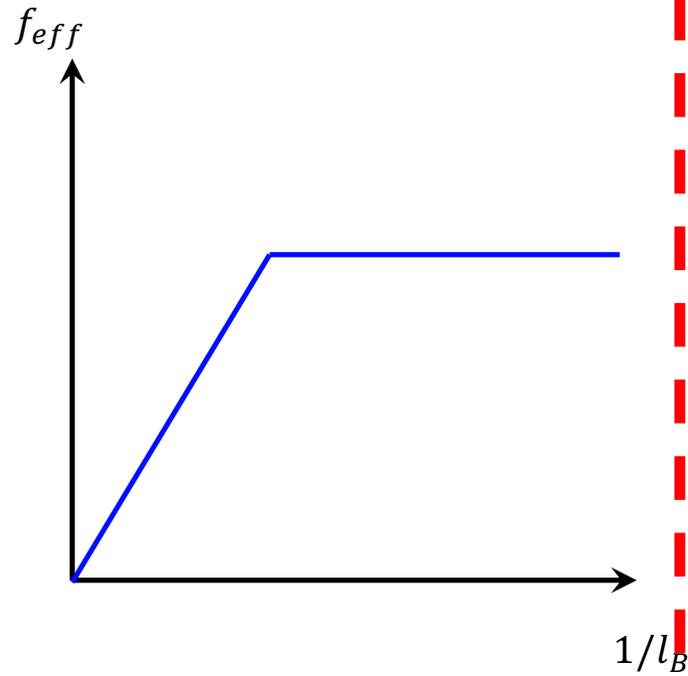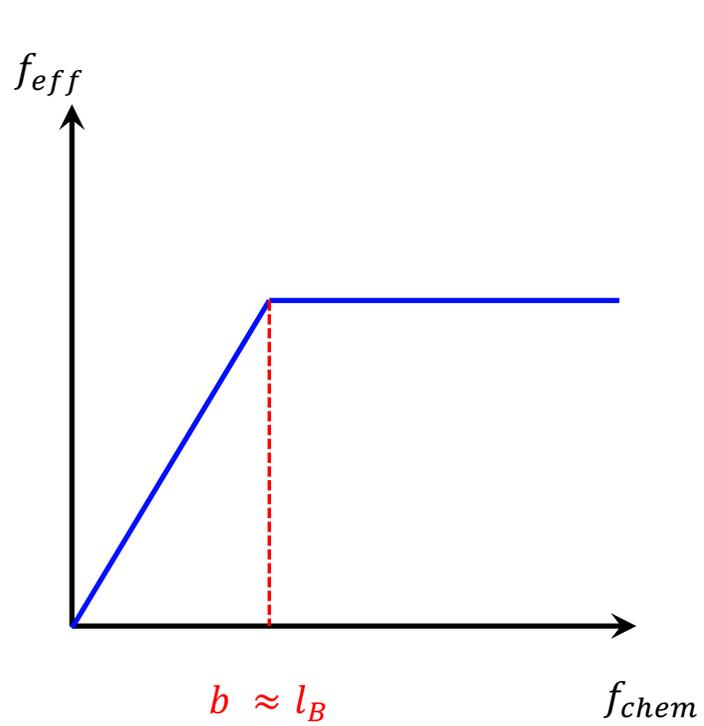$$f \sim \frac{1}{b} \; if \; \frac{b}{l_B} > 1$$

Experiments show a somewhat less sharp transition

b – distance between charges
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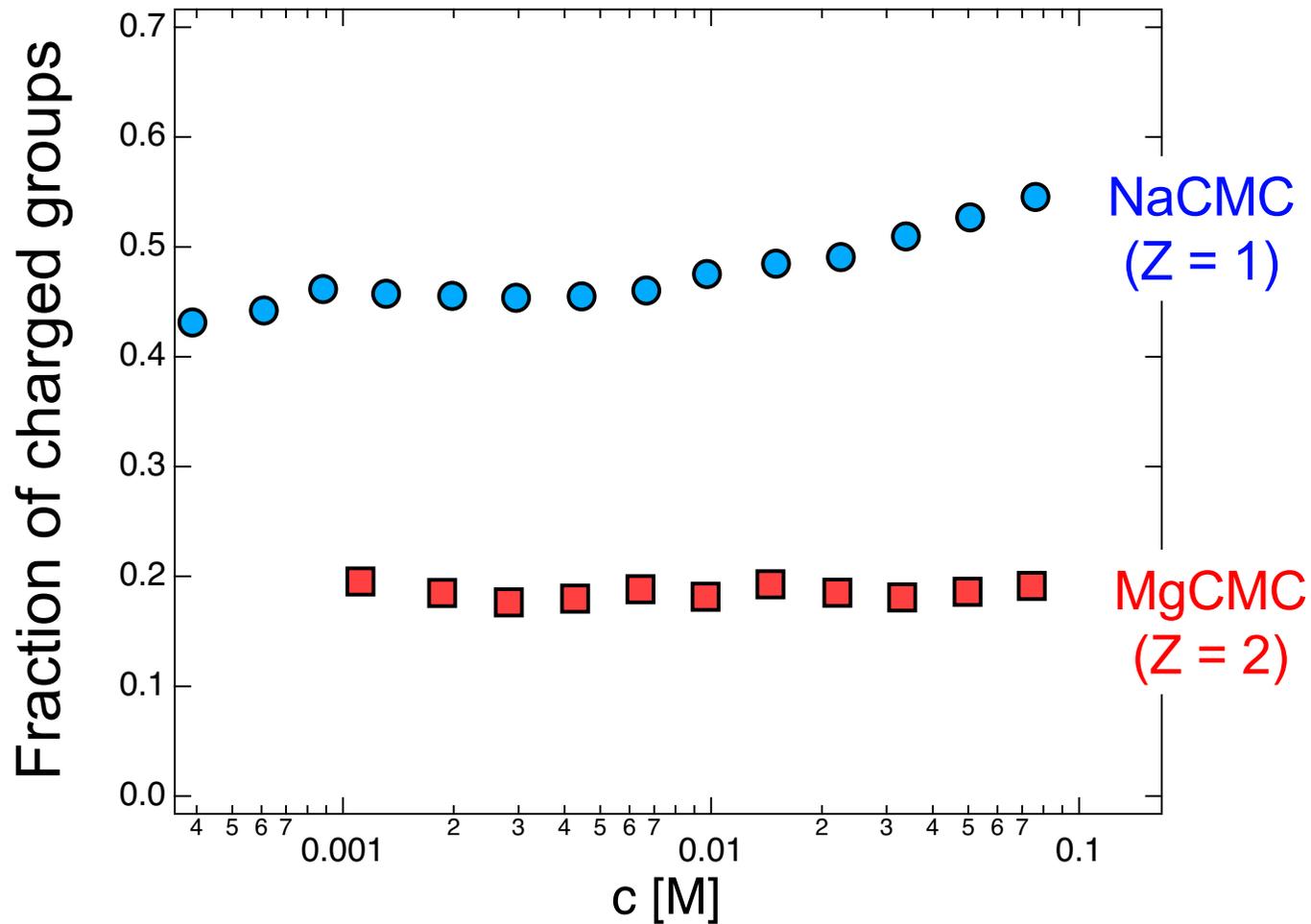
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$$l_B = \frac{e^2}{4\pi\epsilon_0 \epsilon_r k_B T}$$

