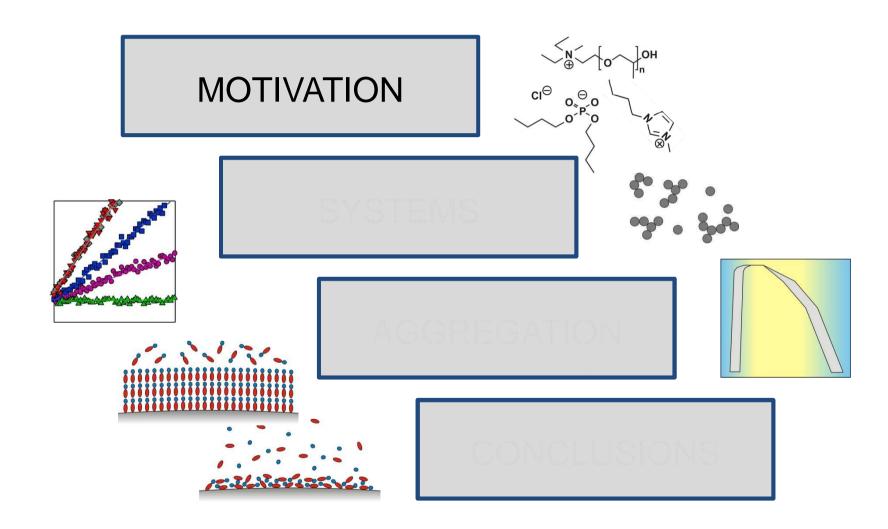
# EFFECT OF IONIC LIQUIDS ON AGGREGATION OF LATEX COLLOIDS

## ISTVÁN SZILÁGYI

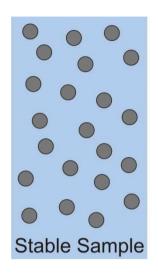
LABORATORY OF COLLOID AND SURFACE CHEMISTRY
UNIVERSITY OF GENEVA
SWITZERLAND

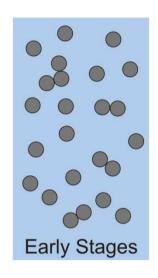


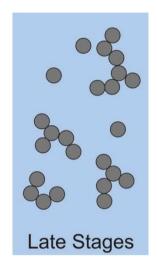




## Particle Aggregation in Water



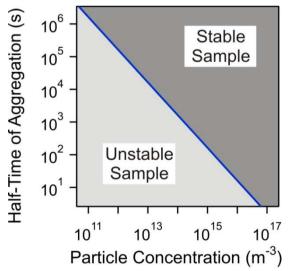




stabilization of colloids foods, cosmetics, paints...

destabilization of colloids wastewater treatment, papermaking...

particles as catalysts stability during the run & removal by aggregation



#### von Smoluchowski

$$T_{1/2} = \frac{2}{kN_0}$$
  $k = \frac{8k_BT}{3\eta} \approx 1.23 \times 10^{-17} \text{ m}^3/\text{s}$ 

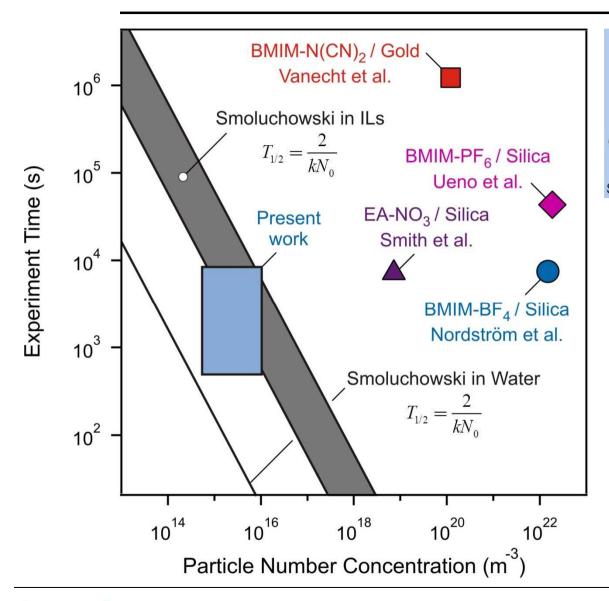
Derjaguin, Landau, Verwey and Overbeek (DLVO)

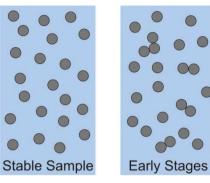
$$F = F_{\rm vdW} + F_{\rm dl} \qquad F_{\rm vdW} \sim H \ F_{\rm dl} \sim \Psi^2$$