INFLUENCE OF COUNTERION VALENCE
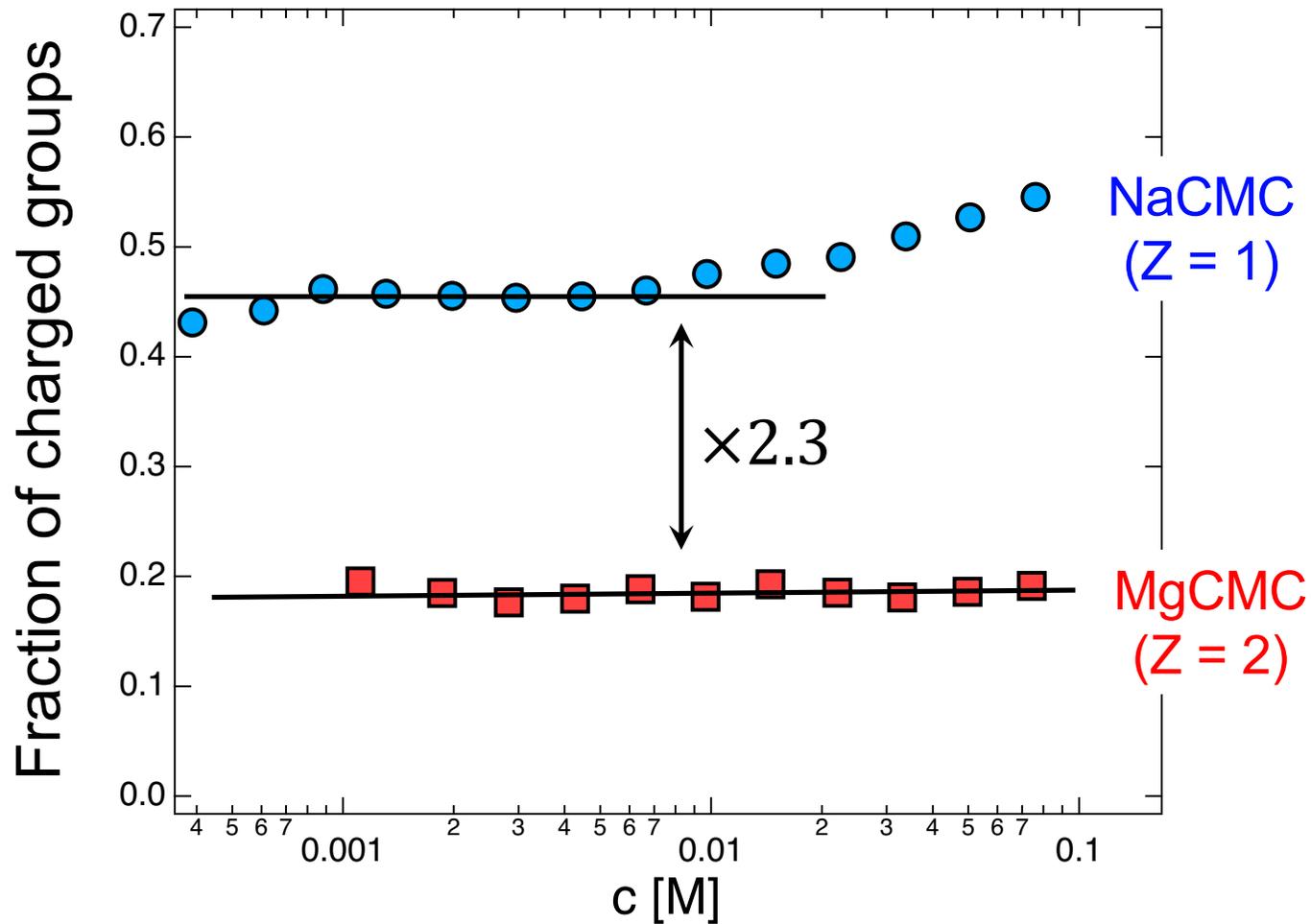
Oosawa-Manning prediction:

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

INFLUENCE OF COUNTERION VALENCE

Fraction of charged groups vs c [M]

NaCMC
(Z = 1)

MgCMC
(Z = 2)

Oosawa-Manning prediction:

$$f_{eff} = \frac{b}{l_B \mathbf{Z}_{counterion}}$$

9

INFLUENCE OF COUNTERION VALENCE

Oosawa-Manning prediction:

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

Experimental result:

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

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INFLUENCE OF COUNTERION VALENCE