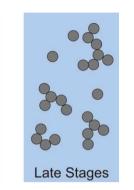




## Particle Aggregation in ILs







$$N = \frac{N_0}{1 + t / T_{1/2}}$$

$$N = N_1 + N_2 + N_3 + \dots \quad N_0 = N_1 + 2N_2 + 3N_3 + \dots$$

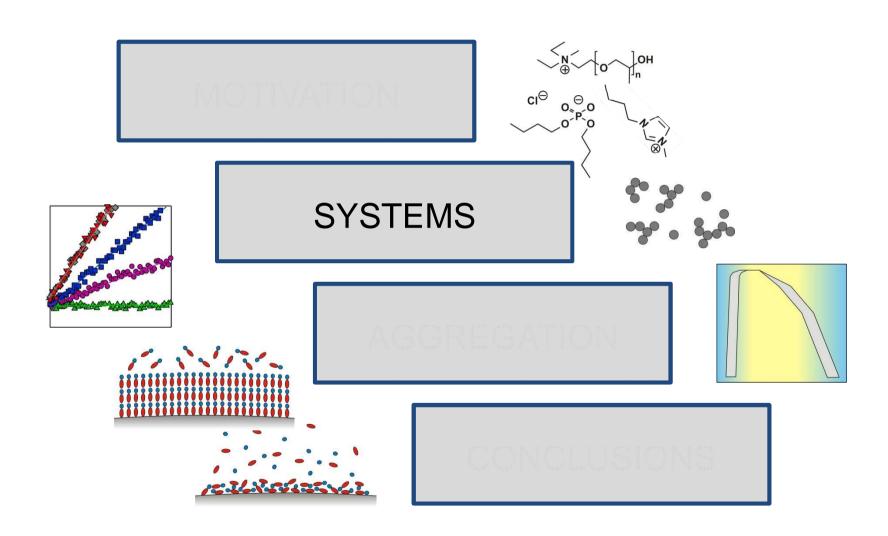
$$T_{1/2} = \frac{2}{kN_0}$$

$$k = \frac{8k_{\rm B}T}{3\eta} \approx 1.23 \times 10^{-17} \text{ m}^3/\text{s}$$

in aqueous electrolyte







# PARTICLES SUSPENDED IN ILS

ILS – room-temperature, water miscible ILs & their aqueous solutions

SCN
$$^{\odot}$$

BMIM-SCN

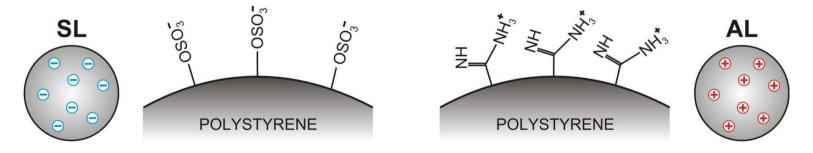
N(CN) $_{2}^{\odot}$ 

BMPY-DCA

BMIM-DCA

BMIM-BF<sub>4</sub>

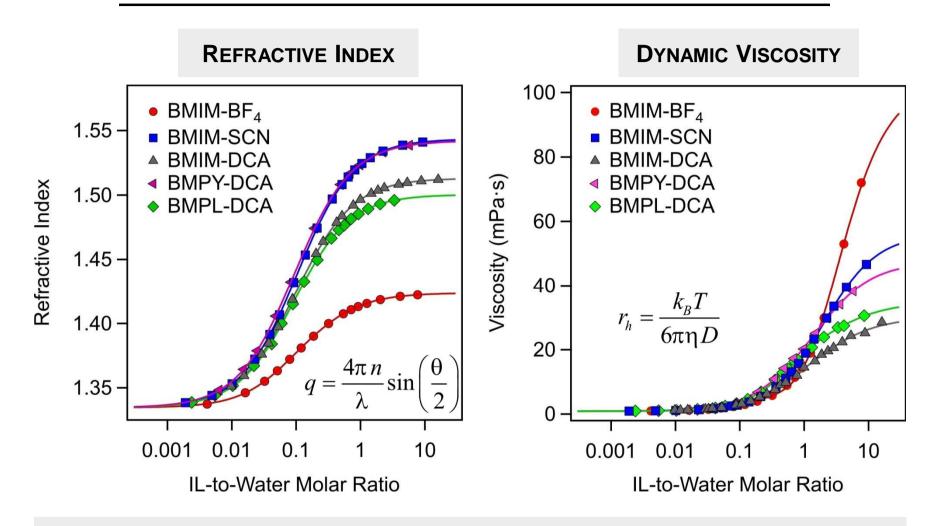
Particles – polystyrene latexes of 265 (SL) & 110 nm (AL) in radius