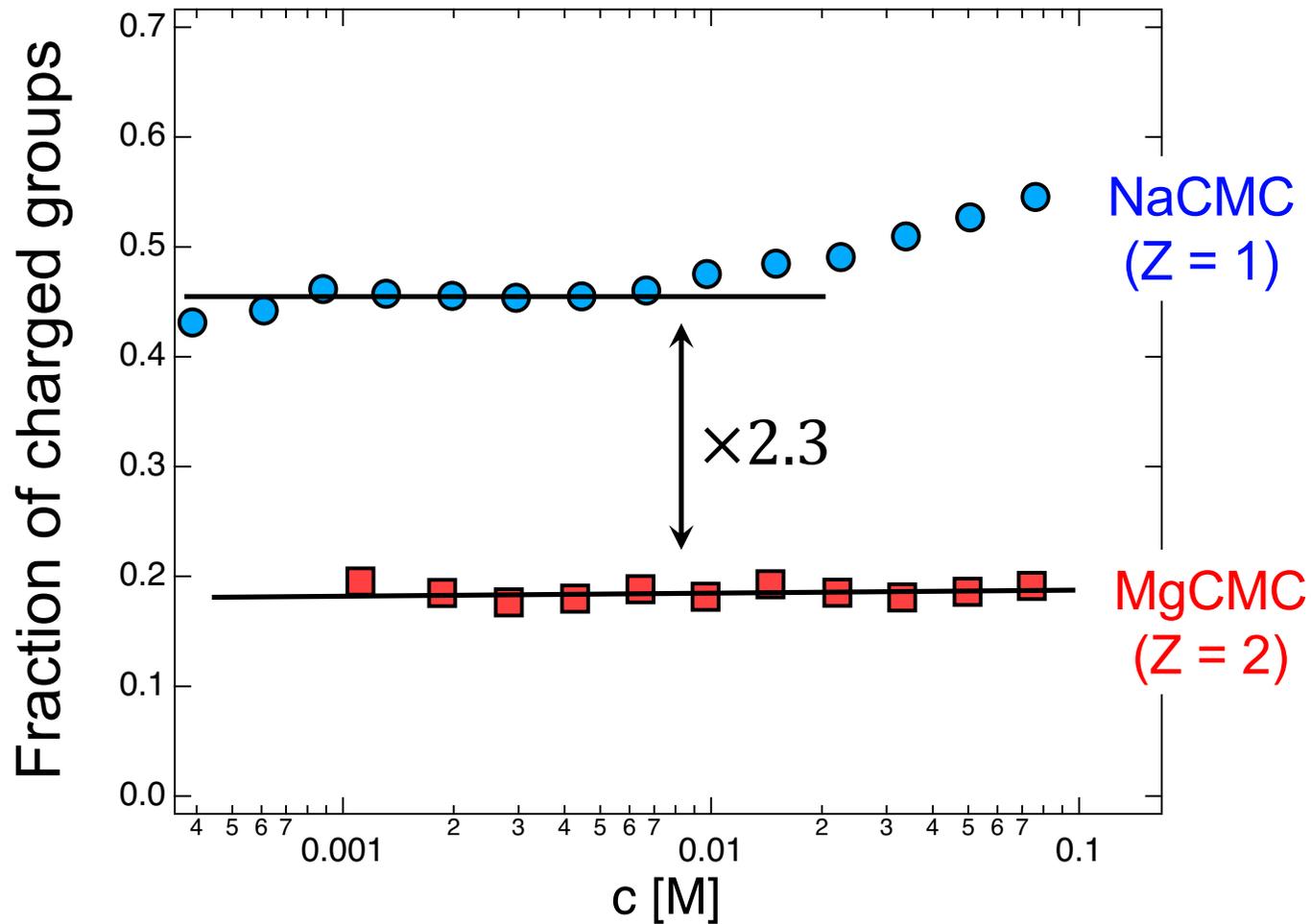

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NaCMC (Z = 1)

MgCMC (Z = 2)

×2.3

9

INFLUENCE OF COUNTERION VALENCE
(comparison with other systems)

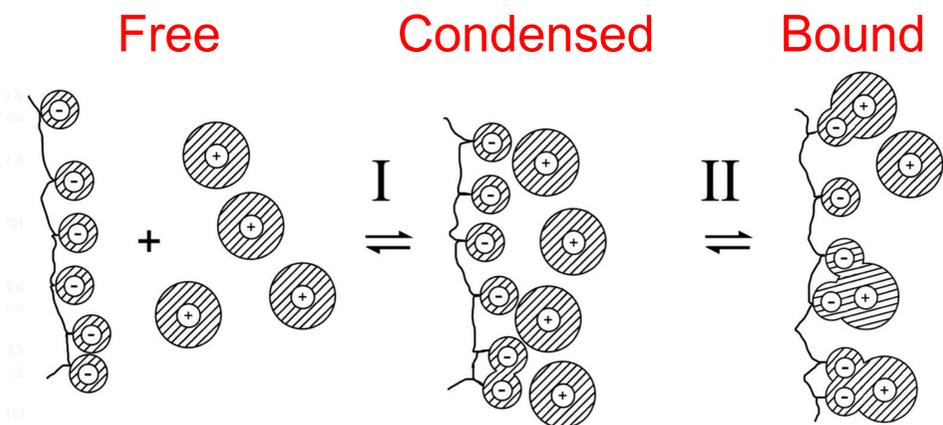| Polymer	f_{M^+}	$f_{M^{2+}}$	Ratio
Carboxymethyl cellulose	0.45	0.19	2.3
Carboxymethyl amylose	0.3	0.16	1.9
Carboxymethyl dextran	0.58	0.3	1.9
Alginate	0.3	0.16	1.9
Polyvinyl sulfate (50%)	0.44	0.22	2

10

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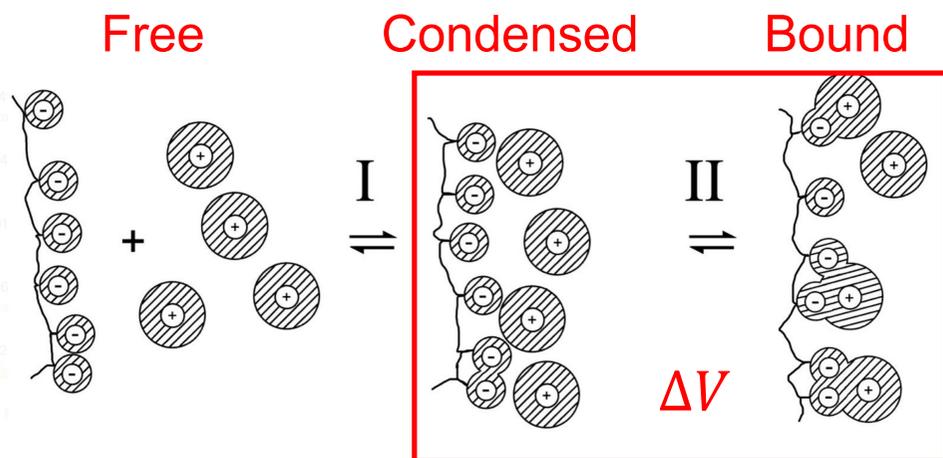- Scattering properties: condensation & delocalisation