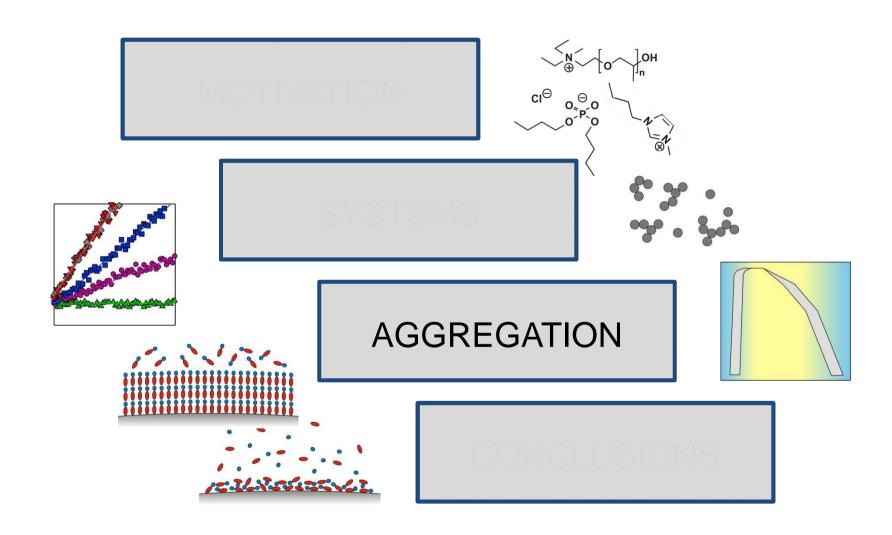
## PHYSICO-CHEMICAL DATA



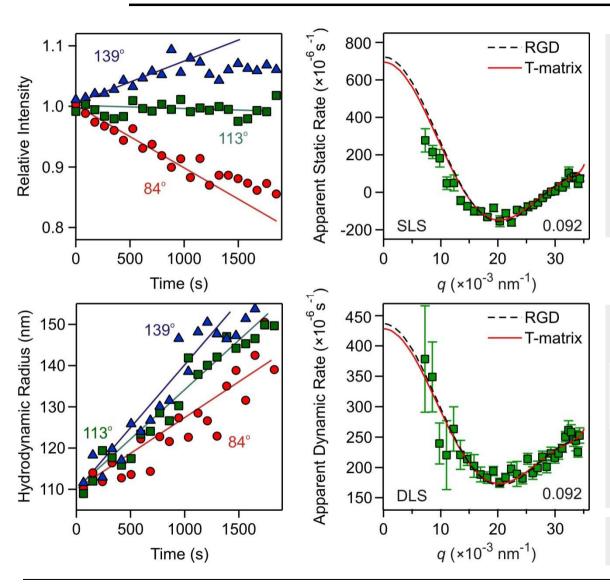
refractive index & viscosity – scattering vector & hydrodynamic radius in LS







# PARTICLE AGGREGATION RATES BY LS



#### STATIC LIGHT SCATTERING

$$\left. \frac{1}{I(q,0)} \cdot \frac{dI(q,t)}{dt} \right|_{t \to 0} = kN_0 \left( \frac{I_2(q)}{2I_1(q)} - 1 \right)$$

optical factor: RGD or T-matrix aggregation rate: least-squares fit



#### **DYNAMIC LIGHT SCATTERING**

$$\left. \frac{1}{r(q,0)} \cdot \frac{dr(q,t)}{dt} \right|_{t \to 0} = kN_0 \left( 1 - \frac{r_1}{r_2} \right) \frac{I_2(q)}{2I_1(q)}$$

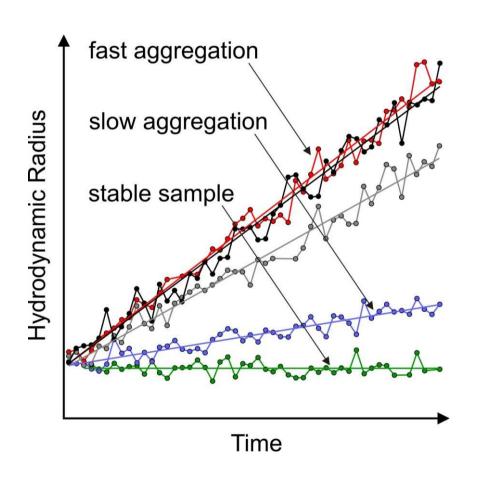
aggregation rate: from SLS hydrodynamic factor: fit

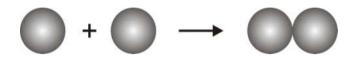
**COMBINATION OF SLS & DLS** 





# PARTICLE AGGREGATION RATES BY DLS





#### aggregation rate constant

$$\left. \frac{1}{r(q,0)} \cdot \frac{dr(q,t)}{dt} \right|_{t \to 0} = kN_0 \left( 1 - \frac{r_1}{r_2} \right) \frac{I_2(q)}{2I_1(q)}$$

#### Smoluchowski's constant

$$k_{\rm S} = \frac{8k_{\rm B}T}{3\eta}$$

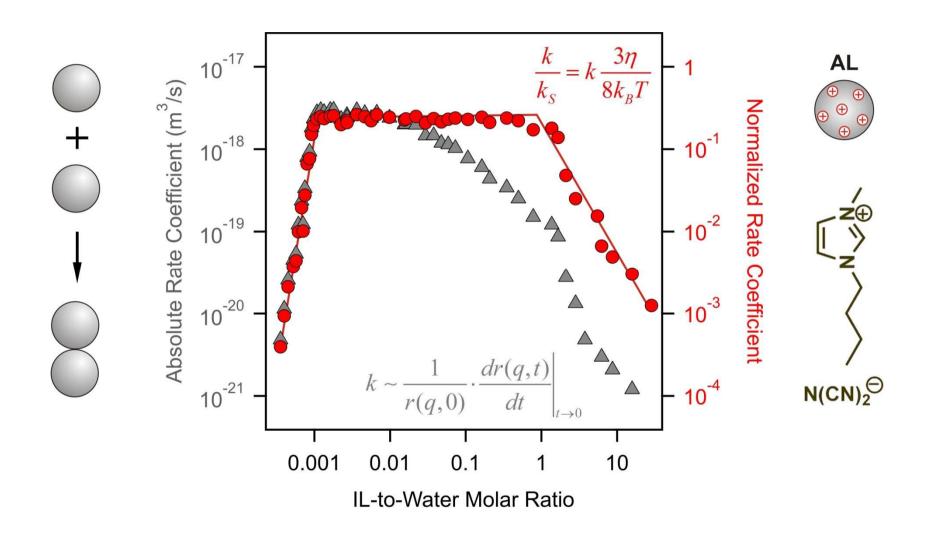
#### normalized rate constant

$$k_{normalized} = \frac{k}{k_{s}}$$





# NORMALIZED AGGREGATION RATES



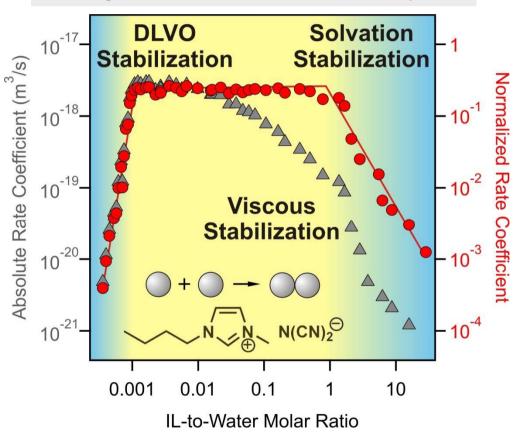




# STABILIZATION MECHANISMS

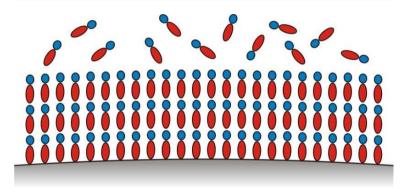
#### Stabilization Effects

Low IL Dose – Electrical Double Layers Intermediate IL Dose – Viscosity Effect High IL Dose – Interfacial Assembly