ION PAIR FORMATION

Free   Condensed   Bound

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

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

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

11

ION PAIR FORMATION

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ION PAIR FORMATION

Free   Condensed   Bound


ΔV
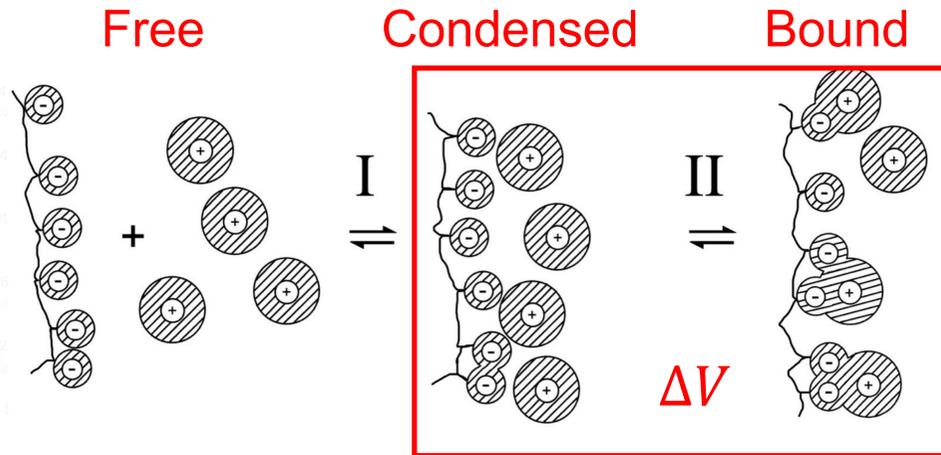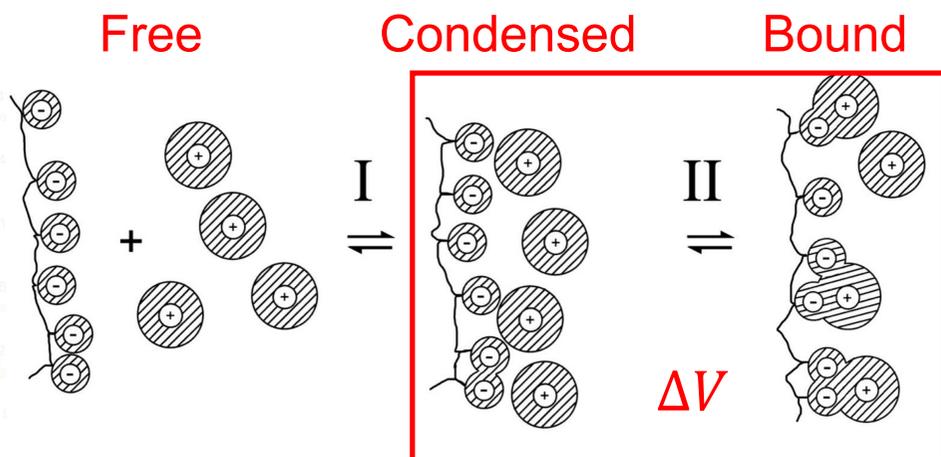
Electrostricted water ($\rho \approx 1.1\ g/mL$)

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

Ultrasound absorption

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

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ION PAIR FORMATION

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

ΔV increases
$\rightarrow$ stronger ion binding

Degree of neutralisation

$$Li^+ > Na^+ > K^+ > Cs^+$$

Atkinson, G., Baumgartner, E. and Fernandez-Prini, R., 1971. *Journal of the American Chemical Society*, 93(24), pp.6436-6443.
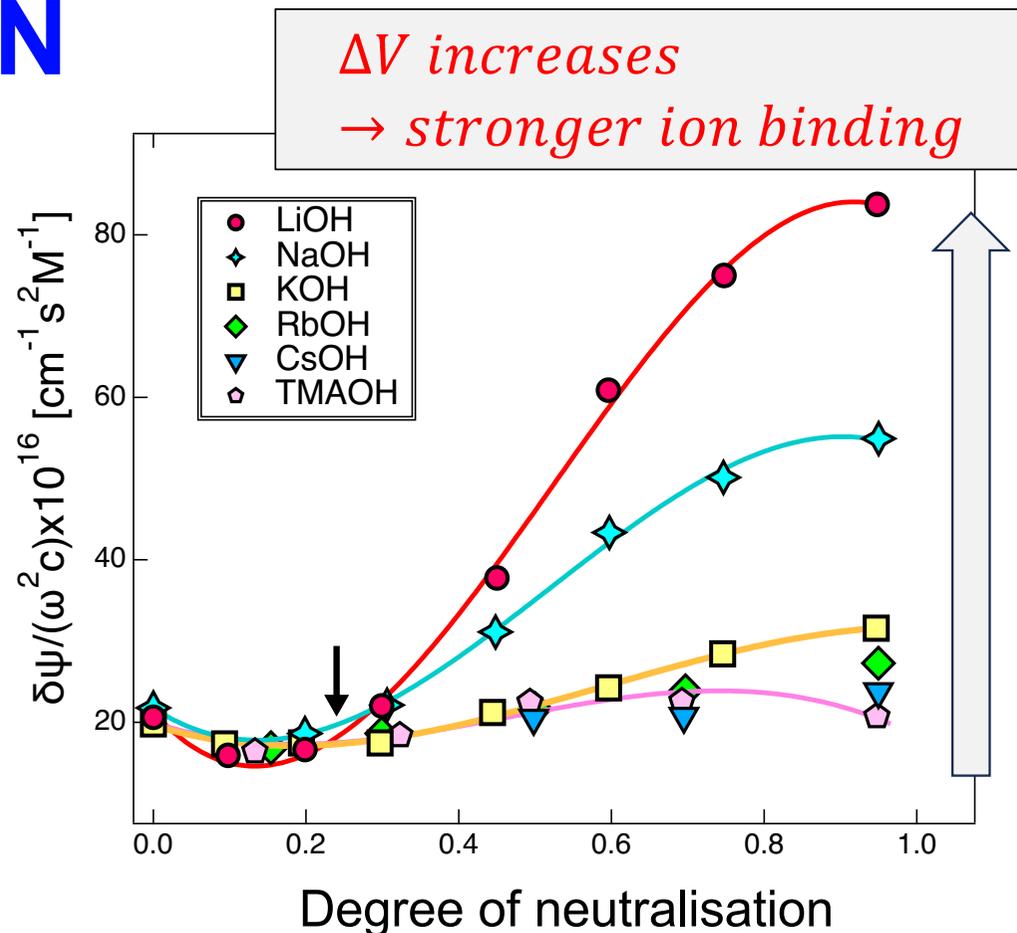
Zana, R., Tondre, C., Rinaudo, M. and Milas, M., 1971. *Journal de Chimie Physique*, 68, pp.1258-1266.

11

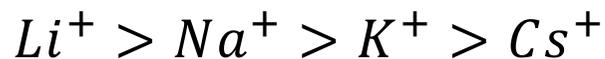# INFLUENCE OF COUNTERION TYPE ON CHARGE FRACTION
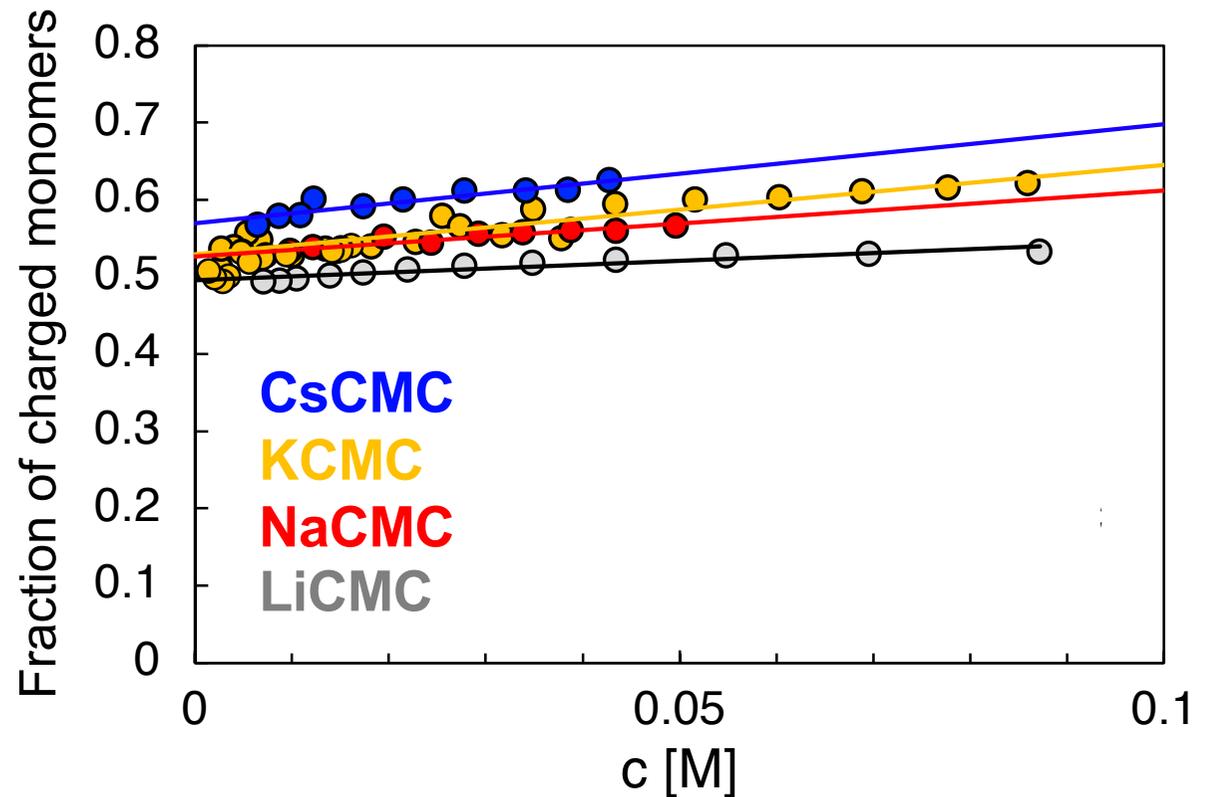
Ion pair formation strength:

$$Li^+ > Na^+ > K^+ > Cs^+$$
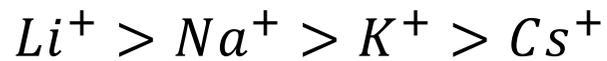
~ 40% ion-pairs   No ion pairs