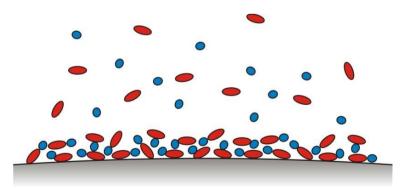
#### Interfacial IL Layers

Science 322 (2008) 424 & JPCC 111 (2007) 5162



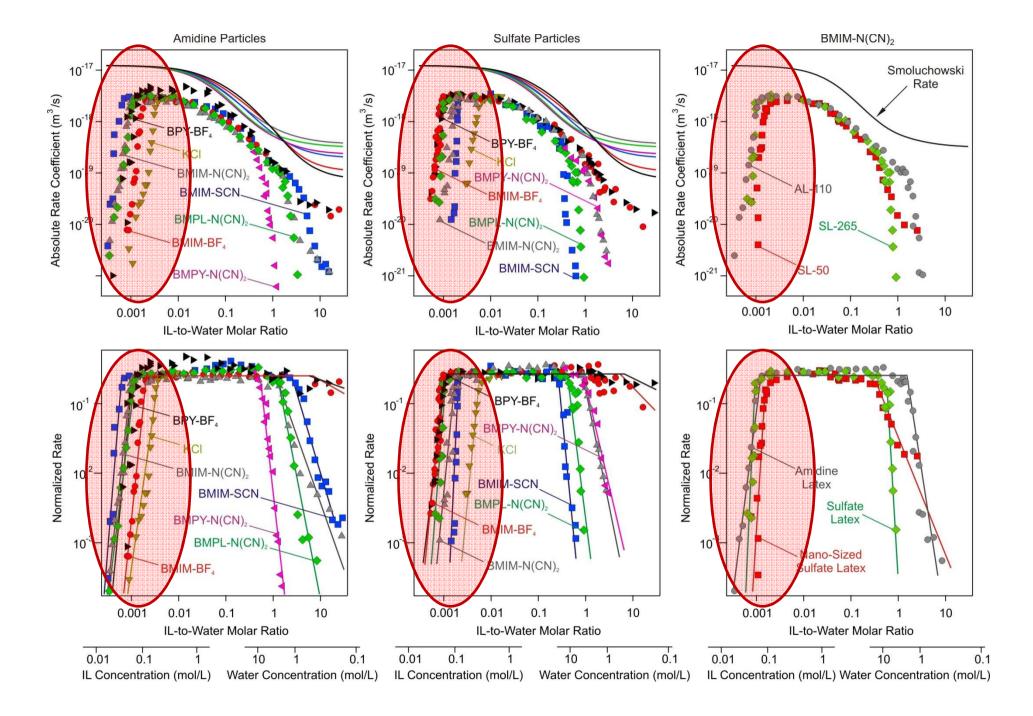
#### **Electrical Double Layer**

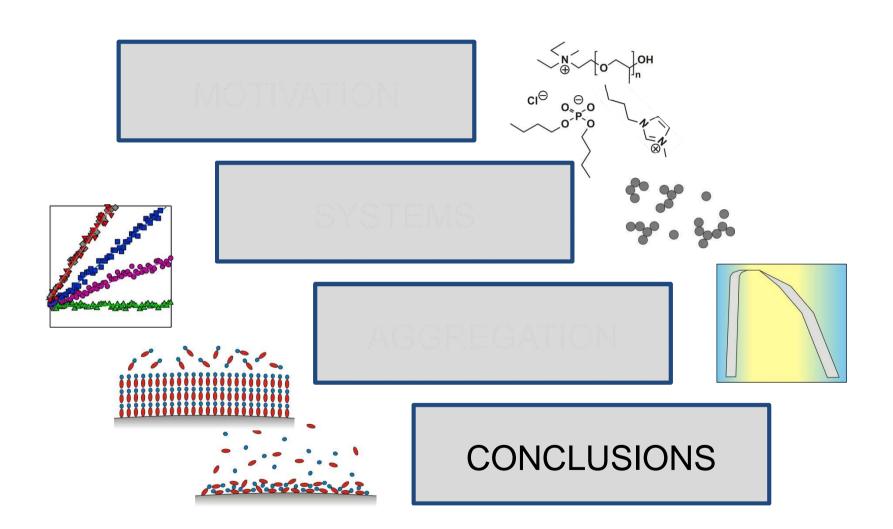
PNAS 110 (2013) 9674 & JPCC 113 (2009) 16445











## **CONCLUSIONS**

### **ABSOLUTE AGGREGATION RATES CAN BE DETERMINED**

BY LIGHT SCATTERING IN IL-WATER MIXTURES

## COLLOIDAL STABILITY IS INFLUENCED BY THE IL DOSE

DILUTED – DLVO-TYPE FORCES

INTERMEDIATE – VISCOUS STABILIZATION

PURE – SOLVATION STABILIZATION

## INCREASING IL HYDROPHOBICITY LED TO LOWER CCCS

EXTENDED HOFMEISTER SERIES

 $OMIM^{+} < HMIM^{+} < BMIM^{+} < BMPL^{+} < EMIM^{+} < MIM^{+} < N(CH_{3})_{4}^{+} < NH_{4}^{+} < Cs^{+} < K^{+} < Na^{+} < Li^{+}$ 