Ion bound counterions

$$Li^+ > Na^+ > K^+ > Cs^+$$

≈ 10% difference

CsCMC
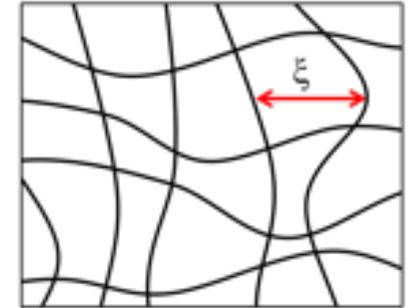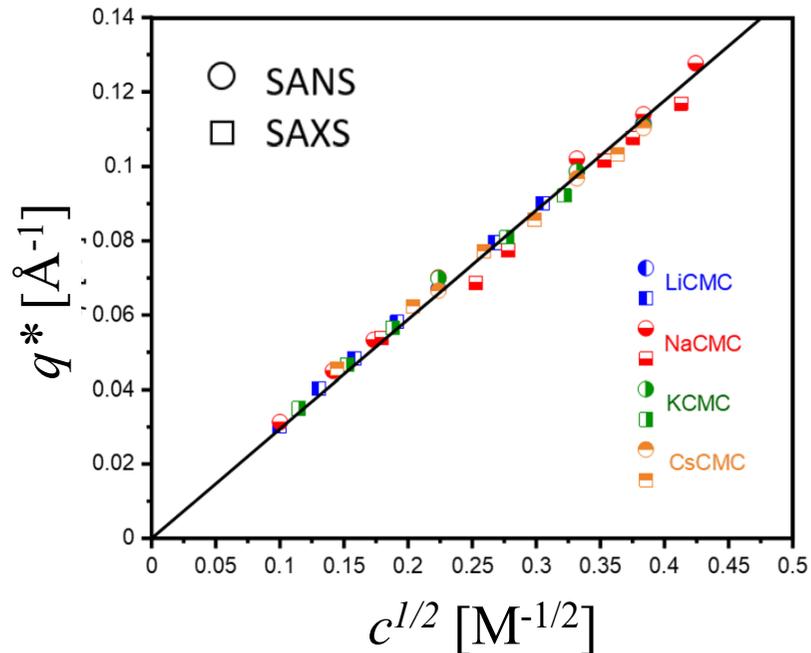**KCMC**
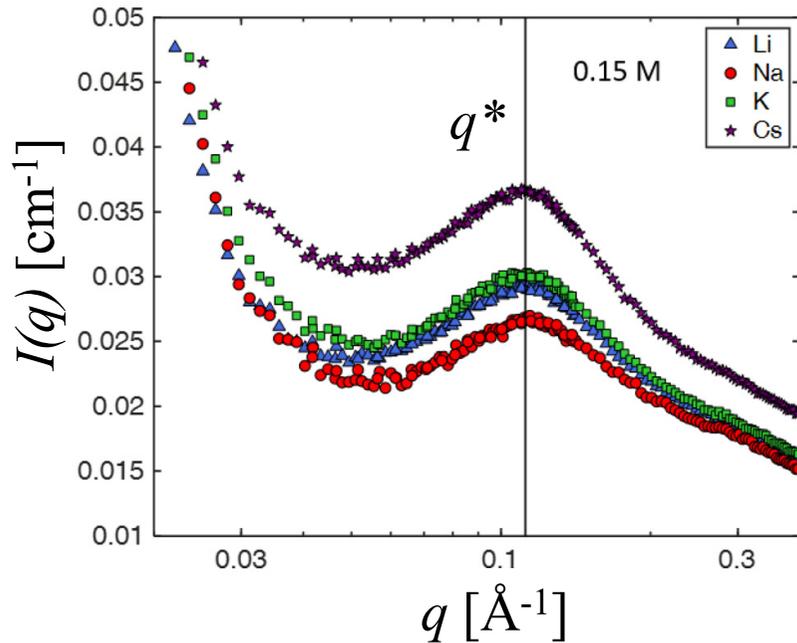**NaCMC**
LiCMC

12

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the Carreau n
model for $h = $
rate dep ... n
but different v
4.2.1 Salt free

NFLUENCE OF COUNTERION TYPE
(alkali metals)

q^*

0.15 M

- Li
- Na
- K
- Cs

$I(q)$ [cm^{-1}]

q [Å^{-1}]

0.03   0.1   0.3

q^* [Å^{-1}]

○ SANS
□ SAXS

LiCMC
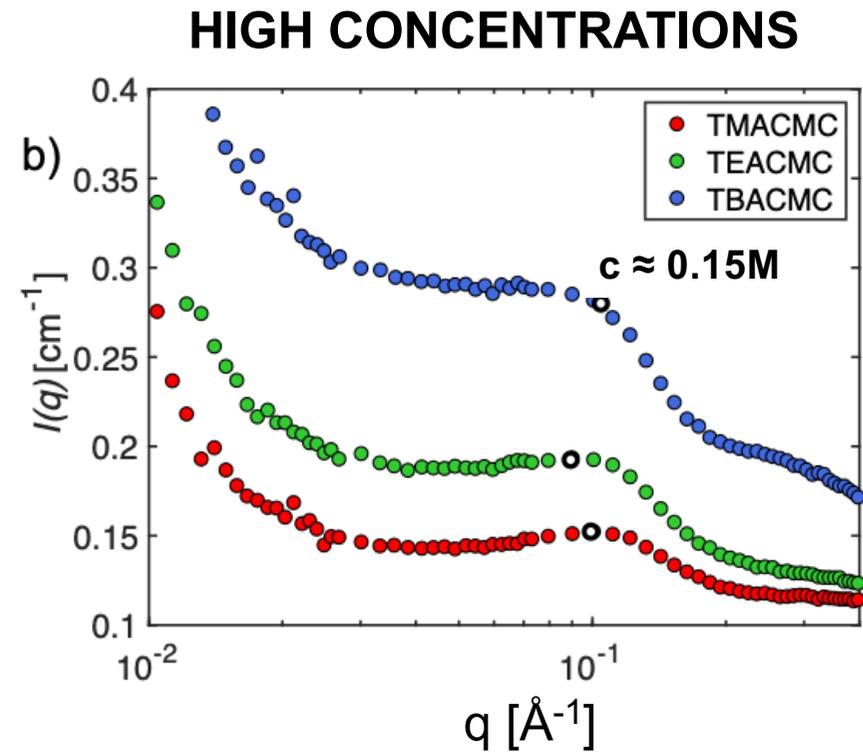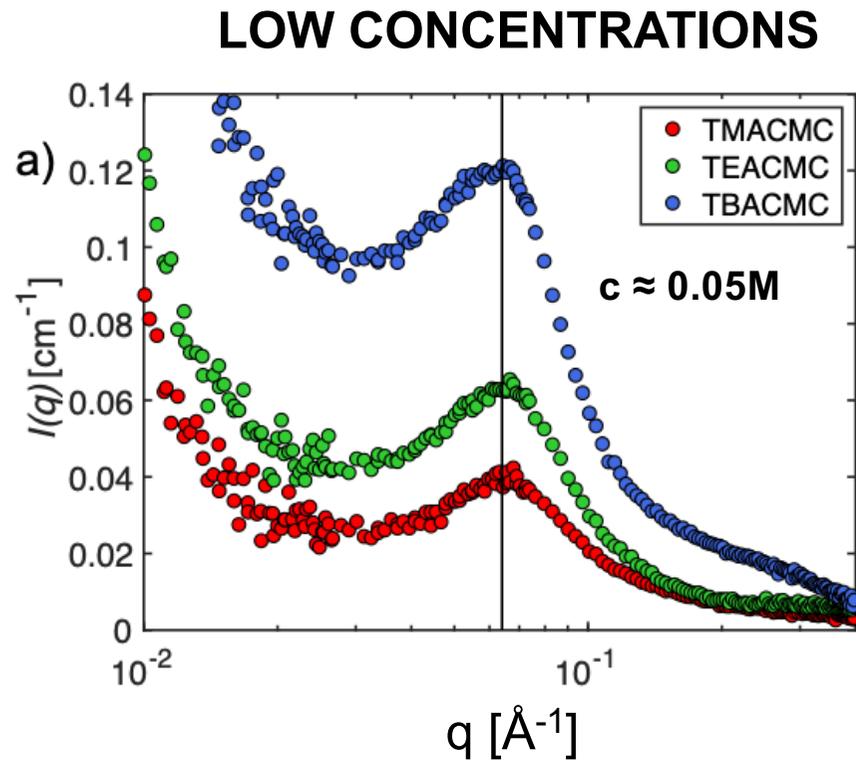NaCMC
● KCMC
CsCMC

$c^{1/2}$ [M$^{-1/2}$]

$\xi = \dfrac{2\pi}{q^*}$

$\xi \approx (bc)^{-\frac{1}{2}}$

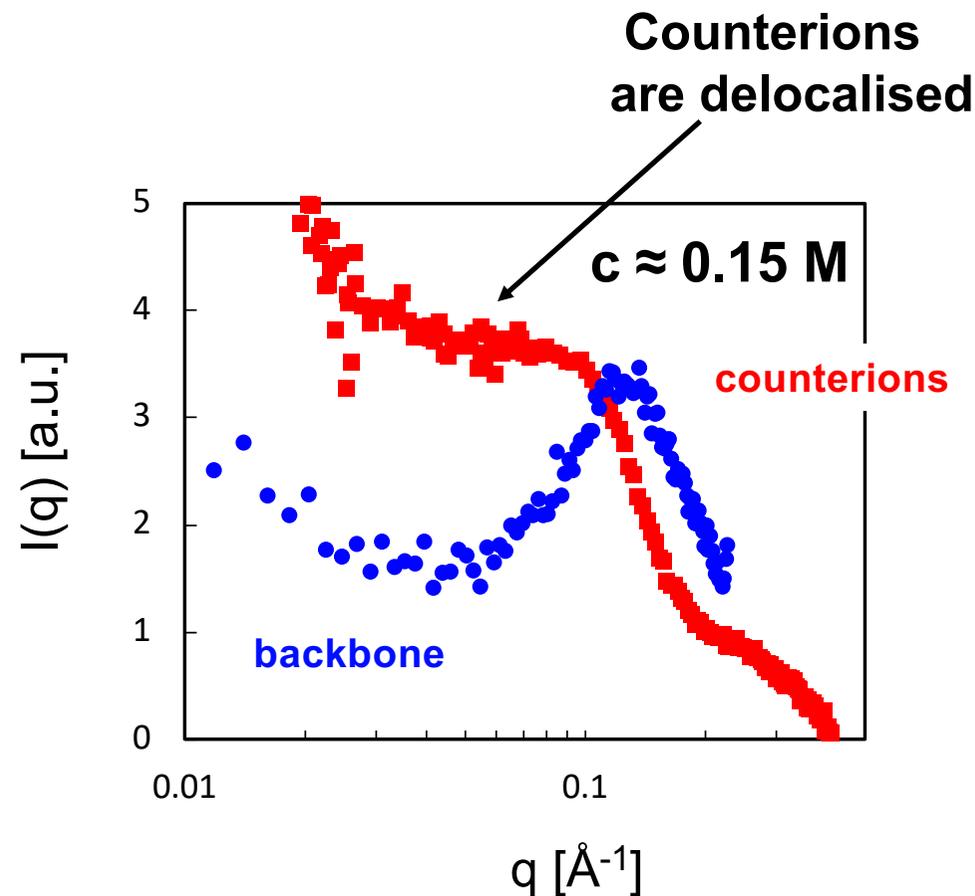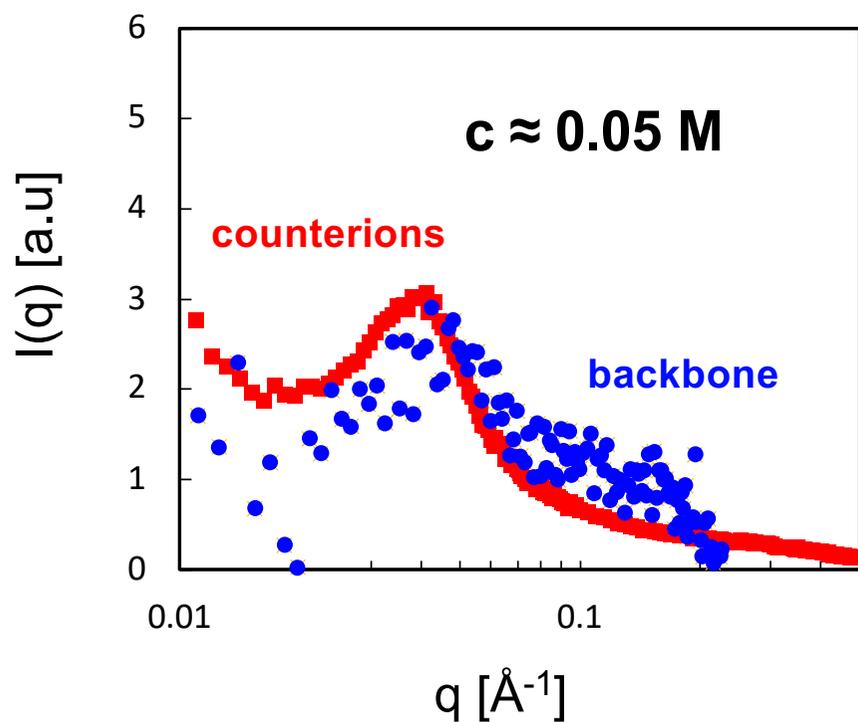- Scattering properties are independent of counterion type

Gulati, A., Douglas, J.F., Matsarskaia, O. and Lopez, C.G., 2024. Influence of counterion type on the scattering of a semiflexible polyelectrolyte. *Soft matter*, 20(43), pp.8610-8620.

14

MgPSS (SANS)

INFLUENCE OF COUNTERION TYPE
(tetra-alkyl-ammoniums)

Decoupling of concentration fluctuations of monomers and counterions at high concentrations
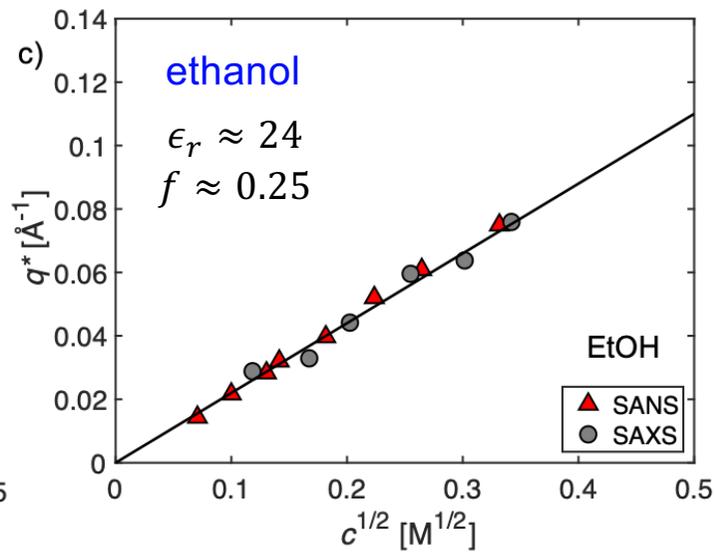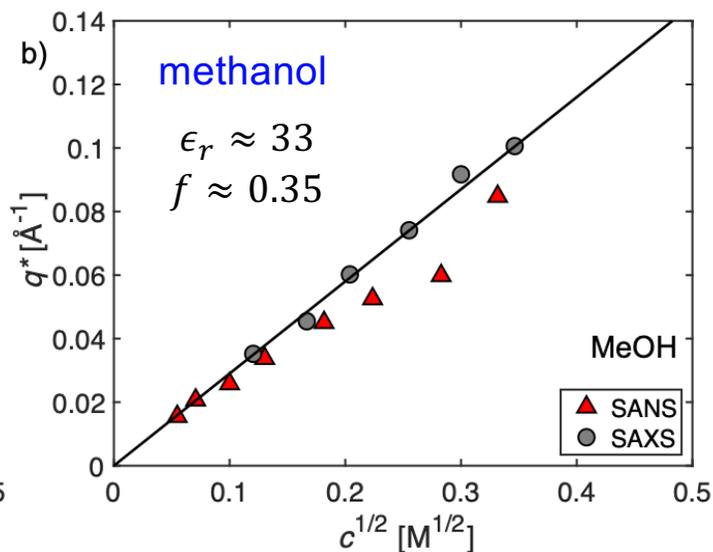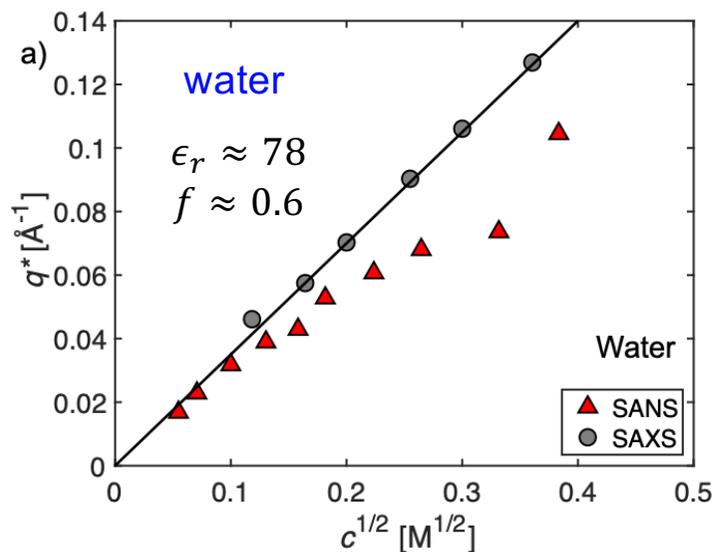
15

COUNTERION DELOCALISATION: TBACMC

Counterions are delocalised

c ≈ 0.05 M

counterions

backbone

c ≈ 0.15 M

counterions

backbone

Decoupling of concentration fluctuations of monomers and counterions at high concentrations

16

POLYMER-COUNTERION DECOUPLING

Contrast from polymer backbone
Contrast from counterions

Dielectric constant decreases

Polymer & counterion fluctuations de-couple

Gulati, A., Douglas, J.F., Matsarskaia, O. and Lopez, C.G., 2024. Influence of counterion type on the scattering of a semiflexible polyelectrolyte. *Soft matter*, *20*(43), pp.8610-8620.

17

SUMMARY & OPEN QUESTIONS

- **Oosawa-Manning** condensation correctly predicts the dependence of polyelectrolyte effective charge on <u>dielectric constant</u>, <u>bare charge density</u> and <u>counterion valence.</u>

- **Ion-pairing** due to solvation shell sharing takes place but has a minor effect on the effective charge of the polyelectrolytes.

- At high concentrations in high dielectric constant solvents, **concentration fluctuations of polymer and counterions decouple.**
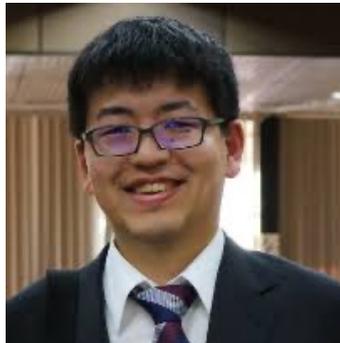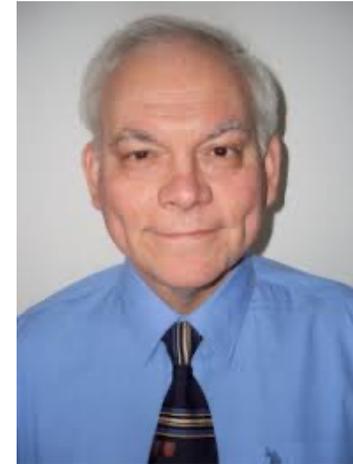
13

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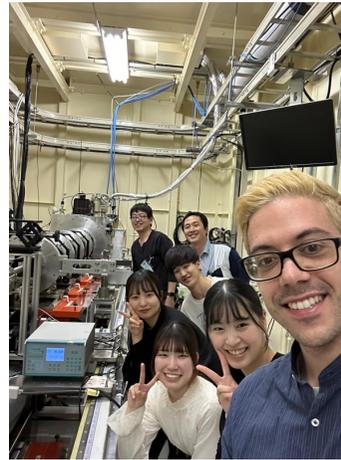
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14